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Wool fibres for the sorption of volatile organic compounds (VOCs) from indoor air

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Wool fibres for the sorption of volatile organic compounds (VOCs) from indoor air

*Being a thesis submitted in candidature
for the degree of Doctor of Philosophy*

by

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Abstract

This thesis reports the investigations of sheep wool's ability to sorb volatile and very volatile organic compounds (v/VOCs). Indoor air quality and occupants health can be adversely affected by the presence of even low gaseous concentrations of v/VOCs. Sheep wool's fibres, with their keratinous chemical functionalities, provide platforms for sorption of the said compounds.

Wools from different breeds of sheep are studied with regards to the sorption of four volatile organic compounds in their gaseous state, which represents a wide range of polarity and basic chemical diversity: formaldehyde, toluene, limonene and dodecane. A gas-tight set-up was constructed and analytical techniques were optimised. It was found that there is variation between the different wool types in addition to difference between scoured and unscoured wools. Total sorption capacity of formaldehyde is also examined, with variations opposing the trend seen for the sorption of the more non-polar VOCs at low concentrations. Sorption patterns were studied with respect to increasing concentrations. Characteristics of the different wool types are reported and linked to the observed sorption behaviour.

Moisture uptake is studied across different wool types and the use of the Vrentas-Vrentas mathematical model is discussed. The mean cluster size of water molecules in the wool fibres is compared. The sorption kinetic behaviour of the wool fibres is analysed using the Parallel Exponential Kinetic model, and the sorption parameters were used to calculate the modulus of the wool fibres.

Chemical and mechanical modifications along with the use of additives are studied to enhance wool's sorption ability. Adding polar functionalities onto the fibres' surface hinders total sorption capacity of formaldehyde and the sorption of all four v/VOCs at low concentrations. Adding a large non-polar functionality also hinders total sorption capacity of formaldehyde, but increases the sorption at low concentrations of non-polar compounds without reducing the sorption of polar formaldehyde. Ball milling increases surface area and the sorption of all four compounds at low concentrations. Carbon fibre as an additive excels at the sorption of non-polar compounds, whereas a coating of chitosan increases the total sorption capacity of formaldehyde without effecting the sorption patterns of any of the v/VOCs at low concentrations. The effect of the modifications on other fibre properties is also reported.

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List of publications

Book section

Mansour, E., Ormondroyd, G., 2017. Wool - Nonwood biobased building materials, in: Performance of Bio Based Building Materials.

Journal articles

Mansour, E., Curling, S., Stéphan, A., Ormondroyd, G., 2016. Absorption of Volatile Organic Compounds by Different Wool Types. *Green Mater.* 4. <https://doi.org/10.1680/jgrma.15.00031>

Mansour, E., Loxton, C., Elias, R.M., Ormondroyd, G.A., 2014. Assessment of health implications related to processing and use of natural wool insulation products. *Environ. Int.* 73, 402–412. <https://doi.org/10.1016/j.envint.2014.08.004>

Ormondroyd, G.A., Curling, S.F., Mansour, E., Hill, C.A.S., 2016. The water vapour sorption characteristics and kinetics of different wool types. *J. Text. Inst.* 108, 1198–1210. <https://doi.org/10.1080/00405000.2016.1224442>

Conference proceedings

Clauder, L., Mansour, E., Ormondroyd, G., Pfriem, A., 2015. Emissions from bio-based building products, in: European Conference on Wood Modification. European Conference on Wood Modification 2015, Helsinki, Finland.

Curling, S., Mansour, E., Ormondroyd, G., 2016. Effect of different natural insulation products' density in relation to thermal conductivity. COST Action FP1303 Meeting, Poznan Poland.

Loxton, C., Mansour, E., Elias, R., 2013. Research into natural bio-based insulation for mainstream construction. SB 13, Guimarães, Portugal.

Mansour, E., Curling, S., Ormondroyd, G., 2015a. Absorption of formaldehyde by different wool types. International Panel Products Symposium, Llandudno, UK.

Mansour, E., Marriott, R., Curling, S., Ormondroyd, G., 2015b. Natural insulation fibres for the absorption of indoor volatile organic compounds. FEMS EUROMAT, Warsaw, Poland.

Mansour, E., Marriott, R., Ormondroyd, G., 2016. Sheep wool insulation for the absorption of volatile organic compounds. Young Researchers' Forum III 2016 Innovation in Construction Materials.

Ormondroyd, G., Mansour, E., Curling, S., 2017a. Wool in Interiors and the effects on Indoor Air Quality. IWTO Annual Congress, Harrogate, UK.

Ormondroyd, G., Stefanowski, B., Mansour, E., Spear, M., Curling, S., 2017b. An Industry Prioritised Survey of Thermal, Mechanical, Hydro and Decay Properties of Natural Fibre Insulation Materials. International Panel Products Symposium, Llandudno, UK.

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My biggest thanks is for the Creator. As I learn more about any aspect of life and science, I find that believing in Him takes less faith than not to (Hebrews 11:1). He sure does things in style.

Onwards and upwards – despite the bumps along the road!

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Abbreviations

Abbreviation	Expansion
°C	Degrees centigrade
µg	Microgram
µl	Microliter
µm	Micrometre
18-MEA	18-methyleicosanoic acid
Å	Angstrom
AgBB	Ausschuss zur gesundheitlichen Bewertung von Bauprodukten
ANOVA	Analysis of variance
BRE	Building Research Establishment
BTEX	A mixture of benzene, toluene, ethylbenzene, and xylenes
BTX	A mixture of benzene, toluene and xylenes
C=O	Carbonyl group
C-C	Carbon-carbon bond
CH ₂	Methylene group
cm	Centimetre
cm ⁻¹	Reciprocal centimetres
cm ³	Cubic centimetre
CN	Carbon-nitrogen bond
C-N-H	Carbon-nitrogen-hydrogen bond
CO	Carbon monoxide
C-O	Carbon-oxygen bond
C-O or C-O-C	Ether group
-C-OH or OH	Hydroxyl group
COO ⁻	Carboxylate ion group
COOH	Carboxyl group
DDSA	(2-dodecen-1-yl)succinic anhydride
EMC	Equilibrium moisture content
EPA	Environmental Protection Agency (US)
F	F-Statistic
FKM	Fluorocarbon rubber
FTIR	Fourier transform infrared spectroscopy
g	Gram
ID	Inner diameter
kg	Kilogram

Abbreviations continued	Expansion continued
m³	Cubic meter
MC	Moisture content
mg	Milligram
ml	Millilitre
mm	Millimetre
MVOCs	Microbial Volatile organic compounds
NBR	Nitrile rubber
ng	Nanogram
NH	Nitrogen-hydrogen bond
NH₃	Amino group
nm	Nanometre
NO₂	Nitrogen dioxide
NO_x	Mono-nitrogen oxides
NPT	National pipe thread
O=C-R	Acyl group
-O-C=O	Ester group
OD	Outer diameter
O-O⁻	Peroxide group
p	probability
PM₁₀	Particulate matter less or equal to 10micron
PM₂₅	Particulate matter less or equal to 25micron
ppb	Parts per billion
ppm	Parts per million
PTFE	Polytetrafluoroethylene
SBS	Sick building syndrome
SEM	Scanning electron microscope
SO₂	Sulphur dioxide
TEAM	Total Exposure Assessment Methodology
UV	Ultraviolet
v/VOCs	Volatile and very volatile organic compounds
VOCs	Volatile organic compounds
vVOCs	Very volatile organic compounds
WHO	World Health Organisation

Chapter 1: Aims of the study

1.1 Introduction to indoor air pollution

Indoor air quality (IAQ) has been of concern to scientists since the mid-1800s (von Pettenkofer, 1858) with further interest shown in the 1930s, with the main concern being the spread of microbial agents within dwellings and public buildings (Shurtleff, 1933; Wells, 1943). Historical developments, such as the London smog of 1952, lead to substantial air pollution investigations, and differences in the health of people working indoors and outdoors were explored (Fairbairn and Reid, 1958). There has been a mild interest in the capacity of construction materials to contribute to a better atmospheric environment (Braun and Wilson, 1970); but the main studies investigating volatile organic compounds (VOCs) in buildings didn't start until relatively recently, whereby 50 studies were conducted between 1978 and 1990 (Brown *et al.*, 1994). Unfortunately, indoor air pollution remains a recognised socio-economic problem (EEA, 2013; Franchi *et al.*, 2006), causing the loss of a projected \$10 billion to \$20 billion annually due to efficiency and productivity setbacks in the US alone (Fisk and Rosenfeld, 1997). Based on further scientific findings, the World Health Organisation (WHO) compiled a set of statements emphasising the right to breathe healthy indoor air and the obligations of responsible authorities (WHO, 2000). The organisation also published information about the effects of pollutants including particulate matter, ozone and nitrogen dioxide for the protection of public health (WHO, 2013).

The media reflected concerns over this issue, quoting WHO that air pollution is “the world's largest single environmental health risk”, where 3.3 million deaths are blamed on indoor air pollution in contrast with 2.6 million deaths blamed on outdoor pollution in 2012 (Helen Briggs BBC, 2014). Some news items furthered the public's interest and fears with quotes such as “Air inside contains more than 900 potentially harmful chemicals” (Lizzie Parry Mail Online, 2015), “Smell of death: 99K Europeans die each year from toxic household fumes” (RT News, 2016), and “Potential dangers: Research in York found raised levels of a Volatile Organic Compound called limonene, which is used heavily in air fresheners and scented candles” (Sean Poulter Mail Online, 2016). This was accompanied by a push to clean indoor air in efforts to reduce related global death rates exhibited as strokes, heart diseases, chronic obstructive pulmonary diseases, acute lower respiratory infections in children and lung cancer. Most of the recent media accounts reference a report by the Royal College of Physicians (*Every breath we take*, 2016) that recognises the currently poor controls on indoor pollution and the push to reduced ventilation to save on energy. Another report stresses the situation more by indicating that “as outdoor air pollutant concentrations (CO, PM₁₀, PM_{2.5}, NO₂, SO₂, and volatile organic compounds) are generally predicted to decrease in the future in the UK

(with the exception of ground level ozone), the impact of internal sources, such as cooking, smoking and chemical emissions from indoor materials, on indoor air quality is likely to become proportionally more important” (Vardoulakis and Heaviside, 2012).

As with any risk, we can prioritise indoor air quality by considering both the level of exposure and how hazardous the pollutants are. In basic terms, risk can be defined as the exposure factor multiplied by the hazardousness factor, where the exposure factor can be defined as the time factor multiplied by the pollutants’ presence factor (Anastas and Warner, 2000).

1.1.1 Exposure

A large survey (performed in the United States with n=9,386) points out that the public spend 87% of their time in enclosed buildings and 6% of their time in enclosed vehicles (Klepeis *et al.*, 2001). Studies show that atmospheric pollutants concentrate indoors to high levels. Indoor concentrations are usually 2-5 times and sometimes 100 times higher than outside concentrations, as fresh air is not introduced as much as it was 30 years ago (Franchi *et al.*, 2006). Keeping in mind that there are other environmental issues to tackle, legislation pushes towards more energy efficient buildings (UK Government, 2013; US Department of Energy, 2014). Compared to air change rates of 0.5 to 1 air changes per hour recommended for homes built in the 1980-1990s, the American Society of Heating, Refrigeration, and Air conditioning Engineers Handbook recommends air changes rates for low rise residential homes between 0.15 to 0.2 air changes per hour (Lstiburek, 2002); Passivehaus standards specify that houses must have a maximum fresh air change rate of 0.6 air changes per hour (Mead and Brylewski, 2011). Consequently, air-tight building designs are emerging along with increasing IAQ concerns.

According to the European Respiratory Society, pollutants “may have an important biological impact even at low concentrations over long exposure periods”. They localised these pollutants mainly to homes, schools, congregating halls and residences, and vehicles – almost everywhere we spend most of our time at (European Respiratory Society, 2013).

1.1.2 Sources

Figure 1.1 and Figure 1.2 summarise the sources of indoor air pollutants which include dust, particulates, fibres, dander (loose scales formed on the skin and shed from the coat or feathers of various animals), bacteria, viruses, mould, mildew, CO, NO_x, radon, volatile organic compounds (VOCs) and very volatile organic compounds (vVOCs, where the combination of VOCs and vVOCs is referred to as v/VOCs). All buildings including domestic, industrial and work places are contaminated at varying levels depending on the activities performed. A project conducted in of 167 office buildings in 8 European countries concerning dry eye complaints found the key factors that increase such complaints to include absence of operable windows, exposed concrete and/or plaster, dispersion and/or emulsion paint as wall covering,

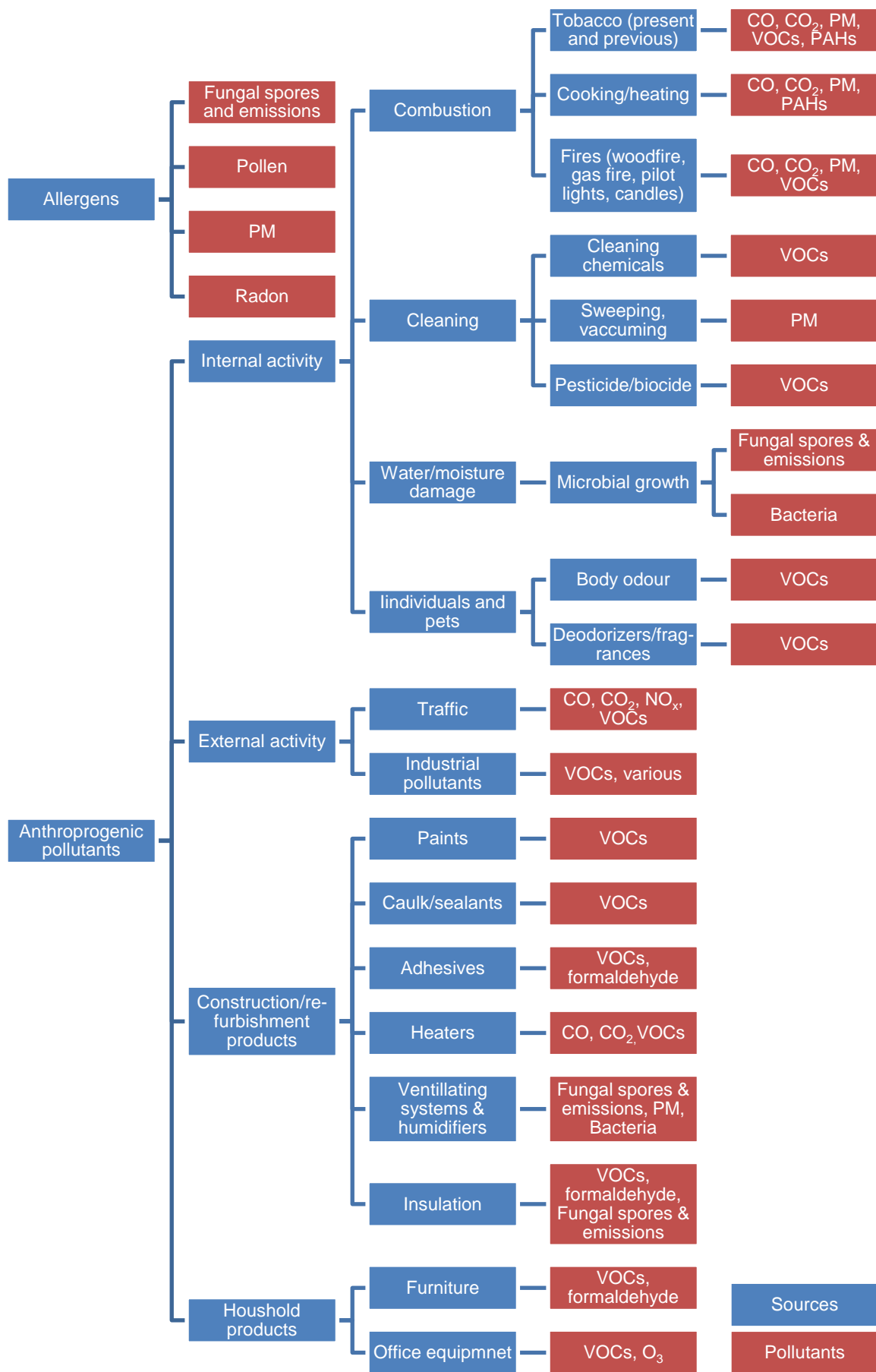


Figure 1.1: Sources of indoor pollution (Bluyssen *et al.*, 1996; European Respiratory Society, 2013; Franchi *et al.*, 2006). PM: particulate matter; PAHs: polycyclic aromatic hydrocarbons.

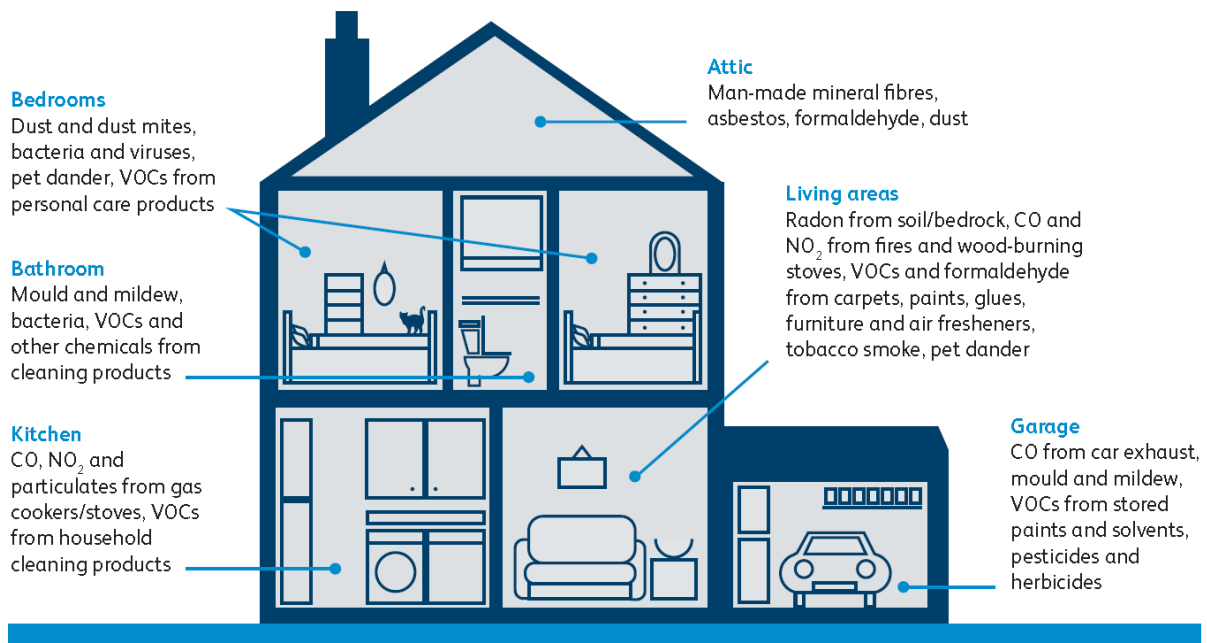


Figure 1.2: A graphical representation of some indoor air pollutants and their sources (Every breath we take, 2016).

and lack of cleaning (de Kluizenaar *et al.*, 2016). Another European study of 56 office buildings reports that 50% of visitors and 30% of occupants found the air quality unacceptable even in well ventilated buildings, and concludes: “Meeting existing ventilation standards is therefore no guarantee for acceptable indoor air quality” (Bluyssen *et al.*, 1996).

There are multiple and complex factors that affect the range and magnitude of indoor pollutants and associated health problems. Dampness is known as a major factor contributing to this, but the relationships are not fully understood (Bornehag *et al.*, 2004; National Academy of Sciences, 2004). It is known though, that dampness alters a building’s VOC profile (Claeson *et al.*, 2007), probably caused by the microbial decay of indoor materials and products.

1.1.3 Hazards

Hazards induced by these pollutants vary, but can be summarised to exacerbating known respiratory diseases, sensitising to airborne agents, and reducing lung functionality (Table 1.1). A comprehensive Italian study on children (n = 20,016, mean age = 7 years) and adolescents (n = 13,266, mean age = 13 years) concludes that avoiding mould and dampness alone decreases the occurrence of related illnesses by 4 to 7% (Simoni *et al.*, 2005). Solid biomass burning in poor European countries caused the death of 3.5 million in 2010 because of high levels of CO and particulate matter, and Radon is responsible for up to 2,900 deaths/year in the US and 1,100 deaths/year in the UK (European Respiratory Society, 2013).

Table 1.1: Classification of hazards induced by indoor agents (European Respiratory Society, 2013; Franchi *et al.*, 2006).

Classification	Agents	Example of symptoms
Environmental agent induced diseases	Microbial, CO, CO ₂ , NO _x , v/VOCs, SO ₂ , PM, radon	Legionnaire's disease, CO intoxication, cancer, chronic obstructive pulmonary disease, other serious diseases
Allergic reactions	Fungal spores/emissions, pollen, particulate matter, NO ₂ , v/VOCs	Asthma, rhinitis, tightness of the chest, shortness of breath, extrinsic, allergic alveolitis, cough
Sick building syndrome	v/VOCs	Acute health and comfort effects that are not identifiable
Multiple chemical sensitivity	v/VOCs	Sensitivity to extremely low concentration of chemicals (in fragrances, etc.) following a massive dose or chronic exposure.

Of course, the actual case of exposure is to a wide array of different pollutants in situations where complex social factors are at play (Adger *et al.*, 2009). The effect can be a synergistic sum, although that is very weakly characterised in the literature. For example, there are indicators pointing to the combination of radon gas and tobacco smoke being the causation of lung cancer, and some VOCs and NO₂ have increased potency when present with allergens that act as adjuvants (*Every breath we take*, 2016). Information gaps appear for other agents, but enough is known to recognise a risk; that is why the scientific community encourages international organisations to establish guidelines, categories, and clear emission limit values for building materials (Franchi *et al.*, 2006).

1.1.4 Current methods to address the problem

Since we interact with many of these agents simultaneously, the overall remedy must comprise of multiple solutions, each targeting specific agents or indeed multiple agents. Out of the many factors influencing indoor air quality, such as climate and social behaviour (European Respiratory Society, 2013), the industry can only manipulate building materials and construction techniques or introduce new products specifically designed to minimise associated risks.

The industry in response has already introduced a wide range of 'air cleaning/treating' products to the market, and the removal of both chemical and biological indoor contaminants

remain a subject of interest (Carslaw *et al.*, 2013). A plethora of devices have been designed to enhance indoor air quality through the use of filters, UV light, chemical or biological agents. Such devices can be energy intensive, contribute to some other form of contamination, and have a short operational life span compared to the building's life. Also, improvement has already been shown achievable without resorting to higher energy expenditure (Bluyssen *et al.*, 1996). It is possible that a passive solution can overcome such limitations. For example, scavengers reduce formaldehyde emissions from building products such as MDF boards (Costa *et al.*, 2013), and photo-catalytic coatings have been designed with the aim of degrading VOCs (Li *et al.*, 2005).

1.2 Aim of study

It is evident from Figure 1.1 and Table 1.1 that indoor v/VOCs present a health threat when considering that 99% of human exposure to VOC results from direct inhalation (Carrer *et al.*, 2000). Compared to other pollutants, v/VOCs induce an array of illnesses ranging from mild symptoms to carcinogenic risks, which can be caused at exposure levels that the general public are currently exposed to.

1.2.1 Scope

The aim of this study is to contribute to enhancing indoor air quality by reducing v/VOC levels. A passive solution would not increase energy consumption nor increase the impact on the building itself. Therefore, I selected a material that is already incorporated in building structures – sheep wool.

The potential of using wool fibres as part of indoor building materials as indoor VOC sorptive material is investigated. It is often used in many household furnishings such as carpets, and is growing in its use as a insulation product (Karus and Kaup, 2002; Research and Markets, 2011). The fibre surface offers a complex and diverse platform of sorption, and it shows promising initial results in the literature (Curling *et al.*, 2012; Ingham *et al.*, 1994; McNeil, 2011; Thomé, 2006).

This thesis considers the sorptive ability of wool fibre, on a small scale, to sequester a range of gaseous v/VOCs, linking trends to other fibre properties, mathematically describing water sorption kinetics, and enhancing fibre sorption potential.

1.2.2 Objectives

I am starting by expanding on the information presented in the literature concerning v/VOC, the hazards they impose on human health when present at levels encountered indoors, and the current procedures to address this problem. Next, I am going to present detailed

information on the structure of wool fibres, how they may be affected by their surroundings, and what contributes to their variation.

For my experimental approach, firstly I will establish the analytical techniques I will use to assess gaseous v/VOC sorption by fibres. In this regard, I am going to select the v/VOCs to be sorbed experimentally and produce sources of them that emit stable gaseous concentrations at similar levels to what is encountered indoors. I am also building a gas-tight setup, linking the v/VOC sources to a controlled flow in order to expose a specimen to the said concentrations. I aim to use v/VOC trapping systems to collect those not sorbed by the specimen and quantify them using either thermal desorption, connected to gas chromatography, or liquid chromatography. In addition to sorption of low concentrations, I will assess the maximum sorption capacity of a v/VOC fibres have by cyclically exposing them to high concentrations and calculating their weight change using Dynamic Vapour Sorption.

Next I am going to investigate the sorptive behaviour of different wool types and compare it to their physical and chemical properties. It is of interest to quantify the variation of sorption profiles of different wool types as different blends are used by different manufacturers. I will further look into the differing trends of v/VOC sorption with regards to the nature of the v/VOCs, as well as the changes in sorption trends as the concentration is altered at low levels. This is done to acquire a comprehensive understanding of wool's potential at contributing to cleaner indoor air. I will also expand on what structural dynamics must occur during sorption to allow maximum sorption capacity.

After that, to better understand the sorption interactions between the fibre and its environment, I am going to perform an in-depth study of the kinetics of water sorption for different wool types. Water sorption is the simplest as only physi-sorption is involved and no chemi-sorption, which may occur with v/VOCs. I aim to achieve satisfactory fits for moisture sorption isotherms and sorption hysteresis using the Vrentas and Vrentas model, and use the Zimm-Lundberg model to define when water clustering in the fibres occurs. I also aim to employ the parallel exponential kinetics model to provide fits to the experimental data and segregate the effects the fast and the slow process have on the isotherms and hysteresis. I will additionally calculate fibres elastic moduli and compare the values with those found in the literature.

After assessing wool fibres' sorption potential, I am going to investigate means to enhance this property using chemical and mechanical modifications alongside the use of additives. I will start by reviewing what routes the literature highlight in order to employ the most promising. The selected enhancements will be quantified using the same tests to be done for different wool types. I will also look at the effect of these modifications have on other fibre properties. Figure 1.3 illustrates the workflow carried out.

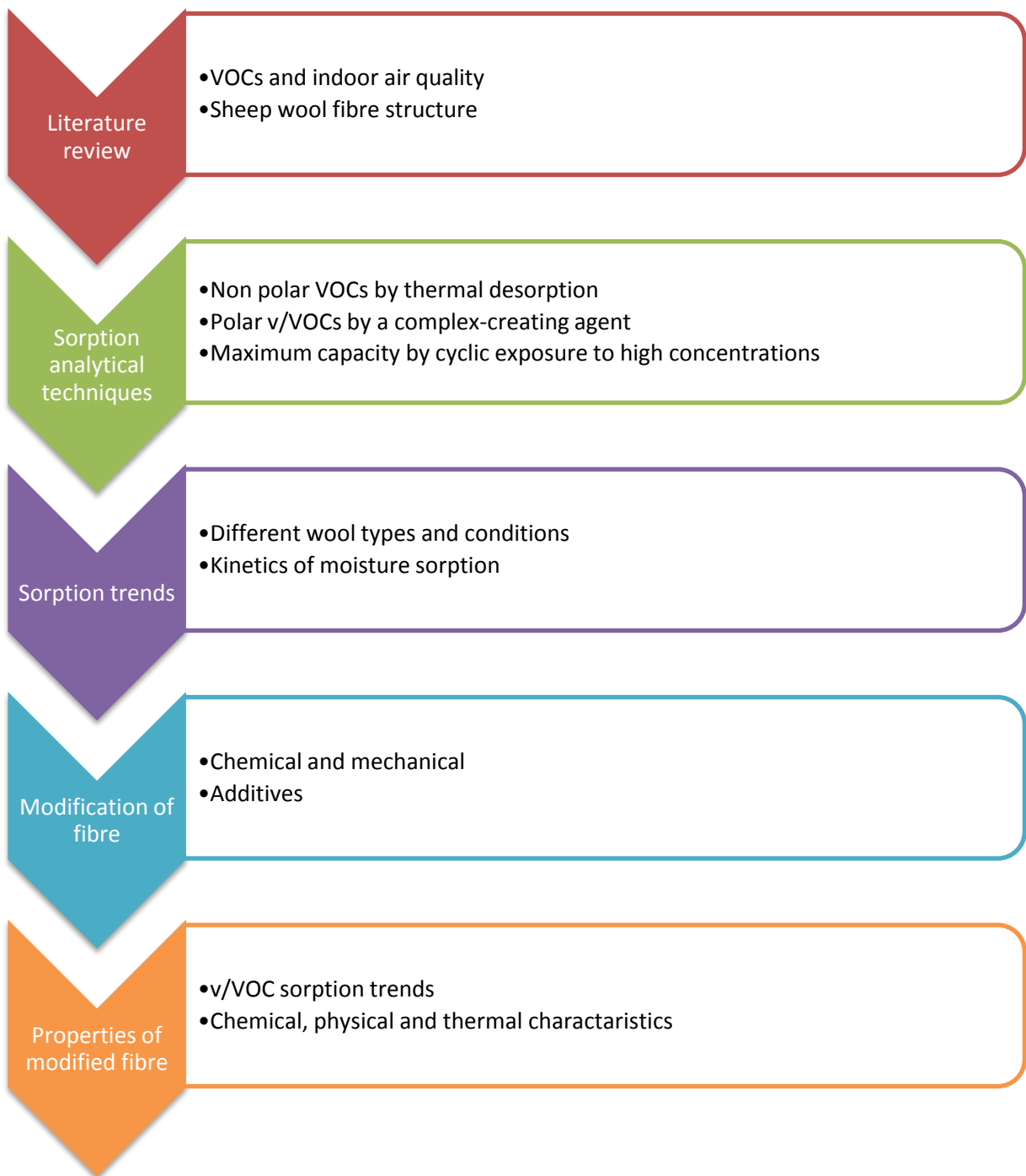


Figure 1.3: Workflow diagram of work carried out to assess and enhance sheep wool fibres' ability to sequester VOCs from the indoor built environment.

Chapter 2: Literature review - VOCs and sheep wool fibre for their sorption

2.1 VOCs and indoor air quality

VOCs are frequently linked to what is termed “sick building syndrome” (SBS), which refers to a collection of symptoms that include eye irritation, stuffy or runny nose, dry skin, headache, fatigue, and difficulty to concentrate. The first noticeable case of SBS was in the 1970s, Sweden (Sundell *et al.*, 1990), where SBS was observed in preschools with “large number of cases of eye irritation, stuffy nose, fatigue, and other conditions”; the cause was attributed to casein that was emitted from self-levelling cement. Several similar cases were thereafter reported such as 10,000 Canadian buildings in the mid-1990s, and the Environmental Protection Agency’s (EPA) U.S. headquarters, which reported an estimated incurred cost of \$1 million due to decreased productivity (Wallace, 2001).

2.1.1 The spectrum of VOCs

The relationship between VOCs and health risks is far from a direct one, primarily because we are not completely aware of the individual and synergistic health effects of VOCs. This is due to the simple fact that there are too many of them, which raises the question: what defines if a chemical substance is a VOC? Different organisations vary in their views.

WHO define VOCs as organic compounds with boiling points from 50°C to 260°C (World Health Organization, 1989), but this definition was based on analytical limitations rather than health effects (Wolkoff and Nielsen, 2001). Figure 2.1 lists other categories.

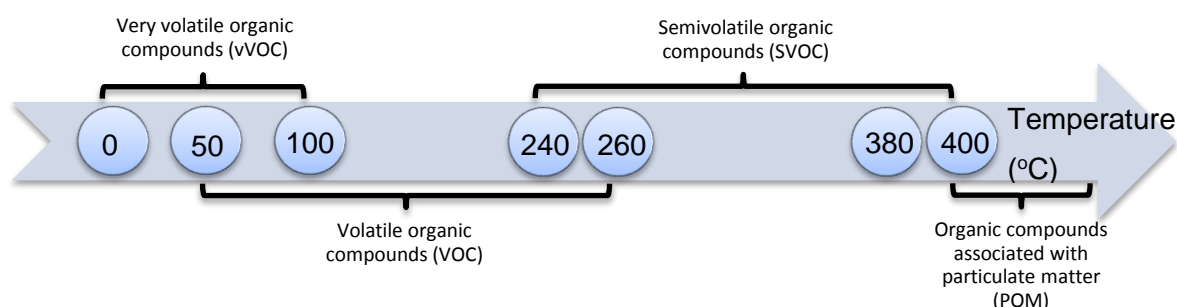


Figure 2.1: WHO's categorisation of VOCs based on their boiling points.

The EPA's definition has been influenced by the policies it has been implementing. It initiated a policy on volatile organic compound reactivity in 1971, but set no guideline limits for non-industrial settings (US EPA, 2012). It recommended the reduction of VOCs, and pays special

attention to those which photochemically form oxidants – mainly ozone. It also allowed the exemption of some VOCs if they can substitute an already-used more reactive compound. However, later research proved that some of these exempt VOCs indirectly produced as much ozone as the former ones, which eventually led EPA to limit the definition of non-VOCs: a compound capable of producing ozone equal to or less than ethane does when present at a concentration not exceeding 4 parts per million (ppm) (Dimitriadis, 1999).

Another definition is found in a working document supporting the European Mandate M/366 that describes the technical specifications for horizontal measurement/test methods concerning indoor air emissions (Technical Committee CEN/TC 351, 2012). It defines VOCs according to their elution through a gas chromatography capillary column coated with 5% phenyl and 95% methyl-poly-siloxane (Figure 2.2).

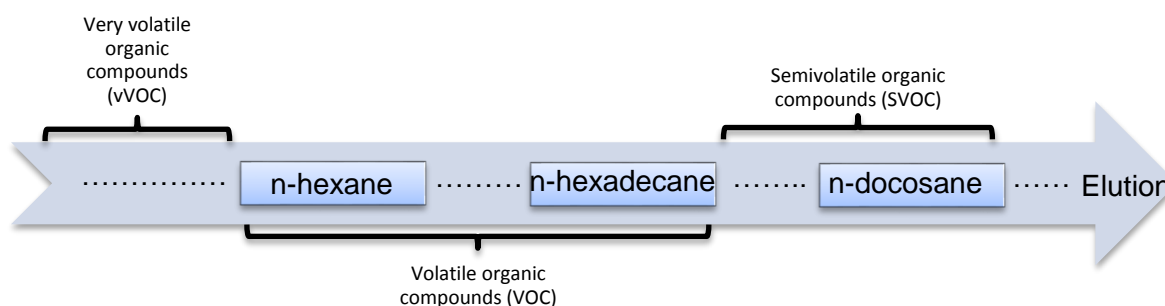


Figure 2.2: VOC categorisation according to European Mandate M/366 technical committee, based on their elution through a GC column.

There are several European indoor emission labelling schemes, adopting their own definition of VOCs. The scheme set by the German federal ministry of transport, building and urban development (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB), 2012) is tied to legal requirements of building codes. They include as VOCs “compounds within the retention range of C₆ to C₁₆” and as SVOCs compounds within the “retention range from C₁₆ up to C₂₂”. Other schemes are mentioned later on under section 2.1.5.1

2.1.2 Minor hazards and low levels

In most cases, levels of exposure are very low compared to what the public perceives as poor indoor air quality. A study looking at controlled short-term exposure to Microbial VOCs (MVOCs) - those that are emitted from microorganisms, including alcohols, ketones, sulphur compounds, terpenes and their derivatives (Claeson *et al.*, 2009, 2002) - lead participants to perceive poor air quality such as stale air and smells only when concentrations are 10-100 times higher than what is normally encountered (Claeson *et al.*, 2009). In another study looking

at exposure to 3-methylfuran at a high concentration, although no subjective symptoms were noted, objective measurement of eye and airway irritation were significant (Wålinder *et al.*, 2005), indicating that SBS effects might not always be perceived although they do actually exist.

As in the case of other pollutants, synergistic effects can exacerbate symptoms at such low levels (Cometto-Muñiz *et al.*, 2004, 1997). Adding to that, not every indoor compound and pollutant has been identified (Wolkoff *et al.*, 1997). This might explain why some studies show a change in perceived air quality, increase of headaches, and diminished efforts when a source of a mixture of VOCs is introduced (Wargocki *et al.*, 1999). Also individual characteristics of the occupants plays an obvious role; it seems that women for example suffer more with SBS than men (Brasche *et al.*, 2001) and genetic factors play a major role (Rohr *et al.*, 2008). Observations change when considering long term exposures (Claeson *et al.*, 2009). Hence, the overall picture is far from being comprehensively understood.

2.1.3 Major hazards

Some VOCs are known or suspected carcinogens, with the top three frequently identified to be benzene, chloroform, and para-dichlorobenzene (Guo *et al.*, 2004; McCann *et al.*, 1986; Tancredi *et al.*, 1987; Wallace, 1991); each contributes to hundreds of annual cases, and VOCs in general contribute to thousands of annual cases – roughly similar to the cancer cases radon gas causes non-smokers (Wallace, 2001). Unlike the costs of about \$500,000 per test to study carcinogenetic effects of chemicals, mutagenicity tests are much less expensive. Therefore, several VOCs are labelled as confirmed mutagenic. Remarkably, of chemicals tested for both carcinogenetic and mutagenic effects, 80% exhibit both characteristics (Gold *et al.*, 1984).

2.1.4 Measuring human health exposure

Measurement of VOCs is frequently reported in the literature. The EPA started off by investigating outside sources such as building ventilation outlets, industrial smoke emissions, water emissions, etc. (Wallace, 2001). The American National Academy of Sciences later directed the attention to personal exposure, leading to the development and use of personal monitors (Wallace and Ott, 1982). In 1986, in a major U.S. study, Total Exposure Assessment Methodology (TEAM) used this equipment and surprised the scientific community with the results. As a case study, as some areas were surrounded by numerous petroleum refineries, benzene was of particular interest. The remarkable observation was a vivid contrast between emissions levels from sources and human exposure from these sources (Figure 2.3): “even non-smokers living with a smoker were receiving more benzene from that source than from the major industrial sources just down the street” (Wallace, 2001). Weighted exposure takes

into consideration the levels of VOCs and the time spent exposed to them. For gasoline-related VOCs, 35-56% of exposure is attributed to homes, 22-49% to offices, and 5-20% to commuting even though higher concentrations are encountered whilst commuting (Carrer *et al.*, 2000; Chan *et al.*, 1991; Marchand *et al.*, 2006). Logically then, indoor emissions are of far greater importance.

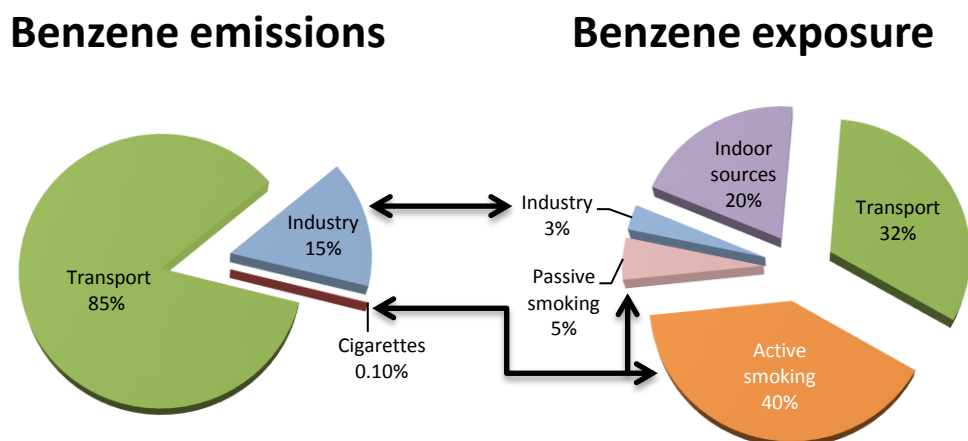


Figure 2.3: Benzene emission and exposure, showing that exposure from passive smoking is greater than from industry even though the opposite relationship is true for emissions. Derived from (Klepeis *et al.*, 1996; Wallace, 2001).

2.1.4.1 Techniques and limitations

A great number of studies of indoor VOC measurements resulted over the years, many of which are published in the Journal of Exposure Analysis and Environmental Epidemiology and Journal of Environmental Monitoring. Some focused on a group of indoor products such as polymeric materials (Yu and Crump, 1998). Studies differ (Table 2.1) in their scope, surrounding conditions (e.g. ozone concentrations), analytical techniques, and sampling methods: different adsorbents (Table 2.2), passive collection (diffusion) or active collection (pumping a specific amount of air through). A number of these differences impact the results; for example, measurements of personal exposure tend to be less than those of indoor air sampling. Other factors such as seasonal variation and difference in temperature or humidity do not relate as much (Fellin and Otson, 1994). The overall results are quite varied, as Figure 2.4 and Figure 2.5 show noticeable differences both between different studies and between mean and highest recorded values. Therefore, it is recommended that comparisons between studies “should be done on a compound-by-compound basis” (Jurvelin *et al.*, 2001a).

Table 2.1: Differences between some major exposure measurement studies (Jurvelin *et al.*, 2001a).

Study	Sampling method	Analytical technique	Scope	Reference
Total exposure assessment methodology (TEAM), 1986	Active sampling using Tenax GC adsorbent tubes	GC	20 toxic, carcinogenic, or mutagenic organic compounds in air and water of 1000 residents in 10 U.S. cities	(Hartwell <i>et al.</i> , 1987; Wallace <i>et al.</i> , 1991, 1987, 1986)
German Environmental Survey (GerEs II), 1990-1991	Passive sampling using OVM-3500 badges	GC-FID	74 VOCs for 113 individuals	(Hoffmann <i>et al.</i> , 2000)
Concord Environmental Corporation and Health Canada study, 1991	Passive sampling using OVM-3500 badges	GC-MS	26 VOCs in 754 Canadian homes at different seasons	(Fellin and Otson, 1994)
EXPOLIS study, 1996-1998	Active charcoal (Carbotech) in Basel, Tenax TA in Athens, Helsinki, Milan and Prague	GC-FID and GC-MS	30 VOCs (out of 323 detected) for 401 individuals, their residence and workplace in European cities	(Jurvelin <i>et al.</i> , 2001a)

2.1.4.2 Sources and categorisation of VOCs

The huge diversity of v/VOCs naturally complicates the attribution of specific VOCs to specific sources. Their diversity largely outnumbers the different classifications other pollutants have, making them the least categorised. A great number of these VOCs are introduced by household products. An EPA survey aimed at 31 VOCs and 1159 common household products (Sack *et al.*, 1992) found toluene, xylenes and dichloromethane present in over 40% of the products. VOCs comprising over 20% of the weight of the products included the latter plus acetone, 2-butanone, hexane, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, and 1,1,2-trichlorotrifluoroethane. The vast majority, if not all, of the other indoor VOCs are introduced by building products.

Table 2.2: Different sampling methods used for atmospheric VOC measurements (Wallace, 2001).

Method	Advantages	Limitations
Activated charcoal	<ul style="list-style-type: none"> Used for active or passive sampling, where VOCs are concentrated, and are then desorbed by a solvent (such as CS₂). Cheap 	<ul style="list-style-type: none"> Manufacturing leaves background contamination; when sampling low concentrations (non-occupational environments) passively, longer test times are required to compensate.
Tenax	<ul style="list-style-type: none"> Has low background contamination. More reliable recovery of sorbed VOCs. No need for solvent; allows thermal desorption as it is stable at temperatures up to 250°C Reusable 	<ul style="list-style-type: none"> Reacts with some chemicals (benzaldehyde, phenol, etc.) Does not retain vVOCs, which reduces total VOC values
Multi-sorbent systems	<ul style="list-style-type: none"> Employs a combination of Tenax for most VOCs and activated charcoal for those incompatible with Tenax 	
Direct air sampling	<ul style="list-style-type: none"> No sorption/desorption involved, reducing contamination 	<ul style="list-style-type: none"> Requires very sensitive detectors

Table 2.3 categorises them based on the most common found in worldwide studies; the top most repetitive being a mixture of benzene, toluene and xylenes (BTX), acetone, tetrachloroethylene, and hexane. Toluene has been found indoors at an average of 70µg/m³, which is equivalent to about 10% of the average total VOC concentrations (Lorimier *et al.*, 2005). Table 2.4 on the other hand lists the identified major sources for some of the more hazardous indoor VOCs, all of which are known or suspected carcinogens.

Table 2.3: Most common VOCs, by order, detected (Wolkoff and Nielsen, 2001).

Australian review (Brown, 2007)	European audit (Bernhard <i>et al.</i>, 1995)	U.S. review (Holcomb and Seabrook, 1995)	BASE study, U.S. (Girman <i>et al.</i>, 1999a)	Swedish housing (Bornehag and Stridh, 2000)	German study: Selected VOCs (Reitzig <i>et al.</i>, 1998)
Benzene	Acetone	o-Xylene	Acetone	Toluene	Group 1: Phenoxyethanol Butyldiglycol acetate Longifolene Dimethyl phthalate
Tetra-chlorethylene	Isoprene	Benzene	Hexane	Decane	
p-Dichlorobenzene	2-Methylpentane	Tetrachloroethylene	Toluene	Dodecane	
Ethylbenzene	Hexane	m-, p-Xylenes	1,1,1-Trichloroethane	Nonanal	
m-, p-Xylenes	2-Methylhexane/benzene	Ethylbenzene	Methyl chloride	Undecane	
1,1,1-Trichloroethane	Heptane	Trichloroethylene	Benzene	Limonene	Group 2: α -Pinene Camphene β -Pinene 3-Carene
o-Xylene	Toluene	Toluene	Ethanol	C11-Alkane	
Decane	m-, p-Xylenes	1,1,1-Trichloroethane	2-Propanol	C12-Alkane	
Toluene	o-Xylene	Dichlorobenzenes	Dichlorofluoromethane	Xylenes	
1,2,4-Trimethylbenzene	Decane	Styrene	m-, p-Xylenes	C10-Alkane	
Hexane	Trimethylbenzene	Undecane	2-Butanone	Trimethylbenzenes	Group 3: Styrene o-Xylene C12-Alkanes
Nonane	Limonene	Dodecane	Trichlorofluoromethane	Butoxyethoxyethanol	
Limonene		Octane	o-Xylene Undecane	Butoxypropanol C7-Alkane	
			Tetrachloroethylene		Group 4: 1,2,3-Trimethylbenzene 1,2,4-Trimethylbenzene Methylcyclohexane
			Methylene chloride		
			1,2,4-Trimethylbenzene		
			Decane		

Table 2.4: Most important sources of exposure of indoor VOCs identified by TEAM studies (Wallace, 2001).

VOC	Most important source of exposure	Quantity contributed
Benzene	Smoking	45% of total exposure
Chloroform	Chlorinated water (bathing/showering and drinking)	33µg/l of treated water entering soft drink manufacturing plants and 24µg/l of soda drinks
Tetrachloroethylene	Dry-cleaned clothes	100µg/m ³ to 1.5mg/m ³
Para-dichlorobenzene (p-DCB)	Mothcakes and deodorizers	500µg/m ³
Dichloromethane (DCM)	Paint strippers and solvent-based cleaners	100mg/m ³
Polyaromatic hydrocarbons (PAHs)	Smoking and uncontrolled burning of biomass	Up to thousands fold of levels of developed countries

Likewise but on a larger geographical scale, the INDEX project subcategorises VOCs according to their assessed health risks throughout Europe (Koistinen *et al.*, 2008). Table 2.5 summarises the findings.

Household products VOCs are not always the same as construction VOCs – those emitted from construction materials. Prioritisation of building materials as indoor pollution sources (BUMA) (University of Western Macedonia, 2006) was a European project of large importance that created a database of 400 building materials, 400 emitted substances and 8,000 emission data. It found that “all measured VOC substances exhibit high concentrations in houses”, particularly in the winter. The most used building materials are identified as water based paint, plaster and particleboards, and the VOCs emitted were varied depending on emission sources and outdoor concentrations. The most abundant were formaldehyde, acetaldehyde, acetone and d-limonene; carbonyls comprised 40 to 80% of the VOCs, followed by aromatics, whereas hydrocarbons such as a mixture of benzene, toluene, ethylbenzene, and xylenes (BTEX) and terpenes seem to reach low levels with time (see Figure 2.4 and Figure 2.5 for exposure studies summaries) (Missia *et al.*, 2010). The project concludes that building material emission must be prioritised based on no less than both formaldehyde and total VOC (TVOC) concentrations. Also noted was ozone, which contributes to several relevant indoor reactions, oxidising up to 1/3 of indoor VOCs to formaldehyde and aldehydes at relatively low concentrations (28-44 ppb). It also reacts with unsaturated hydrocarbons (wood, linoleum, resins, detergents, waxes, lubricants, etc.) (Weschler *et al.*, 1992). Still, the project faced some limitations that depreciate the actual impacts: (1) it did not assess the health impact of all the measured VOCs, and (2) it disregarded the health impact of combined VOCs.

Table 2.5: Categorisation of VOCs in Europe according to their health risks.

	Compounds	Considered a concern when present at a concentration of	Comments
High priority pollutants	Formaldehyde	1 µg/m ³	Most important sensory irritant. It is present in the background of rural areas at 1 µg/m ³ .
	Benzene	N/A - carcinogen	Significantly increases the risk of leukaemia in highly trafficked urban areas.
	Naphthalene	10 µg/m ³	Some subpopulations are highly sensitive.
Low priority pollutants	Acetaldehyde	200 µg/m ³	Not enough available European studies, but levels are presumed to be 10-20 times lower.
	Toluene	300 µg/m ³	Effects central nervous system. Levels are 16 times lower.
	Xylenes	200 µg/m ³	All isomers and mixtures cause mild effects on central nervous system and mild irritation. Levels are 20 times lower.
	Styrene	250 µg/m ³	Causes neurological effects; genotoxicity is observed at low concentrations, but no evidence of being carcinogenetic is established. Levels are 100 times lower.
Pollutants requiring further research	Limonene	450 µg/m ³	Widely used in consumer products. No neurological effects observed at background levels (10 times lower). May form irritants when O ₃ is present.
	α-Pinene	450 µg/m ³	Widely used in consumer products. No irritation effects observed at background levels (40 times lower). May form irritants when O ₃ is present.

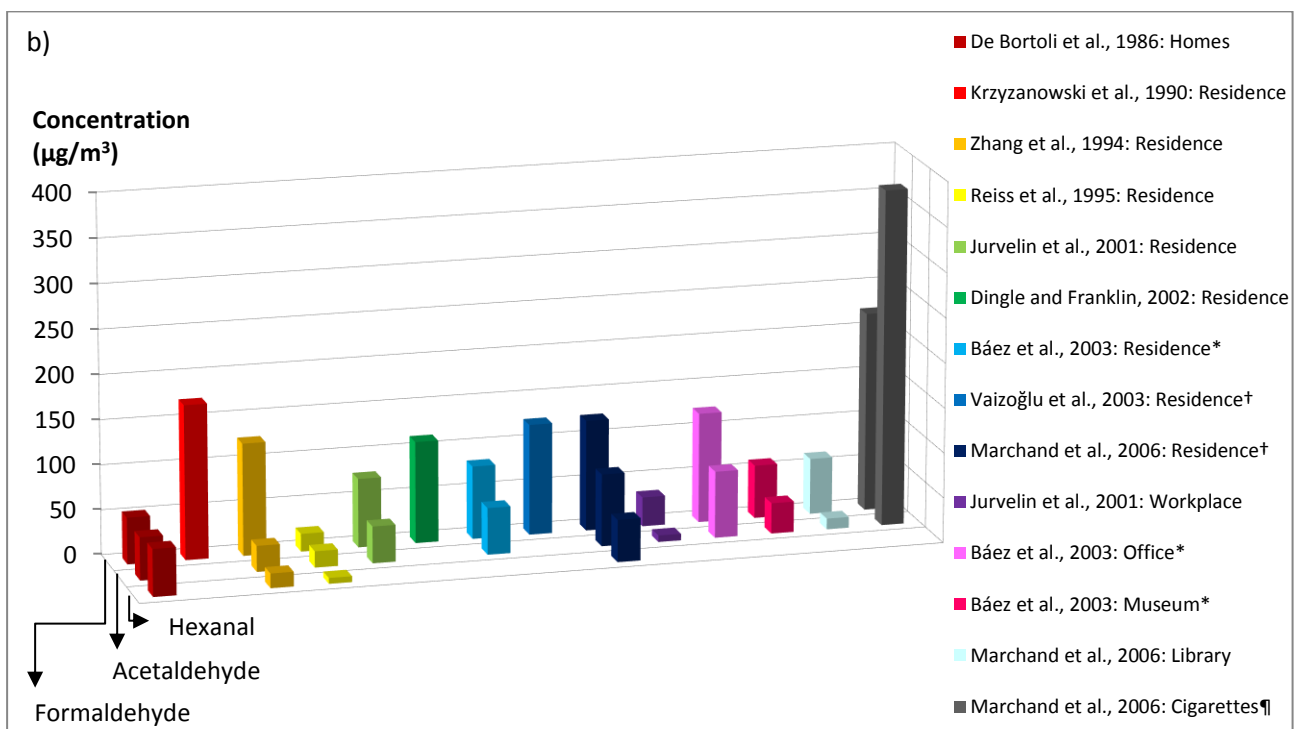
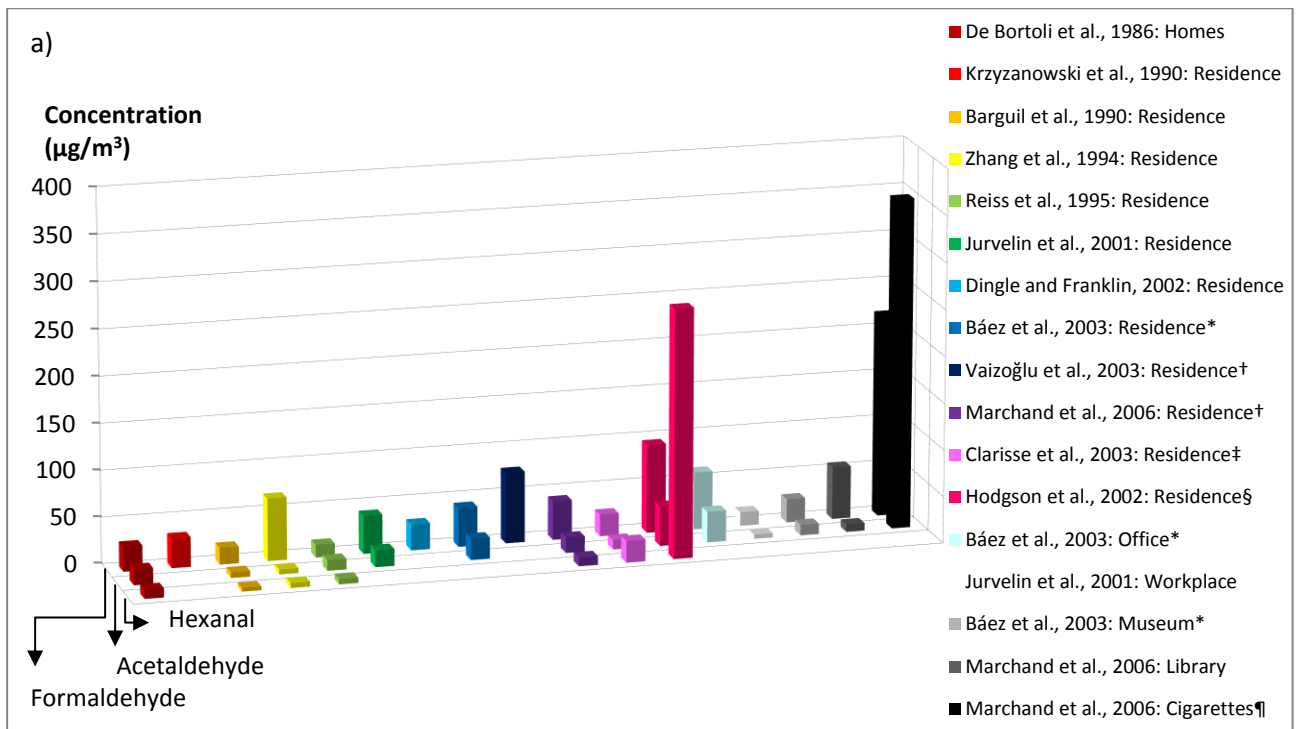


Figure 2.4: Common carbonyl measurements primarily arranged by the place studied and in ascending date of study within each category: (a) mean values, (b) highest recorded values. (Báez *et al.*, 2003; Barguil *et al.*, 1990; Clarisse *et al.*, 2003; De Bortoli *et al.*, 1986; Dingle and Franklin, 2002; Hodgson *et al.*, 2002; Jurvelin *et al.*, 2001; Krzyzanowski *et al.*, 1990; Marchand *et al.*, 2006; Reiss *et al.*, 1995; Vaizoğlu *et al.*, 2003; Zhang *et al.*, 1994)

* Averages of 2 or 3 structures' means

† Mean average of ranges

‡ 2/3 of flats were recently refurbished

§ Newly manufactured residence

¶ After 5 cigarettes in a closed room

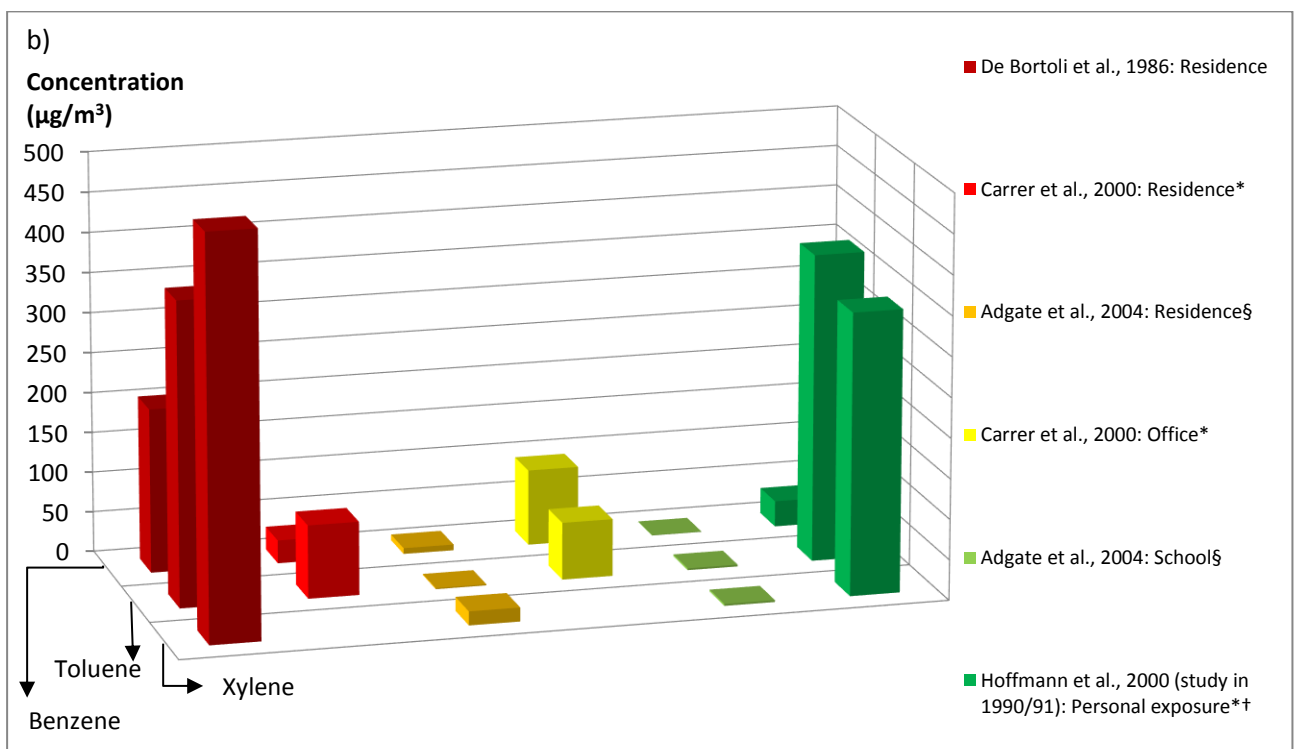
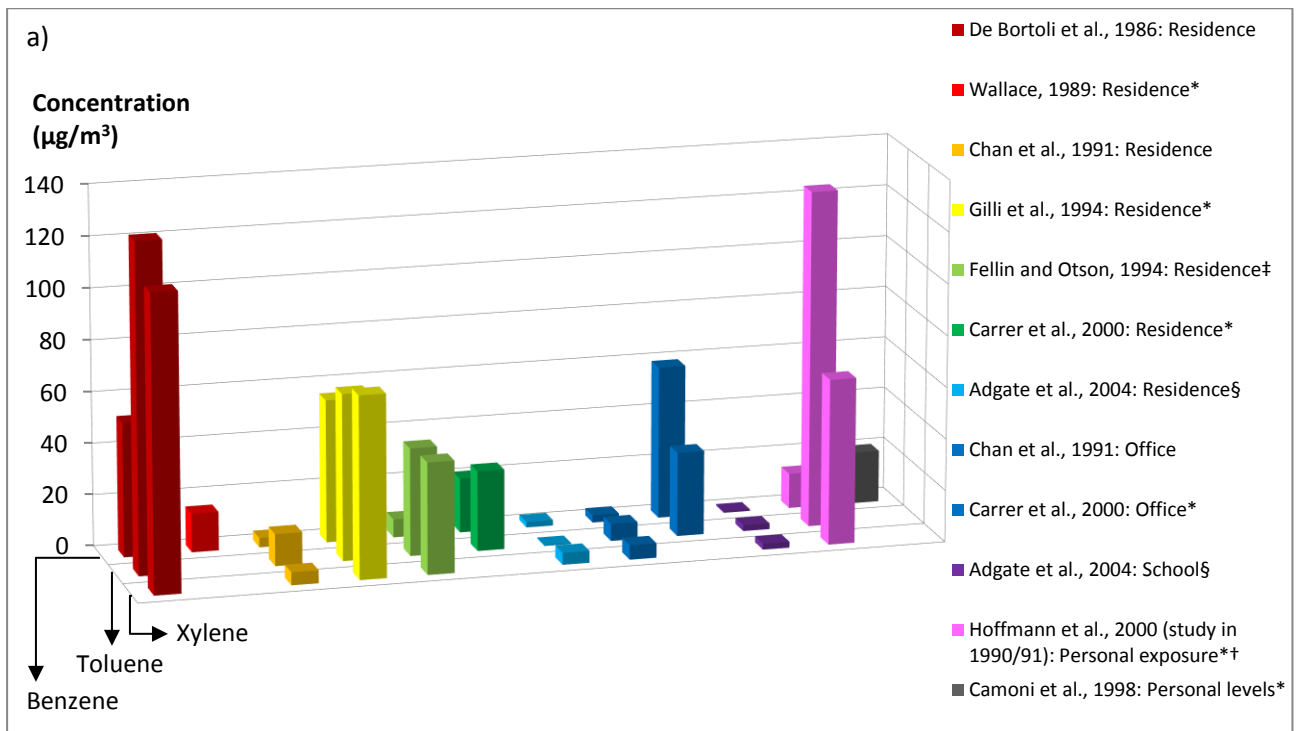


Figure 2.5: BTX measurements primarily arranged by the place studied but also arranged in ascending date of study within each category: (a) mean values, (b) highest recorded values. (Adgate et al., 2004; Camoni et al., 1998; Carrer et al., 2000; Chan et al., 1991; De Bortoli et al., 1986; Gilli et al., 1994; Wallace, 1989)

*Personal exposure

†No constraints on individual activity; high variation due to smoking, traffic emissions, and work conditions

‡Highest seasonal average, during fall

§Average of winter and spring measurements

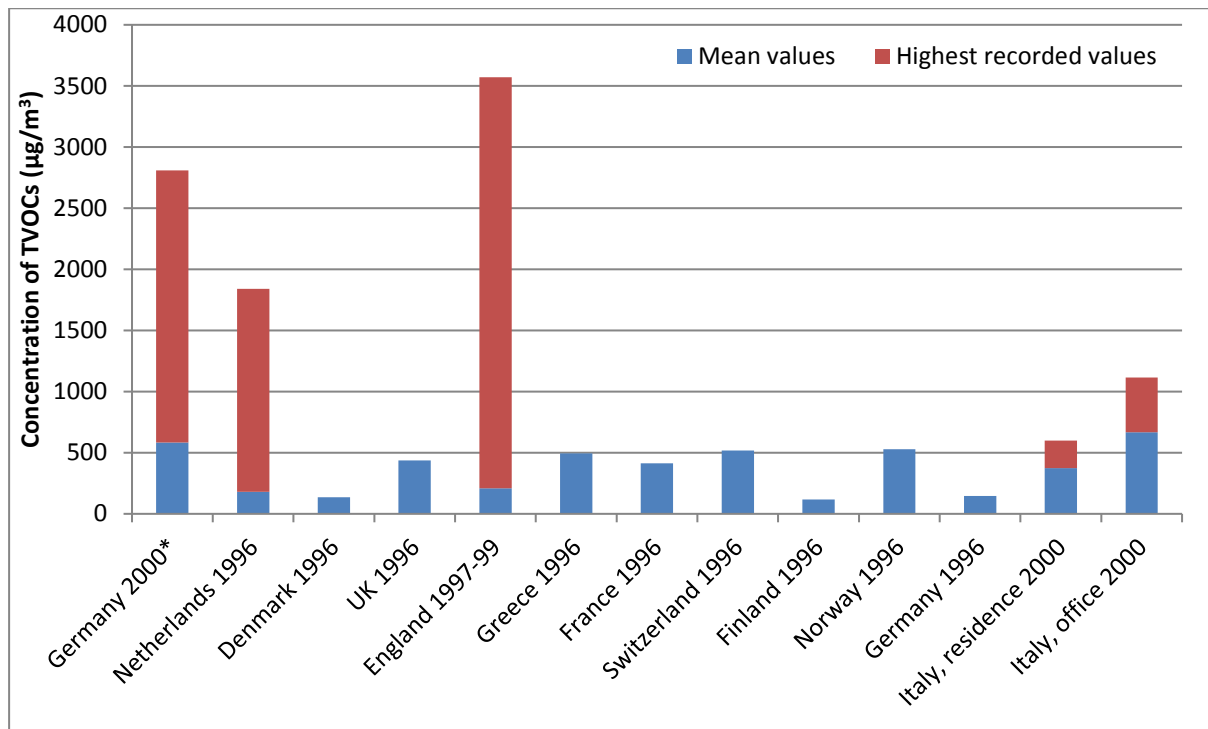


Figure 2.6: TVOC measurements (Bluyssen *et al.*, 1996; Carrer *et al.*, 2000; Coward *et al.*, 2001; Hoffmann *et al.*, 2000)

* Personal exposure, no constraints on individual activity; high variation due to smoking, traffic emissions, and work conditions

A Chinese study addressed another real-life aspect of buildings as it conducted its measurements in a developing city where refurbishments and decorations are frequent (Chi *et al.*, 2016). They were able to categorise TVOC and formaldehyde emissions based on categorised time scales: ‘decoration pollution’ being the main contributor during the first year, ‘transition pollution’ being emitted from composite sources during the second year, and ‘consumption pollution’ being the main supplier in the third year onward. Combustion was found to be the main source of ‘consumption pollution’ although concentrations are so irregular they could not be predicted.

2.1.4.3 Challenges of combining abundance and hazardousness categories

Although some of the aforementioned studies attempt to categorise VOCs by abundance, exposure and hazards, trying to establish which VOC is responsible for which symptom is not straightforward and is scarcely researched. For example, in the case of terpenoids (dicarbonyls diacetyl, 4-oxopentanal (4-OPA), glyoxal, glutaraldehyde, and methyl glyoxal, and similar oxygenated compounds), some have been associated with the release of proinflammatory mediators by lung epithelial cells, and potential effects may be caused by cumulative exposure to small amounts of these chemicals (Anderson *et al.*, 2010).

Since SBS symptoms are frequently reported for recently renovated buildings, studies sensibly relate them to VOC concentrations (Berglund *et al.*, 1984; Zweers *et al.*, 1992). One such study successfully pinpointed the significant VOCs and sources responsible for the symptoms via a multivariate regression analysis: styrene from carpets and 2-butoxyethanol and 2-propanol from

cleaning products (Brinke *et al.*, 1998). Still, the exact identity of VOCs responsible for indoor irritation is not fully established (Wolkoff *et al.*, 2006). The fact is, indoor VOCs are always present in unpredictable mixtures, and undoubtedly analytical techniques do not detect all components (Wolkoff *et al.*, 2006).

As noted earlier, real-life mixtures of VOCs and other elements complicate things even more, through poorly understood synergistic effects. For example, mixtures of 2-butene, NO_x and UV light cause airway irritation similar to formaldehyde, which is not observed if 2-butene is replaced with butane (Kane and Alarie, 1978a); and a mixture of 2-butene, butadiene and ozone cause eye irritation (Stephens *et al.*, 1961).

An imperative factor that is usually ignored is reactive atmospheric chemistry. This is significant because building products emit more secondary emissions than primary during their lifetime, with the latter being more likely to affect perceived air quality (Knudsen *et al.*, 1999; Wolkoff, 1999). A study on photochemical oxidants (Kane and Alarie, 1978b) showed that the following hydrocarbons and UV light adversely affected the lung function of mice in the this order of magnitude: propene > 1,3-butadiene = 1-butene = cis-2-butene > ethylene. It also demonstrated that exposure to formaldehyde for 3 hours/day on 4 days caused irritation.

Another study on isoprene and ozone mixtures (Rohr *et al.*, 2008) report cumulative irritation in mice exposed for 3 hours/day on 4 days. Isoprene is emitted by plants, animals and humans, and is therefore expected to become concentrated in areas with higher population density, such as in the case of congregation halls.

Ozone levels vary considerably even from room to room, and the related reactions are quite fast (Weschler, 2000). The major sensory active compounds resulting from ozone reactions are unknown, and may include radicals. However, formaldehyde is known to be a major product of alkene oxidation, which adds to its significance. Such reactions are dependent on surrounding factors – low relative humidity is shown to increase irritation symptoms.

Wolkoff *et al.* (Wolkoff *et al.*, 2012a, 2008a) showed that neither *d*-limonene nor ozone on their own showed consistent health effects. But residual *d*-limonene and formaldehyde produced from their reaction account for 75% of the decrease in respiratory frequency. They later concluded that the reaction products isopropyl-6-oxo-heptanal and 4-oxopentanal contribute to irritation and irreversible lung damage respectively (Wolkoff *et al.*, 2007). The effects were not cumulative in this case (possibly due to exposure time being only 1 hour/day), and they disappeared when the aerosol was separated from the gas using a denuder. They therefore conclude that “ultrafine particles that are generated from ozone-initiated *d*-limonene chemistry and denuded are not causative of sensory effects in the airways”. So the synergistic effect of solid particles with VOCs appears to be yet another important factor. Interestingly, another study concerning limonene and other terpenes showed that

when they are mixed with ozone, 0.1-0.2 μ m particles are formed, and when ozone is introduced again results in 0.2-0.3 μ m particles (Wainman *et al.*, 2000; Weschler and Shields, 1999). Combining that with predictions that ground level ozone is on the rise in the UK (Vardoulakis and Heaviside, 2012), this increase in particle size with the availability of more ozone could well be a key complement to SBS.

A way forward might be combining exposure and symptom results with studies investigating VOC levels in the breath (Bikov *et al.*, 2013; King *et al.*, 2012), blood (Blount *et al.*, 2006, p. 31; Sexton *et al.*, 2005), and mother's milk (Kim *et al.*, 2007).

2.1.5 Current procedures to address indoor air quality

There exist occupational concentration limits for common VOCs, but such limits are aimed at industrial buildings where known pollutants are predicted to rise to very high concentrations. Therefore, occupational limits are set at much higher concentrations than those generally encountered when assessing indoor air quality. When talking about such smaller concentrations, there is no established relationship between quantity and symptoms or perceived air quality as explained above. Still, there are some guidelines for TVOC exposure: 200mg/m³ based on toxicological data (Mølhave, 1991), and 300mg/m³ based on expected achievable levels (Seifert, 1992).

2.1.5.1 Guidelines and limits

The EPA set the bar at 5mg/m³ for a mixture of 22 common VOCs, exposure to which causes headaches (Otto *et al.*, 1990). Some individual VOC concentration limits are also recommended. WHO set quantitative guidelines for some of the major indoor VOCs (World Health Organization, Regional Office for Europe, 2010), summarised in Table 2.6. The INDEX project mentioned previously sets recommended limits for some VOCs as summarised in Table 2.5 (Koistinen *et al.*, 2008).

Under the German AgBB scheme (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB), 2012), buildings with TVOC concentrations greater than 3mg/m³ are labelled as questionable, and the same limit is used by certification bodies such as Deutsche Gesellschaft für Nachhaltiges Bauen (DGNB, 2012). Lowest permissible concentrations of interest for individual VOCs are also specified. A recent French regulation placed a mandatory labelling of construction products installed indoors (excluding untreated metals and glass), floor and wall coverings, paints and lacquers according to emission testing as per ISO16000 (Ministère De L'écologie, Du Développement Durable, Des Transports Et Du Logement, 2011). A new draft Belgian regulation on VOC emissions has also been notified to the European Commission (Federal Public Service Of Health, Food Chain Safety And Environment, 2012).

Table 2.6: Quantitative guidelines set by WHO regarding common indoor VOCs (World Health Organization, Regional Office for Europe, 2010).

VOC	Recommendations	Notes
Benzene	<p>No safe level of exposure can be recommended.</p> <p>Unit risk of leukaemia per 1 µg/m³ air concentration is 6 × 10⁻⁶</p> <p>Airborne concentrations associated with an excess lifetime risk:</p> <p>1/10 000: 17µg/m³; 1/100 000: 1.7µg/m³; 1/1000 000: 0.17µg/m³</p>	<p>Indoor concentrations are generally higher than those in outdoor air.</p> <p>Typical indoor concentrations are below the lowest levels showing evidence of adverse health effects.</p>
Formaldehyde	<p>0.1 mg/m³ as a 30min/day average to prevent sensory irritation in the general population.</p> <p>Around 0.2mg/m³ to preventing risks such as cancer.</p>	<p>Indoor exposures are the dominant contributor through inhalation.</p> <p>No indication of accumulation of effects over time with prolonged exposure</p>
Naphthalene	<p>0.01mg/m³ as an annual average of continuous exposure.</p>	<p>Use of mothballs increase indoor concentrations increase up to 100-fold over typical 0.001mg/mg³</p>
PAHs (especially benzo(a)pyrene)	<p>No safe level of exposure can be recommended.</p> <p>Unit risk for lung cancer for PAH mixtures is estimated to be 8.7 × 10⁻⁵ per ng/m³ of benzo(a)pyrene.</p> <p>Concentrations for lifetime exposure to benzo(a)pyrene producing excess lifetime cancer risks:</p> <p>1/10 000: 1.2ng/m³; 1/100 000: 0.12ng/m³; 1/1 000 000: 0.012ng/m³</p>	<p>In view of the difficulties in developing guidelines for PAH mixtures, benzo(a)pyrene was considered to represent the best single indicator compound.</p>
Trichloroethylene	<p>Unit risk est. of 4.3 × 10⁻⁷ per µg/m³</p> <p>Airborne concentrations associated with an excess lifetime cancer risk:</p> <p>1/10 000: 230µg/m³; 1/100 000: 23µg/m³; 1/1 000 000: 2.3µg/m³</p>	<p>Carcinogenicity (with the assumption of genotoxicity) is selected as the end-point for setting the guideline value.</p>
Tetrachloroethylene	<p>0.25mg/m³ as an annual average of continuous exposure.</p>	<p>Carcinogenicity is not used as an endpoint.</p>

Only about 7.5% of green building certifications worldwide address indoor environment quality, limiting optional measurements most frequently to TVOC, formaldehyde and CO₂ concentrations (Wei *et al.*, 2015). In the UK, BREEAM is a voluntary schemes that assesses indoor air quality for new construction, in-use buildings and refurbishments based on standards developed by BRE (“BREEAM,” 2018). For finished construction that is not yet occupied, it gives credit when formaldehyde concentrations are less than or equal to 100µg/m³ (averaged over 30 minutes) and TVOC concentrations being less than 300µg/m³ (over 8 hours), in line with the Building Regulation requirements (“Ventilation,” 2010). Another globally recognised green building rating system is the Leadership in Energy and Environmental Design, part of the U.S. Green Building Council (“LEED | USGBC,” 2017). For finished construction that is not yet occupied, it sets the maximum concentrations guidelines for formaldehyde at 27ppb (16.3ppb for healthcare buildings) and TVOC at 500µg/m³ (200µg/m³ for healthcare buildings; “LEED v4 for Homes and Midrise,” 2013). Other voluntary European schemes include NaturePlus (international), Blauer Engel/Blue Angel Ecolabel (Germany), M1- Emission Classification of Building Material (Finland), CESAT Schema (France), Umweltzeichen/Austrian Environmental Label, Eco Devis (Switzerland), and Indoor Climate Label (Denmark and Norway).

Table 2.7 shows other limit values set by European regulations and schemes, as the European directive leaves these figures to individual authorities. Figure 2.4-Figure 2.6 show that when VOC values are summed up, they more often than not exceed recommended levels; the same case is observed for benzene on its own.

It is interesting that regulations such as the U.S. ones do not require producers to disclose all ingredients present in a consumer product – a mixture termed “fragrance” is deemed sufficient. Steinemann *et al.* (2011) challenged this reasoning by inspecting the VOCs emitted from 25 different fragranced products, and found that only one out of a total of 133 emitted VOCs was listed on product label and that at least one VOC per product is classed as toxic or hazardous.

2.1.5.2 Practical solutions

The problem of indoor air quality is not yet fully and satisfactorily addressed. A recent study investigated the annual indoor concentration of a birth control cohort study of 72 VOCs over a period of 9 years in Germany (Wissenbach *et al.*, 2016). It concludes that about 42% of the VOCs generally decrease in annual concentration over time, but 10% of them were noted to increase. Those on the increase, based on a linear regression and verified with a Mann-Kendal test, include alkanes and cyclohexane (heptane, octane, cyclohexane) aromatics (o-xylene), esters (ethyl acetate with a significantly high increase, methylcyclohexane, 1-methoxy-2-propylacetat), halogenated hydrocarbons (1,2-dichlorobenzene, 1,4-dichlorbenzene), ketones

Table 2.7: Maximum allowable concentrations of VOCs set by European regulations and schemes.

Limit concentrations based on countries' legislation	Germany(Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB), 2012)	Belgium (Federal Public Service Of Health, Food Chain Safety And Environment, 2012)	France (Ministère De L'écologie, Du Développement Durable, Des Transports Et Du Logement, 2011)	Finland (Finnish Society of Indoor Air Quality and Climate, 2010)
TVOC	120 µg/m ³ µg/m ³ after 28 days of storing in test chamber	1,000 µg/m ³ after 28 days of storing in test chamber	2,000 µg/m ³ for class B 1,500 µg/m ³ for class A 1,000 µg/m ³ for class A ⁺	0.2 mg/m ² h for class M1 and 0.4 mg/m ² h for class M2
Formaldehyde	120 µg/m ³ after 28 days of storing in test chamber	100 µg/m ³ after 28 days of storing in test chamber	120 µg/m ³ for class B 60 µg/m ³ for class A 10 µg/m ³ for class A ⁺	0.05 mg/m ² h and 0.125 mg/m ² h for class M2
Acetaldehyde	N/A	200 µg/m ³ after 28 days of storing in test chamber	400 µg/m ³ for class B 300 µg/m ³ for class A 200 µg/m ³ for class A ⁺	-
Toluene	1,900 µg/m ³ after 28 days of storing in test chamber	300 µg/m ³ after 28 days of storing in test chamber	600 µg/m ³ for class B 450 µg/m ³ for class A 300 µg/m ³ for class A ⁺	-
Carcinogens	10 µg/m ³ after 3 days and 1 µg/m ³ after 28 days of storing in test chamber	1 µg/m ³ after 28 days of storing in test chamber	-	0.005 mg/m ² h for class M1 or M2
TSVOC	100 µg/m ³ after 28 days of storing in test chamber	100 µg/m ³ after 28 days of storing in test chamber	-	-

(1-methyl-2-pyrrolidone) and terpenes (α -pinene with a significantly high increase). Some manufacturers replaced the common VOCs their products emit by other longer-lasting chemicals. Unfortunately, these new chemicals can only delay the release of new VOCs that

still retain toxicological properties. One example of this situation was reported for 51 German dwellings, where many complaints were made 2 years after they were renovated (Reitzig *et al.*, 1998). The VOCs detected were completely new: longifolene, phenoxyethanol, and butyldiglycolacetate.

It is worth noting that TVOC measurements can assess the efficiency of ventilation; some studies showed that concentrations were lower in houses that had mechanical ventilation compared to manual ventilation (Tappler, 2014), but others observe that natural ventilation reduced levels by over 20% more than mechanical ventilation (Carrer *et al.*, 2000). Hence, an effective improvement should tackle homes and offices to begin with without relying on ventilation.

The most promising solution lies within the sorption and/or degradation of VOCs from indoors in a lasting manner, as opposed to only having reduced emissions. Some already existing building materials with added value may be used for this end. Although that field is still in its early stages, with literature discussing the idea just over 20 years ago (Darling *et al.*, 2012; Yu and Neretnieks, 1993), some exciting developments have been taken place; sorptive building materials have been used to improve indoor air quality in Korea and Japan (Seo *et al.*, 2010). Based on the use of activated carbon as a sorptive indoor material, computational fluid dynamics was conducted to ascertain the factors depicting optimal installation of sorptive building materials (Park and Seo, 2016). As far as fibres are concerned, commercial 3D printing allows the incorporation of TiO₂ nanoparticles into a readily available filament of acrylonitrile butadiene styrene that was able to degrade rhodamine 6G in solution, an indication to its catalytic ability to degrade VOCs and be extrapolated to a wide variety of applications. (Skorski *et al.*, 2016). Another study (Seo *et al.*, 2009) looking at the sorption of gaseous VOCs report that an activated carbon layer effectively reduce VOC concentrations, and that other sorptive materials such as gypsum board mixed with a given quantity of activated carbon and boards made out of activated carbon are fairly effective as well. Although activated carbon may be expensive and has a large carbon footprint, the study shows that products containing it demonstrate a long lifetime of the sorption capability.

2.2 Sheep wool fibre for the sorption of v/VOCs

Sorbing volatile organic compounds from indoor air is currently not a straightforward process. The challenge is mainly due to the chemical variability of the different gases and their typical low concentrations.

Sheep's wool stands out from other fibres utilised by the natural insulation industry as being the only protein-based fibre, the others being derived from cellulose rich materials. It's already

been demonstrated that sheep's wool has an inherent sorption ability towards organic compounds such as aqueous formaldehyde (Aluigi *et al.*, 2009; Ghosh and Collie, 2014; Jonas *et al.*, 1947; Reddie and Nicholls, 1971), as it is well known to sorb dyes. It's also been shown to sorb formaldehyde in gaseous form (Curling *et al.*, 2012), with the amount sorbed being quantified using dynamic vapour sorption (DVS): 4.9% by weight (Figure 2.7), with 2/3 of that amount being permanently bound onto the surface.

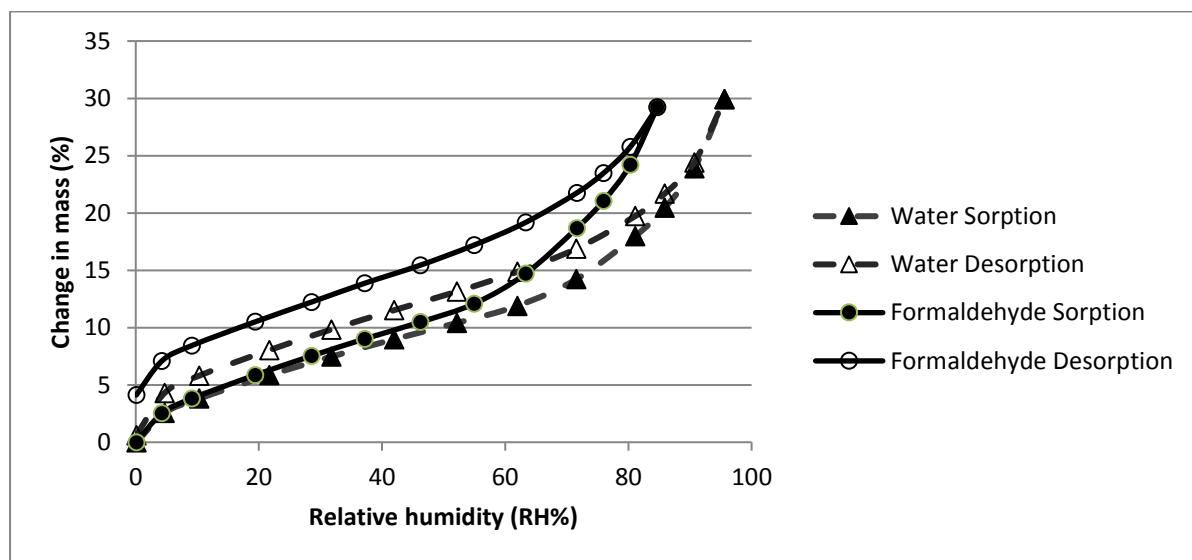


Figure 2.7: Sorption and desorption cycles of sheep wool using DVS, one using moisture and no formaldehyde, while the other using moisture and formaldehyde gas (Curling *et al.*, 2012).

Other gases are reported to be sorbed by wool's protein surface structure, which has a practical application demonstrated in case studies; a rehabilitation school in Bielefeld, Germany, had a reduction of toluene from $1100\mu\text{g}/\text{m}^3$ to $70\mu\text{g}/\text{m}^3$ after the introduction of wool into the building (Thomé, 2006). Wool used in carpets (Ingham *et al.*, 1994; McNeil, 2011) is reported to reduce low levels of formaldehyde (5ppm) to near zero in 30min and high levels (300ppm) to near zero in 4 hours. It is also noted for its rapid absorption of SO_2 and NO_x , and that its absorption capacity remains intact causing no re-emissions for 30 years. Not all studies are conclusive though, as some factors are hard to control. For example, an architectural study (Lu, 2013a) concludes that the use of a wool curtain is ineffective for sorbing indoor formaldehyde; however, many factors were not regulated such as increased relative humidity which is known to increase indoor formaldehyde concentrations (Parthasarathy *et al.*, 2011). Such a factor possibly overshadows the sequestration by wool.

Sheep wool based insulation has been produced and used as an insulation product. Adding to the functionality of such a product is the most effective way of increasing its value. Its use in the construction sector should provide enough of the material to sufficiently sorb v/VOCs, as it may be installed in all lofts and cavity walls. Hence, enhancing sheep's wool property to regulate indoor air quality in a passive manner is a promising solution.

2.2.1 Sheep wool general structure

Sheep wool is known to be composed of about 90% by weight cortical cells (those present underneath the outer surface), surrounded by about 10% flat cuticular cells (those present on the outer surface) aligned in a scale-like fashion as shown in Figure 2.8 (Bonès and Sikorski, 1967; Bradbury and Chapman, 1964; Rogers, 1959). Individual cortical and cuticular cells have a shape as shown in Figure 2.9, where the finger-like extensions interlock with the extensions of another cell.

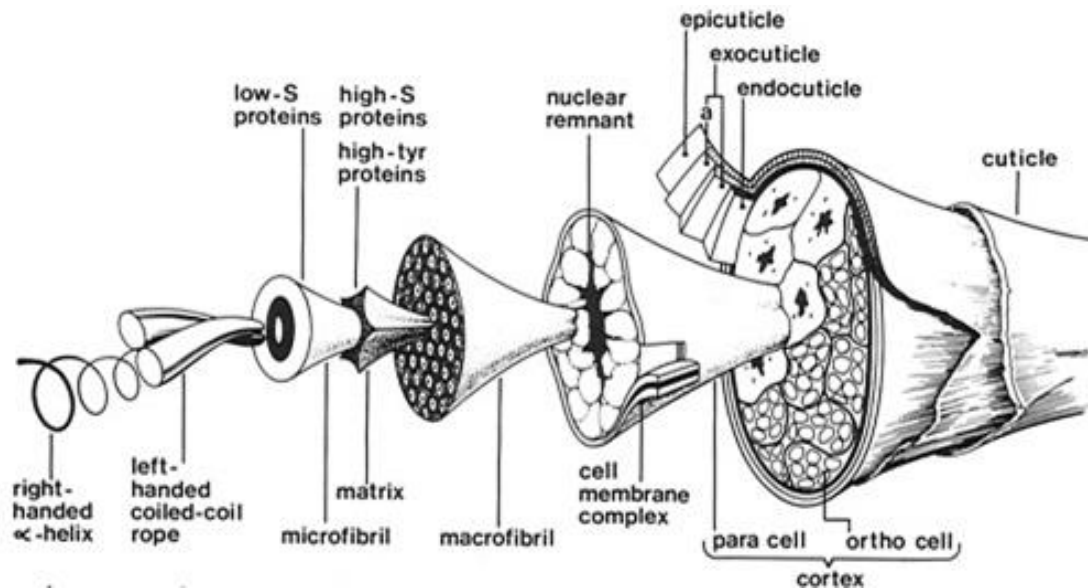


Figure 2.8: Wool fibre structure showing cortical and cuticular parts (CSIRO, 2011)

2.2.2 The cortex

Making up the core of the fibre, cortical cells contain several keratin intermediate filaments. Keratin is a tough fibrous protein that maintains its rigid structure via disulphide bridges, characteristic of the amino acid cystine, in addition to intra- and intermolecular hydrogen bonds (Pauling and Corey, 1951). The keratin intermediate fibres are held together by a matrix that is composed of non-fibrous keratin-associated proteins, and is either of a high glycine/tyrosine type or a high-sulphur type (i.e. rich in cystine) (Rogers and Bawden, 2008) as depicted in Figure 2.9. These fibres are complex and very little is known about them other than that they are composed of two different types of proteins that are not very similar in their amino acid sequence but are similar in their secondary structure. They are stabilised by α -helix hydrogen bonds and disulphide bonds, the latter being the bond that cements them to the surrounding matrix. They group into what is termed microfibrils, which in turn group into what is termed macrofibrils.

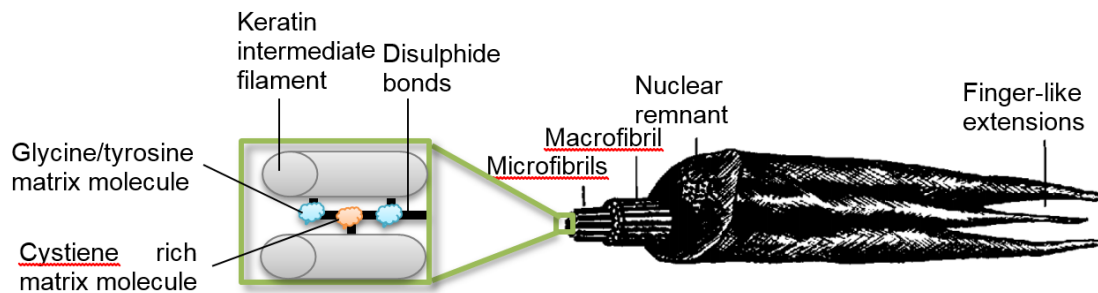


Figure 2.9: Shape of an individual cortical cell (Rogers, 1959; Rogers and Bawden, 2008)

There are two types of cortical cells: ortho and para. Para-cortical cells have a more uniform/fused keratin structure, and are more resistant to chemical and mechanical attack, such as swelling, than the orthocortex (Kulkarni and Bradbury, 1974), which explains why wool fibre crimps: different wool types vary in their fineness, which is attributed to this difference between cortical cells - finer wool fibres have two distinct halves of ortho- and para-cortical cells (i.e. bilaterally distributed, see Figure 2.10) that, when exposed to moisture, swell to different degrees and make the fibre bend. This crimp is what traps air pockets in between the fibres and give wool its insulation properties (Bradbury, 1974).

2.2.3 The cuticle

The whole bundle of macrofibrils is encapsulated by the cuticle, which unlike the cortex is amorphous, but is composed of cells of similar interlocking extensions as the cortex. The outermost membrane on the fibre is the epicuticle, about 13nm thick (Swift and Smith, 2001) and resistant to chemical attack, with 12% of its protein component being keratin (Negri *et al.*, 1993; Ward *et al.*, 1993). The epicuticle is highly insoluble due to isodipeptide crosslinks of 1-amino-(γ -glutamyl)-lysine (Folk, 1977). It is longitudinally striated with ridges about 350nm long, which face away from the root; this helps dirt and water droplets to drop away in one direction. The striation is what gives wool fibres a great frictional force and allows felting.

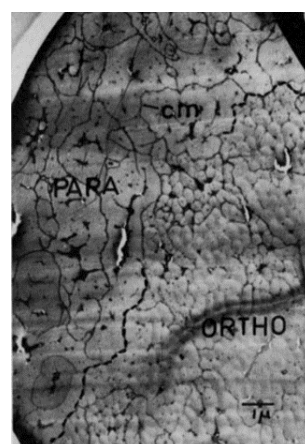


Figure 2.10: Low magnification view of a cross section of a fine crimped Merino wool fibre stained by the thioglycollate-0s04 method. The para-cortical cells are visible on the left as a more homogenised matrix than the ortho-cortical cells on the right (Rogers, 1959)

Below the epicuticle is the dense A-layer, 35% of it being cystine (Negri *et al.*, 1993). This layer is the start of the underlying exocuticle (Bradbury and Chapman, 1964), which is stabilised by disulphide bonds of keratin. The exocuticle contains high-sulphur keratin-associated proteins that are related to the matrix proteins (Rogers and Bawden, 2008). In contrast the layer below that, the endocuticle, does not contain keratin. In between cuticle and cortical cells is a cell membrane complex, which in turn is divided into β and δ layers. However, the cell membrane complex of the cuticle behaves differently than that of the cortex, the former containing citrulline and being resistant to modification with formic acid (Peters and Bradbury, 1976). An illustration of the layers of cuticle cells and an image showing the cell membrane complex in cortical cells are shown in Figure 2.11, and the composition of Merino wool is summarised in Table 2.8.

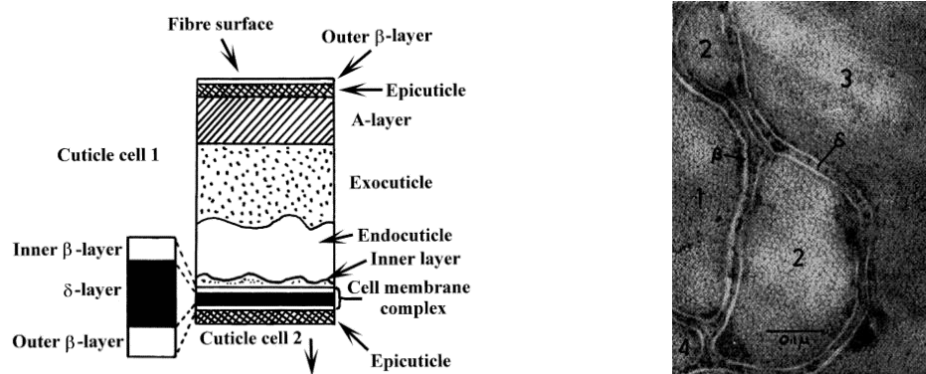


Figure 2.11: Left - A near-surface transverse diagram of a fibre (Swift and Smith, 2001). Right – Electron micrograph of the cortex of Lincoln wool (cross-section) of the cells separated by darkly coloured δ -layer which is sandwiched between lightly coloured β -layers (Peters and Bradbury, 1976).

Table 2.8: Morphological composition of Merino wool (Bradbury, 1974).

Component		Percentage of whole fibre
Cuticle	Epicuticle*	0.1%
	Exocuticle	6.4%
	Endocuticle	3.6%
Cell membrane	Lipid	0.8%
	Soluble protein	1.0%
	Resistant membranes	1.5%
Cortex	Nuclear remnants and intermacrofibrillar material	12.6%
	Microfibrils**	35.6%
	Matrix**	38.5%

*Approximate

**Ratio of microfibrils to matrix is that of Lincoln wool

2.2.4 Composition of separate components

The different components of the fibre can be separated and studied through ultrasonic disruption of wool fibres (Bradbury *et al.*, 1965; Bradbury and Chapman, 1964; Bradbury and King, 1967; Bradbury and Ley, 1972; Bradbury and Kulkarni, 1975; Bradbury and Peters, 1972; Chapman and Bradbury, 1968a; King and Bradbury, 1968; Kulkarni and Bradbury, 1974; Peters and Bradbury, 1976, 1972). Small differences in amino acid composition can be seen between different wool types, but statistically significant differences are noted when it comes to their elemental content (Patkowska-Sokola *et al.*, 2009). However, large differences are observed between the cuticle and cortex compositions of the same wool type as summarised in Table 2.9 (Bradbury *et al.*, 1965). It was concluded that all the amino acids abundant in the cuticle are classed as non α -helix-forming, and that all the amino acids that are scarce in the cuticle – with 2 exceptions – are classed as α -helix-forming; the remaining 3 amino acids were not classified (Blout and Stahman, 1962). This explains why the cuticle is amorphous and less polar than the α -helical cortex.

Table 2.9: Amino acid content of different wool types and differences between the cuticle and the parent fibre of the same wool types (Bradbury *et al.*, 1965).

Amino acids	Scoured Merino		Scoured Lincoln 36's wool 'top'	
	Composition of whole fibre (μ moles amino acid/g dry material)	Difference between cuticle and whole parent fibre	Composition of whole fibre (μ moles amino acid/g dry material)	Difference between cuticle and whole parent fibre
Cysteic acid	7	430%	12	570%
Aspartic acid	560	-31%	603	-47%
Threonine	572	-19%	563	-23%
Serine	902	40%	920	33%
Glutamic acid	1049	-19%	1130	-26%
Proline	522	60%	615	66%
Glycine	757	17%	617	19%
Alanine	469	-	504	-
Valine	486	33%	552	24%
Cystine	922	41%	881	72%
Methionine	44	-18%	44	-45%
Isoleucine	275	-14%	324	-34%
Leucine	676	-16%	708	-29%
Tyrosine	349	-22%	234	-18%
Phenylalanine	257	-30%	229	-45%
Lysine	269	-	252	-17%
Histidine	82	-	66	-24%
Arginine	600	-25%	667	-34%
Recovery of anhydroamino acid	95.5%	-	97.4%	-

The nuclear remnants and inter-macrofibrillar material are digestible by trypsin, which does not digest keratin to any appreciable amount. In comparison with the whole of the fibre, Merino wool's nuclear remnants and inter-microfibrillar material are found to contain more aspartic acid, histidine, isoleucine, valine, twice as much lysine, and three times as more methionine. They are also found to contain less proline, serine, threonine, tyrosine, and to have one-third as much cysteic acid + ½ cystine (Peters and Bradbury, 1972).

The endocuticle, digested by pronase, shows similar constitution to that of nuclear remnants and inter-macrofibrillar material (Bradbury and Ley, 1972). As the endocuticle is the non-keratinous component of the cuticle and the nuclear remnants and inter-macrofibrillar material are the non-keratinous component of the cortex, this result is expected owing to the common origin of these components being the cytoplasmic debris of the once living cells (Rogers, 1959). The exocuticle on the other hand show more cross-links per amino acid residues, about twice of the whole fibre's (Table 2.10). This is what makes it a non-extensible layer, explaining why longitudinal cracks appear in the cuticle of wool fibres which are swollen by more than 30% in diameter (Bradbury and Chapman, 1963). The epicuticle has a lower lysine and higher serine content than that of the membranes that remain undissolved by various degradative procedures; otherwise it is similar, and it is postulated that the presence of lysine leads to the presence of more ϵ -(δ -glutamyl)lysine cross links (Asquith *et al.*, 1970; Peters and Bradbury, 1976).

Table 2.10: Cross-linking and polarity of the cuticle layer of merino wool (Bradbury and Ley, 1972; Chapman and Bradbury, 1968b)

	Whole fibre	Cuticle	Epicuticle	Exocuticle	Endocuticle
Disulphide cross-links (mole %) (cysteic acid+lcystine)	10.05	15.63	11.91	19.95	3.10
Polar residues (mole %)* (Asp+Glu+Arg+His+Lys)	29.02	19.97	26.61	17.97	27.98

*No allowance has been made for the glutamine and asparagine present, which may reduce these values somewhat

The cell membrane complex, which is present in all the regions of the fibre “and probably contains ordered bilayers of lipids which have polar and non-polar regions, has been found to be important in controlling the rate of sorption' of n-propanol into wool” (Bradbury *et al.*, 1971 in: Bradbury and Ley, 1972).

Differences in amino acid content between ortho- and para-cortical cells are too small to contribute to their differing behaviour with water and stress (Chapman and Bradbury, 1968b).

Another cellular component found in coarse wool is the medulla. This section can vary in size and continuation along the fibre, and is open and light but stiff due lacking amounts of proteins during growth (Bradbury, 1974). Although the medulla seems largely amorphous under the

electron microscope, some fibrils may be observed. It contains more citrulline than the cuticle does, and ϵ -(δ -glutamyl)lysine cross links are responsible for its chemical stability as it does not contain appreciable disulphide bonds (Bradbury and O'shea, 1969; Bradbury, 1974).

2.2.5 Outer surface composition and behaviour

In the case of unmodified and undamaged wool, the fibre is covered by a about 0.9nm thick layer of lipids that comprises $\frac{1}{4}$ of the epicuticle (Negri *et al.*, 1993). These lipids, which are mainly 18-methyleicosanoic acid (18-MEA), are covalently bonded to the keratin protein (Evans *et al.*, 1985). The bond is proposed to occur as a thioester linkage with the amino acid cysteine (Figure 2.12); the amino acid cysteine is not to be confused with cystine, the latter being formed by the oxidation of two cysteine molecules. Breakspear *et al.* (2005) conclude that the lipid layer is homogenous and not disordered as depicted in Figure 2.13a.

Still, this explanation does not account for two observations: the good stability of the thioester bond (Bizzozero, 1995a) and that the surface is solid and ionisable when present in aqueous solution (Evans *et al.*, 2002). To improve on these observations Maxwell and Huson (2005) hypothesise that the lipid layer is disordered (Figure 2.13c) and dynamic, changing its position when the surrounding environment changes from wet to dry (Figure 2.13d); when placed in a hydrophobic environment the hydrophobic chains of the lipid layer faces outwards, but "reorients itself upon exposure to an aqueous environment so that the protein (amide) and polar side chain groups of the proteolipid are oriented outwards" (Maxwell and Huson, 2005).

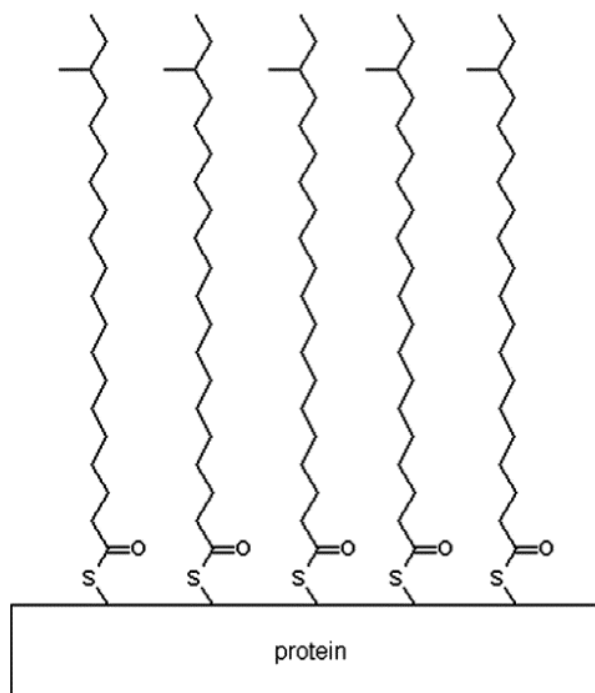


Figure 2.12: 18-MEA covalently bonded to keratin via thioester linkage (Breakspear *et al.*, 2005)

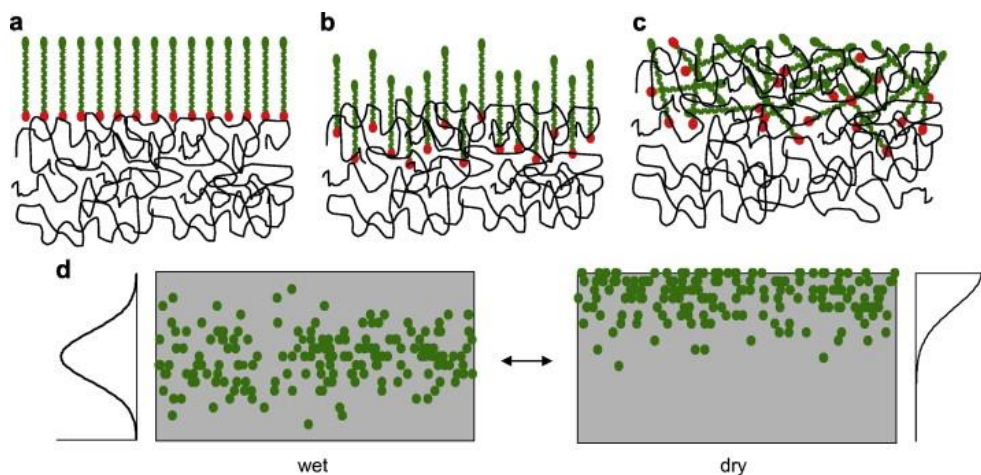


Figure 2.13: Representations of the arrangement of the lipid layer shown in green and underlying protein layer shown in black (Huson et al., 2008). (a) Homogenous layer. (b) Slightly disordered layer. (c) Disordered layer. (d) Dynamic change of the position of the lipids (green dots) in the protein matrix (grey) in response to the surrounding environment.

The lipids are removed by potassium tert-butoxide in tert-butanol or methanolic potassium hydroxide solutions (Ward *et al.*, 1993), as 5 minutes of treatment oxidises the surface cysteine, decreasing the fatty acid content by about half and significantly increases wettability and friction. Therefore similar treatments used in the scouring process get rid of some of this layer. These lipids are not to be confused with lanolin, which are unattached sterols, sterol esters, and other lipids secreted by sebaceous glands that coat wool fibres as they grow (Schlossman and McCarthy, 1978). However, there are claims that this attached lipid layer cannot be physically or chemically removed uniformly without damaging the underlying protein, suggesting that it is an integral part of the structure (Maxwell and Huson, 2005). On the other hand, Swift and Smith (2001) observed “no alteration to the visual appearance of the surface of the fibres as viewed by SEM and SPM” after successive treatments, but agree that the removal is ‘patchy’.

Considering all the information presented in the literature, the surface structure of wool is complex, and the chemical functionalities are still not all understood.

2.2.6 Inner surface composition and behaviour

A past study on the elasticity of wool in various organic solvents concluded that the size of the capillaries in dry wool (English Costwold) is more or less equal to the size of n-propanol (Speakman, 1931). Speakman also calculated the internal surface to be approximately $10^6 \text{cm}^2/\text{g}$., and the maximum moisture sorbed to be about 20% of its weight. In water, the fibres swell, increasing the capillary size from 0.6nm to 4.1nm, which corresponds to an increase in the force required to stretch the fibre. It has also been shown that some organic

liquids that are too bulky to enter the capillaries on their own may gain access and modify the chemical and physical properties of the fibre when water is added. Short chain acids (formic and acetic) showed a reversible collapse of the capillaries, increasing diameters by 40-50%; the physical properties were restored by simply washing with water.

Halogen solutions, such as chlorine or bromine water, react with an undamaged (i.e. unscoured) fibre surface and form raised membrane-bound sacs called Allwörden membranes, depicted in Figure 2.14 (Allwörden, 1916; Negri *et al.*, 1993). The epicuticle, not just the lipid layer covering it, is resistant to halogen solutions but is semi-permeable. It is thought that an oxidation reaction disrupts the disulphide linkage between cystine molecules found in the exocuticle – not the A-layer – and results in water soluble cysteic acid residues. Water molecules and the halogen ions are small enough to pass through the epicuticle, but the cysteic acid residues remain trapped behind the epicuticle. Water therefore passes through the epicuticle because of the concentration difference; this osmosis results in the Allwörden sacs.

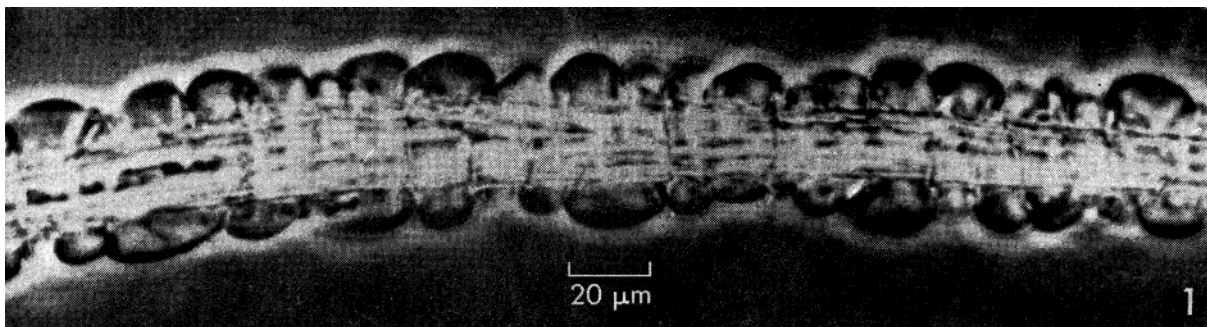


Figure 2.14: Merino wool treated with chlorine water showing Allwörden membranes (Bradbury and Leeder, 1972)

2.2.7 Structural changes due to processing

Wool as a raw natural fibre show structural variation due to sheep breeds and characteristics, in addition to seasonal variations and other factors. In addition, the processing of the fibre by the industry to create consumer products may further alter the structure. All industrial wool fibres in the UK are regulated by the British Wool Marketing Board (“British Wool Marketing Board,” 2016), with similar organisations existing in other countries (Australian Wool Exchange, 2015; Australian Wool Innovation, 2016, NWGA - The National Wool Growers Association, 2016, Wools of New Zealand, 2016). Such organisations ensures that the wool undergoes certain processes especially that of scouring to reduce adverse health effects during processing (Mansour *et al.*, 2014).

2.2.7.1 Scouring

The scouring process essentially cleans the wool from inorganic and organic contaminants: grease, dirt, vegetable matter and manure are removed along with preventable health risks and processing difficulties (large entanglements and debris that can disrupt production or damage machinery) at further manufacturing stages.

Scouring starts with mixing different wool types and grades to obtain a desired blend. The types of wool mixed together determine the blend's grade, which in turn is dependent on the manufacturer and end use application. Textile processors generally opt for the finer grades of wool that are characterised by smaller fibre diameters (fineness), a homogenous colour, and low crimp factor (natural waviness or bend in the fibre). Carpet manufacturers may compromise on the fineness of the blend to a certain extent, but generally remain interested in colour. Insulation manufacturers on the other hand opt for the coarser, lower grade blends with complete disregard for colour. The choice of blend and grade therefore determines physical characteristics of the wool fibre such as density and fragmentation patterns.

The blend is passed through openers that are composed of a relatively large toothed rotating roller that fragment large tufts of wool. Following that it is cross laid and re-blended to ensure proper mixing and washing further down the line. Before washing, the wool is picked up by inclined lattices, allowing the dust to be collected at the bottom. After further mixing, the wool is washed. There are several methods for washing; solvent based systems are usually unpopular due to associated higher costs, unlike aqueous systems (Stewart, 1988). Aqueous treatment involves several steps of mixing with detergents and rinsing. Depending on the wool blend, process parameters such as washing temperatures are adjusted. After the pH is controlled and other treatments (such as brightening) are applied, a sample of wool is tested for colour and bound moisture content. If satisfactory, the batch is dried, checked for the presence of metal and non-conformities, and relieved of large clumps and entanglements. The effluent water is usually treated on site as it is the most expensive process. Further optional treatments can be applied using mechanical systems that apply a partial vacuum to remove dust (Andar Ltd, 2016). After further cross-layering and blending through inclined lattices (which again removes remaining dust) and some final tests, the wool is baled as a final product. Wax, dirt, and water soluble material vary in amount depending on the breed, age, and location of the sheep, but is typically between 30 to 47% (Johnson and Russell, 2008).

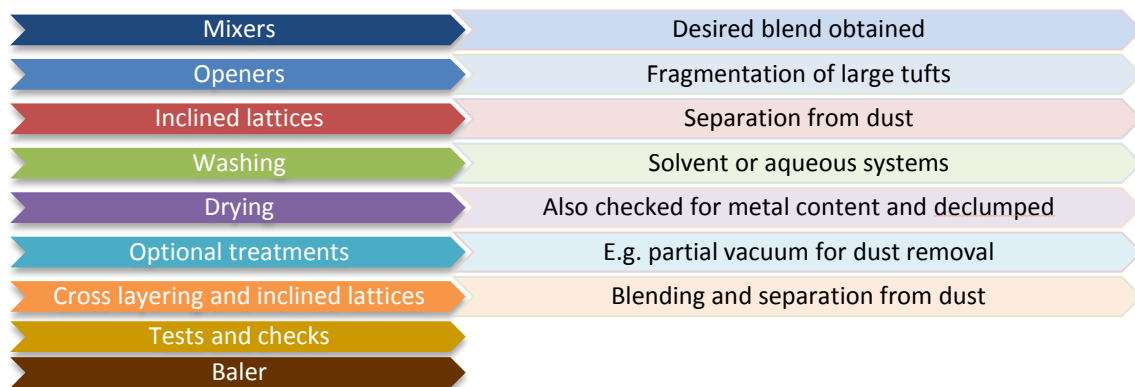


Figure 2.15: Basic process of wool scouring

2.2.7.2 Mechanical and chemical processing

Depending on the industry, wool fibres undergo various random and tensile mechanical stresses, in addition to chemical alterations such as dyeing and the addition of flame retardants, insect repellents, and/or fungicides. Such alterations and additions inevitably cause changes in the fibres' structure. The following is a description of processing of insulation material using sheep wool.

Non-woven insulation is composed of low grade scoured wool mixed with an appropriate proportion of a binder, usually a low melt synthetic fibre such as polyester or a wet adhesive; needle felting is another option that removes the need for a binder, but the thicker the final product the lower structural integrity it will have. Treatments including flame retardants and pesticides may be applied at the mixing stage to ensure proper distribution throughout the thickness of the final product, or may be sprayed on the surface of the final product at later stages. The wool and binder mixture first passes through an opener that partly homogenises the mix in addition to loosening compact fibre bundles. Next, it is scanned for any metal content (as this can damage the machinery) and fed into a carding or an air-laying system.

In a carding system, wool passes through a number of wired rollers that essentially 'comb' the fibres into a single alignment. The advantage of this is higher thermal conductivity values for the final product. The resulting web of aligned fibres are then cross laid into several layers that overlap (Müssig, 2010a), where the degree of overlap depends on the desired density of the product (Müssig and Graupner, 2010). An air-laying system on the other hand is a much simpler process where the fibres are blown out onto a perforated belt forming a web of a certain density and somewhat randomly aligned fibres. This system increases production speed and can result in a thicker final product compared to carding (Müssig, 2010a).

Following web formation by carding or air-laying, the web is conveyed through an oven to allow the binder to melt and thus provide structural integrity to the product. During this process,

the thickness is determined by setting a compression belt over the passing web to the desired measurement. Finally, the web is cut to the required length and width, and is ready for packaging and distribution prior to installation.

2.3 Conclusions and summaries

The literature has large amounts of data both on indoor air quality and indoor VOCs, as well as information regarding the structure of sheep wool fibre. However, no comprehensive or exhaustive understanding is gained about either subject due to their complexities and vast scope.

With regards to indoor VOCs, the following points are deduced:

- Health concerns regarding indoor pollutants and VOCs are increasing due to an anticipated rise in exposure.
- The indoor VOC profile is significantly affected by the wide range of sources, with building materials and household products being the major emitters. This contributes to the complexity of VOCs throughout the life of a building, as refurbishments contributes to varying rises of VOC concentrations.
- Hazards resulting from indoor VOC exposure range from the most serious illnesses in relatively rare occurrences to common SBS symptoms, with ensuing financial and social repercussions.
- Current legislation, schemes and possible alleviation strategies do not fully or satisfactorily address the problem, although they offer an improvement that can be further built on.

With regards to sheep wool, the following points are summarised:

- Sheep's wool fibre shows potential for removal of some VOCs from the indoor environment.
- The fibre structure is complex, having multiple morphological and chemical components, even when the variation between sheep breeds is not taken into consideration as is often the case in the literature.
- Processing parameters such as scouring, mechanical and chemical alterations are subject to the industry and can cause varying changes to the fibres' structure.
- Inner and outer surface structures vary, enhancing the potential of sorbing v/VOCs when surface area and functionalities are taken into account.
- The outer structure is dynamic and responds to surrounding environment; the outer lipid layer changes its position in the protein matrix depending on whether the surroundings are wet or dry (Maxwell and Huson, 2005).

Chapter 3: v/VOC sorption analytical techniques – setup and optimisation

3.1 Introduction to VOC assessment

The numerous studies analysing the amount of VOCs present indoors and those emitted from different products share the basic idea: an adsorbent that has a strong affinity to the VOCs of interest is exposed to a flow of an air/gaseous sample originating from the product or area in question. Depending on the adsorbent used, the collected VOCs are eluted into an analytical instrument such as gas chromatography or liquid chromatography.

Such studies focus on collecting emissions from various sources, but do not directly address how to assess a material for its potential to sorb VOCs. Studies which address such properties are equally varied. Some rely on partition or absorption coefficients where concentrations in the samples are calculated based on mass balance (Dumont et al., 2010; Quijano et al., 2011). And some (Chen and Liu, 2002; Wilson et al., 1992) use gas collecting tubes in conjunction with high-gravity systems (Higee), which was first developed by Ranshaw and Mallinson (1981). These studies, along with many more (Lawson and Adams, 1999; Modelski et al., 2011; Poddar et al., 1996) all employ the same basic concept: a source of VOCs is introduced into a gas flow, subjected to the sorbing material, and the amount sorbed is analysed and calculated one way or another.

3.2 VOC sorption setup

3.2.1 Gas flow setup

A gas tight setup was designed, made and developed as part of the work in order to expose a sample of fibres to a constant gas flow, which in turn can be dosed with fit for purpose concentrations of VOCs. Figure 3.1a details the set-up. 3.175mm (1/8inch) copper tubing and brass fittings were used for connections. A nitrogen source was connected to a hydrocarbon filter followed by a large 254 by 12.7mm (10 by 1/2inch) tube containing Tenax® TA powder (hereby referred to as Tenax). Tenax is a porous polymer resin based on 2,6-diphenylene oxide designed specifically as a trapping agent of volatile substances, and is referred to in several standards including ISO 16000 part 5 (ISO, 2007). This was done to ensure that no residual v/VOCs from the nitrogen cylinder affected results. The flow was then split; both ends were connected to flow controllers with one being first fed into an aluminium container (Figure 3.2b) holding sources of the VOCs in question (see next section). The container was held at a constant temperature using a water bath pump with tubing coiled around (Figure 3.1b).

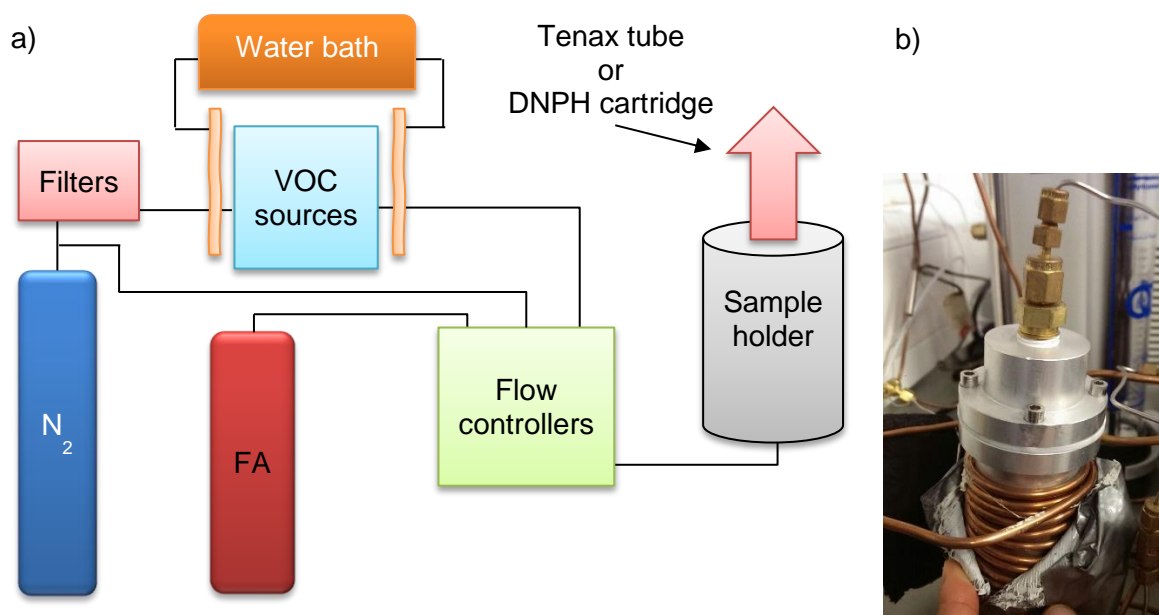


Figure 3.1: a) A schematic diagram of the gas-tight setup created to expose a sample to a known flow of VOCs, where FA is formaldehyde cylinder, and b) photo of sample tubes container with tubing coiled around to allow temperature control using a water bath pump.

The concentration and flow of the nitrogen and VOC mixture was adjusted as required using the flow controllers, which then fed into a sample holder (Figure 3.2a). Both the sample holder and the VOC sources container are designed in a vertical fashion to force the nitrogen flow upwards through the containers and ensuring maximum interaction between the nitrogen, VOCs and material being tested. The sample holder has a fitting at its top to allow the quick attachment and detachment of v/VOC collection sample tubes and cartridges, where O-rings are used to avoid gas leakages. The flow controllers, sample holder and sources container were all wrapped as best possible with bubble-wrap to minimise temperature fluctuations around them. Initially, the sample holder was replaced by a Markes μ -chamber, which is normally used to hold samples at specified temperatures for emission tests (Clauder et al., 2015). However it was found that the flow splitters across the 6 sample holders were not accurate enough to ensure a constant flow of different VOCs.

For analysing samples, 200mg Tenax contained in 89x6.4mm inert coated stainless steel tubes (supplied by Markes) are used to adsorb any toluene, limonene and dodecane that are not sorbed by the sample. A set of 10 of these Tenax tubes were reused for all related sample runs after being cleaned of any v/VOC residues by full thermal desorption (see section 3.3) in between runs. Tenax is also able to sorb formaldehyde as well, but is known to be unreliable for analytical purposes. Hence, 2,4-Dinitrophenylhydrazine (DNPH) cartridges (supplied by Waters) are used to form formaldehyde-DNPH complexes with any formaldehyde that is not sorbed by the sample.

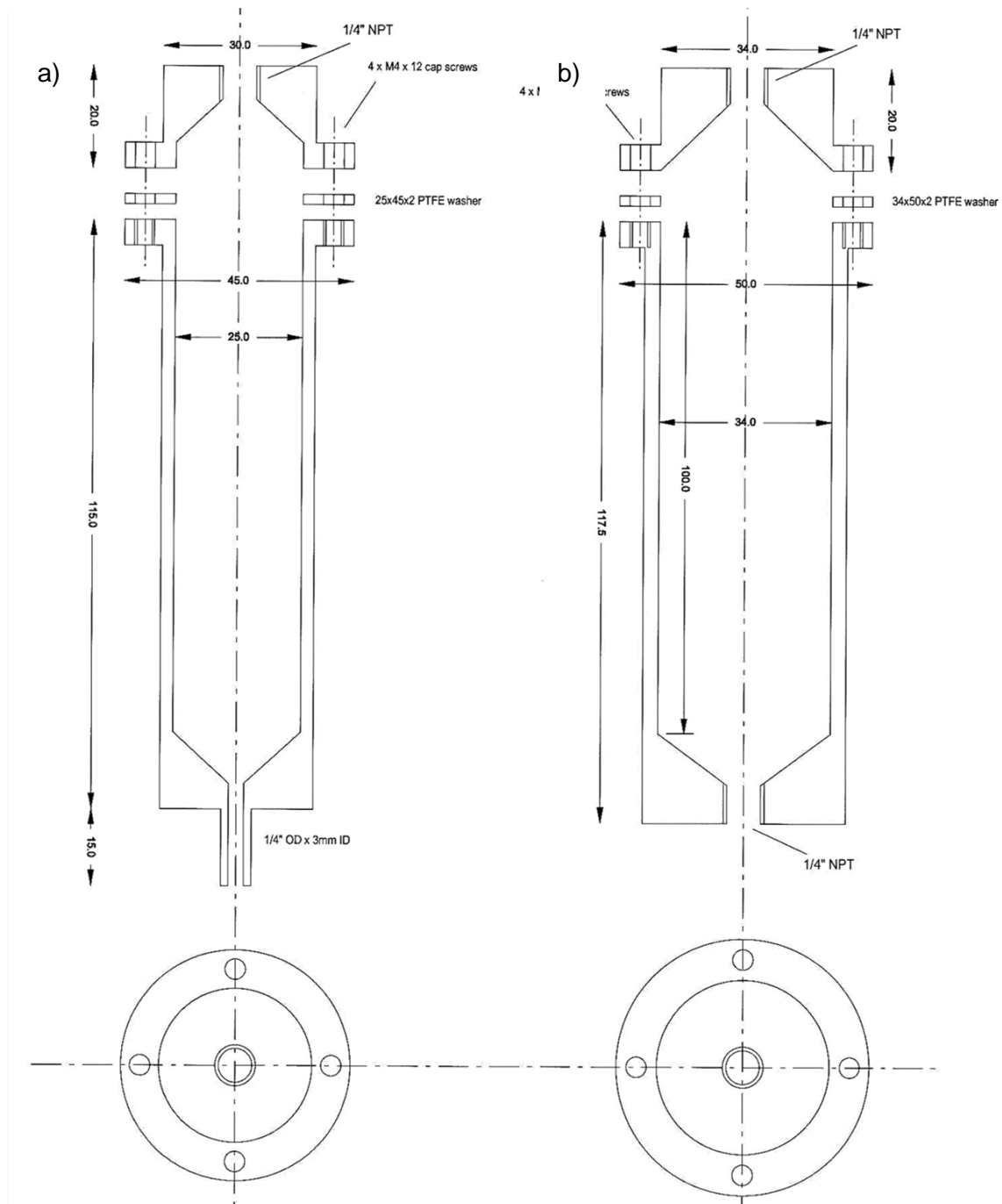


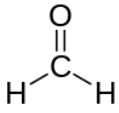

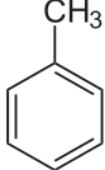
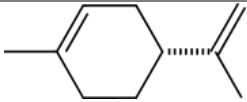

Figure 3.2: Detailed diagrams of a) sample holder and b) sources container used as part of the sorption setup. Where not designated, units are in mm. OD = outer diameter, ID = inner diameter, NPT = National pipe thread, PTFE = Polytetrafluoroethylene.

3.2.2 v/VOC sources

3.2.2.1 Selection of v/VOCs used for assessment

For the purposes of this work, 4 v/VOCs were selected to be assessed for sorption by sheep wool fibre (Table 3.1). The selected v/VOC cover a wide range of polarity, and represent a wide range of chemical structures.

Table 3.1: v/VOCs selected for assessment in this thesis.

v/VOC	Chemical structure	Polarity
Formaldehyde		
Toluene		
Limonene		
Dodecane		

In order of volatility, the first vVOC selected was formaldehyde, a very simple and highly polar molecule. Many building products emit it at significant rates (Meyer and Boehme, 1997). According to the BUMA project (University of Western Macedonia, 2006), referred to in chapter 2, the most abundant emissions from building materials include formaldehyde. Also, up to a third of indoor VOCs, including alkenes (Weschler, 2000), are oxidised when present at low concentrations (28-44 ppb) by ozone into formaldehyde and other aldehydes (Missia et al., 2010). Another point of importance is that formaldehyde is a gas in its natural state, so occupants are easily exposed to it. With regards to its many health effects, concerns over formaldehyde exposure include cancer risk (EPA, 1991).

The next VOC considered is toluene, representing benzene and other cyclic compounds, some that are known to be associated with high health risks and concerns (Petralia et al., 1999; Smith, 2010). Toluene has been found indoors at an average of $70\mu\text{g}/\text{m}^3$, which is equivalent to about 10% of the average total VOC concentrations (Lorimier et al., 2005), and an EPA survey aimed at 31 VOCs and 1159 common household products (Sack et al., 1992) found toluene present in over 40% of the products. The BUMA project also categorised it as an abundant emission, although less so than formaldehyde. Toluene is also used as a reference point in the calculation of TVOC concentrations (ISO, 2011a).

Another VOC considered is (R)-(+)-limonene, representing terpenes and being present and commercialised in countless household products (Wolkoff and Nielsen, 2001), many of which utilise it for the purpose of diffusing a pleasant fragrance indoors. Due to its increasing use and abundance as highlighted by the BUMA project, the media and scientific studies have

highlighted its abundance and potential hazards, including its oxidation to formaldehyde (Grosjean et al., 1993; Sean Poulter Mail Online, 2016). It is also known to have a synergistic effect when present with ozone (Wolkoff et al., 2012b, 2008b).

Representing the very non-polar side of the spectrum, dodecane was selected as a straight chain hydrocarbon. It is reported as being abundant in some studies e.g. in Swedish housing (Bornehag and Stridh, 2000), office buildings in USA (Girman et al., 1999a), and another review conducted in the USA (Holcomb and Seabrook, 1995). Although hydrocarbons of similar nature are noted to reach low levels with time, renovation and refurbishments cause such VOCs to rise in concentrations (University of Western Macedonia, 2006).

3.2.2.2 v/VOC sources

Liquid portions of toluene, (R)-(+)-limonene and dodecane were placed separately inside empty 6.35mm (1/4inch) stainless steel tubes having a brass cap at one end and stoppered with a different plastic plugs of varying lengths (Figure 3.3a). Three source tubes that can be loaded with separate or a mixture of liquid VOCs could be placed inside the gas tight sources container in a vertical manner where the plastic plugs are suspended rather than in contact with the walls of the container (Figure 3.3b). The different types of plastic plugs tested are listed in Figure 3.4 This helps with keeping the emissions rates constant during experimentation.

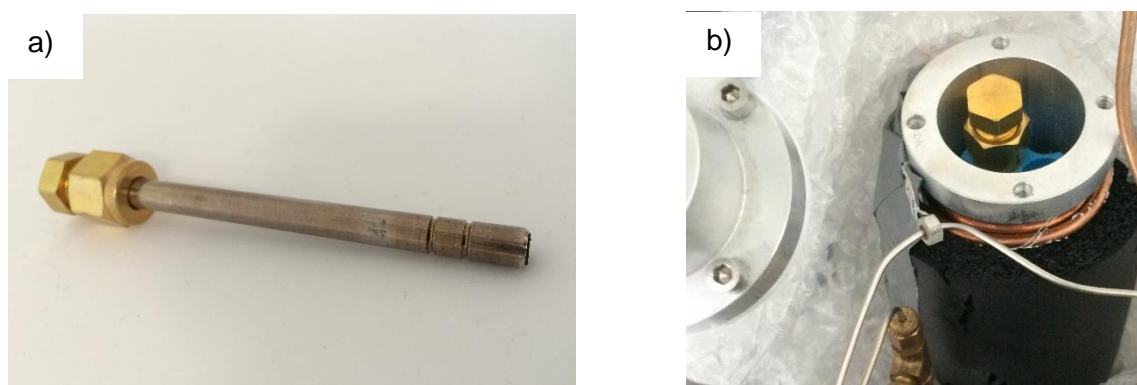


Figure 3.3: a) A source tube and b) a source tube placed inside the source container in a vertical manner.

Mass loss over time gave an indication of the concentration emitted by sources stoppered by 9 and 12mm of the different plastic plugs. The sources were left to emit under a fume hood and weighed using a 6 figure balance periodically to calculate the mass loss. Figure 3.4a shows a relatively steady mass loss per hour for each source after an initial period of equilibrating (c.a. 300 hours). Some sources emit at a completely different scale than others, with sources stoppered with FKM and NBR rubbers emitting the lowest amounts (Figure 3.4b).

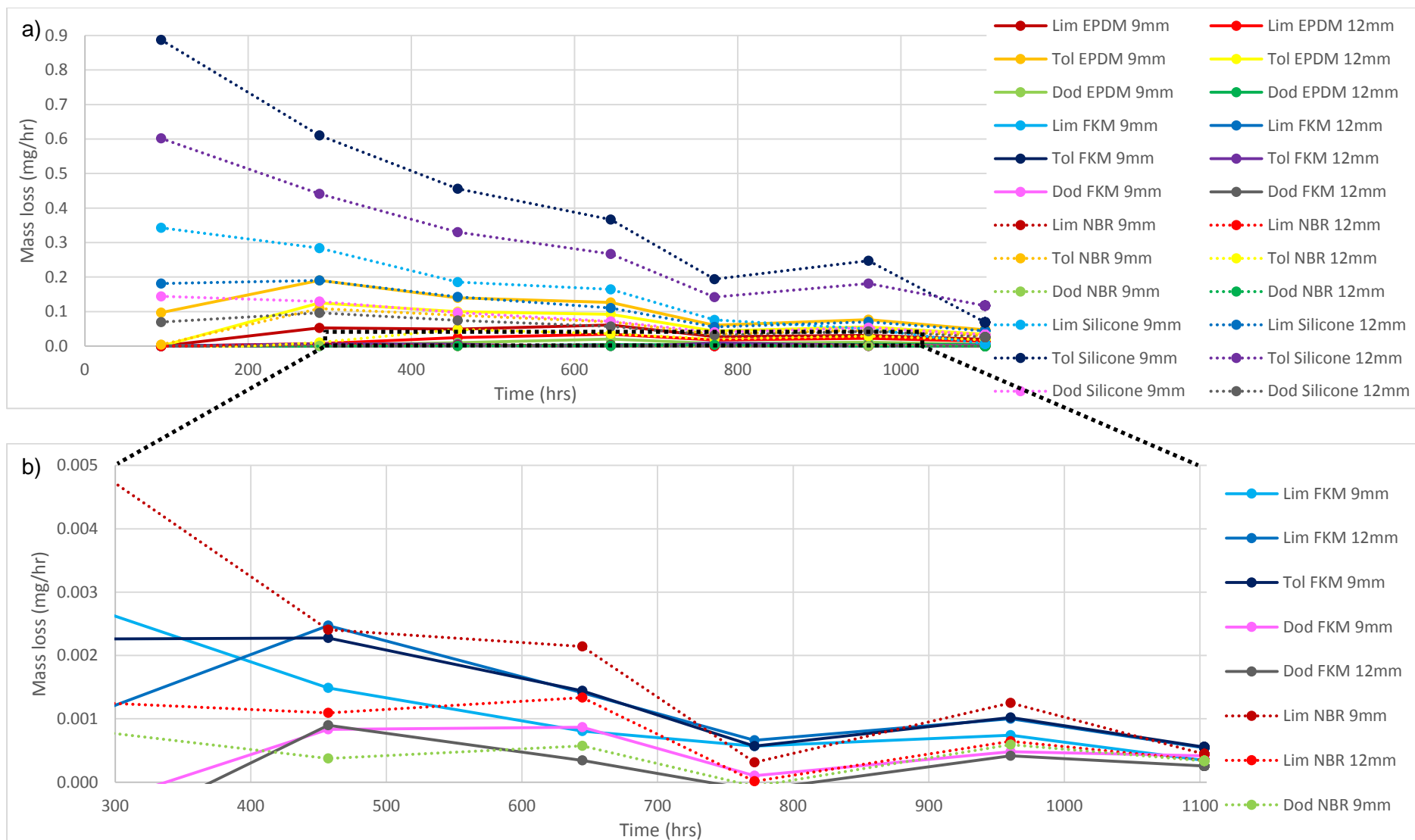


Figure 3.4: a) Mass loss over time of sources stoppered with different plastic plugs and containing liquid VOCs. b) Zoom in to those on the lower scale of graph a. Tol = toluene, Lim = (R)-(+)-limonene, Dod = dodecane, EPDM = ethylene propylene diene monomer (M-class) rubber, FKM = fluorocarbon rubber, NBR = nitrile rubber.

As the interest is in simulating concentrations encountered in real life situations, sources with the lowest emissions were selected; FKM was selected over NBR since toluene – the most volatile of the 3 VOCs being used - was seen to elute at a lower rate when stoppered with the former rubber.

These sources could not be replaced with a gas cylinder containing a mixture of the VOCs in nitrogen due to the differences in partial pressures; toluene does elute out of such a cylinder but limonene and dodecane condense into their liquid state. Prior to any set of experiments, the gas flow and water bath pump were left running over night to ensure stable conditions and that therefore flow concentrations had reached an equilibrated and constant emission state.

A cylinder containing formaldehyde in clean nitrogen was also connected to the flow controllers of the sorption setup, bypassing the hydrocarbon filter and the large Tenax tube to avoid the capture of the formaldehyde by them.

All the v/VOC sources showed constant concentration flows within sets of experiments. Flow concentration differences were noted between one set of experiment and another due to instabilities of the VOC sources over long periods of time and the very short shelf-life of the formaldehyde cylinder.

3.3 Thermal desorption and GC-FID optimisation

For the analysis of toluene, (R)-(+)-limonene and dodecane, Tenax tubes were used to collect the VOC and were desorbed thereafter using a Markes Unity 2 thermal desorber - equipped with a U-T12ME-2S: Materials emissions cold trap - connected to a PerkinElmer Clarus 480 gas chromatography (GC) with a Flame Ionisation detector (FID) and a DB5 column. To ensure optimal desorption of the Tenax tube, the direction of flow for its desorption during analysis was made to be opposite to the direction of flow for its sorption during the experiment.

To remove artefacts seen on the chromatograms, a hydrocarbon filter was connected to the carrier gas (He) flow. Although this is not needed on a normal GC setup, minute concentrations of any flow contaminants accumulate rapidly on the cold trap, and then are injected at higher concentrations in a very fast thermal desorptive manner into the GC. When the carrier gas is directed straight from the cold trap to the GC without passing through a Tenax tube (heat trap run), large peaks of artefacts are detected, which are removed when a filter is installed (Figure 3.5); although some artefact peaks remain due to the thermal degradation of the cold trap, they do not interfere with any of the peaks of interest.

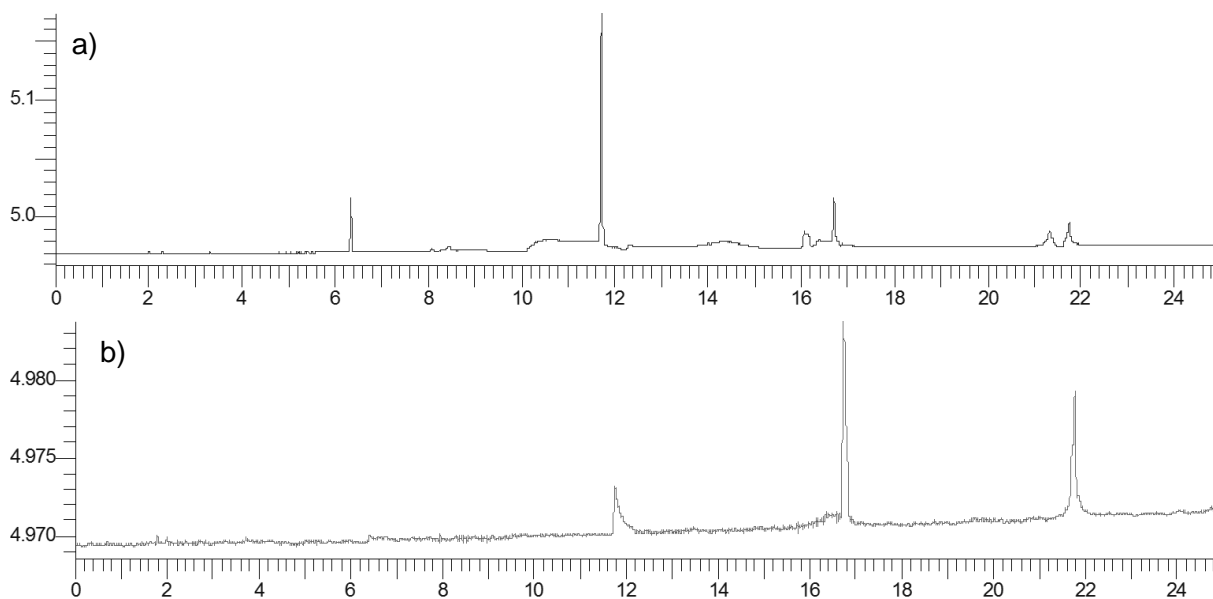


Figure 3.5: Chromatogram of a heat trap run with 10min purge time a) prior to the installing of a hydrocarbon filter to the carrier gas showing large peaks of artefacts th and b) post installing a hydrocarbon trap showing only very small peaks (note the scale difference on the y axis).

3.3.1 Optimal settings and checks

To check if the cold trap is able to successfully deliver all the amounts of the 3 VOCs present on a Tenax tube, two runs were conducted using c.a. 50ng of each VOC directly injected into the Tenax tubes using methanol as a solvent: the first using a cold trap temperature of 0°C and one at -30°C. If some of the volatiles are not being fully trapped, an increase in peak heights would be noted as the temperature is lowered. No such observations were seen except for methanol (Figure 3.6).

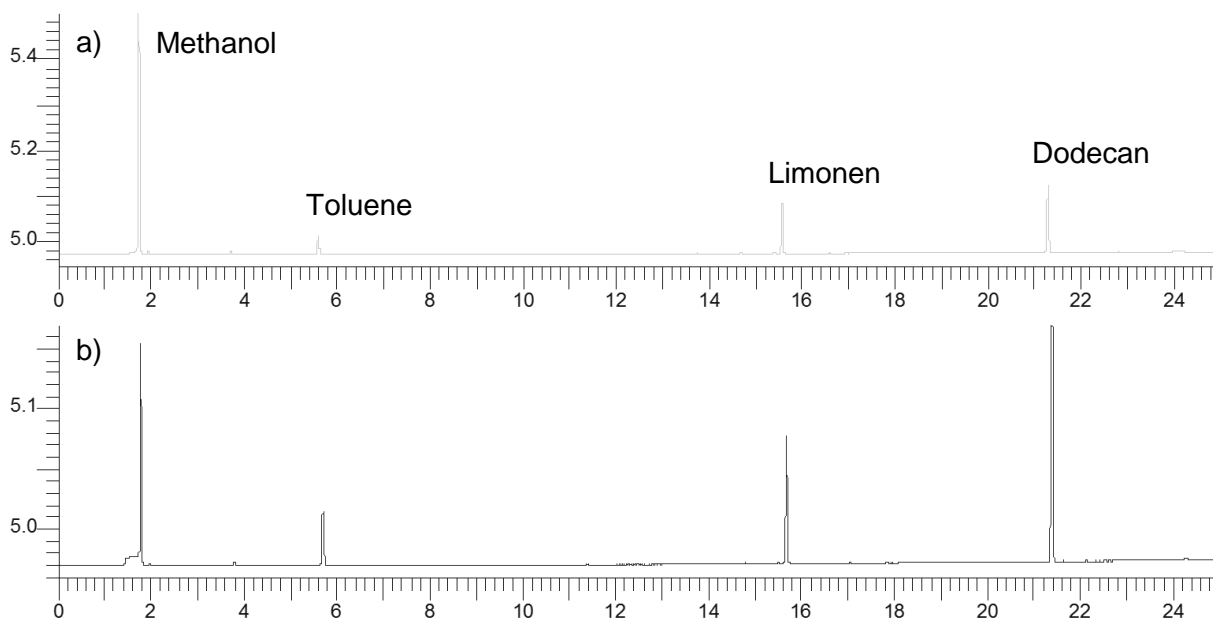


Figure 3.6: Chromatogram of a c.a. 50ng of each of the 3 VOCs a) at 0°C cold trap temperature and b) at -30°C cold trap temperature, showing no difference in peaks heights except in the case of the solvent methanol (note the scale difference on the y axis).

The optimum settings used for the thermal desorption / GC-FID system are detailed in Table 3.2. The GC oven temperature program used was 5min at 40°C followed by a temperature ramp of 10°C per minute for 20mins.

Table 3.2: Optimum settings used for the thermal desorption / GC-FID system.

Setting		Value
GC split	Column flow = Dead volume / Retention time of pentane	0.856ml/min
	Desorb flow	3.6ml/min
	Split flow during trap desorb	33.4 (43.7 for mineral wool tests) ml/min
	Calculated split ratio (using Markes split calculator)	40.0:1 (52:1 for mineral wool tests)
FID	Temperature	200°C
Tube pre-desorption	Pre-purge time (to remove any moisture from the Tenax tube)	1.0min
Tube desorption	Desorption time	8.0min
	Desorption temperature	280°C
Cold trap	Pre-trap fire purge	1.0min
	Trap sorption temperature	-30°C
	Heating rate	MAX°C/s
	Trap desorption temperature	300°C
Flow path	Temperature	200°C
	Minimum carrier pressure	5.0bar

3.3.2 Calibration

The thermal desorption / GC-FID was calibrated in accordance with ISO16000 part 6 (ISO, 2011a) using Tenax tubes injected with known amounts of toluene, (R)-(+)-limonene and dodecane. A parent solution was prepared by consecutively weighing known amounts of each VOC in a 25ml grade A volumetric flask, which was further re-weighed every 5min until 4 weighings were within less than 0.0001g difference. The mass of each liquid VOC within the solution was calculated as an average of the 4 weighings, taking the purity of the solutions used into account. The solution was successively diluted in methanol resulting in 7 differing amounts for each VOC. 0.5µl was directly injected through a septum into a Tenax tube mounted on a Markes CSLR, which was used to run a flow c.a. 100ml/min of clean nitrogen through the tube (Figure 3.7). The syringe was left with the tube for 15min. This ensures that the solvent methanol would escape out the other end of the tube, whilst the 3 VOCs would not

due to their large breakthrough volume through Tenax. Thus, when thermally desorbing, methanol will not interfere with the analysis; it is reported that a higher mass of VOCs than intended is lost with the GC split when high volumes of methanol are present within the Tenax tube, as they preferentially dissolve more with gaseous methanol rather than the carrier gas.

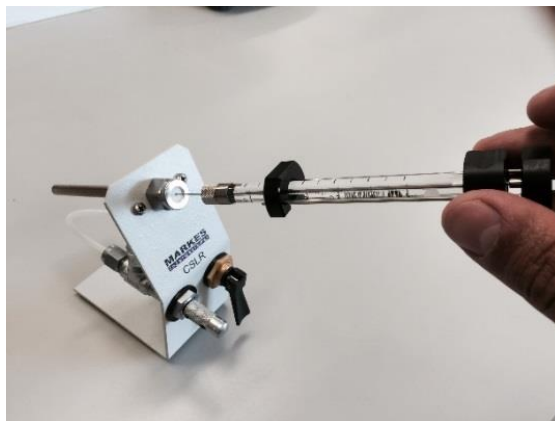


Figure 3.7: Injection of solution into a Tenax tube using Markes CSLR.

Calibration runs were done in triplicates, covering a range of 13.5ng to 2257.0ng. The peak areas were used to obtain a linear calibration fit forced through an intercept of 0. The calibration process was run again for testing mineral wool samples since the apparatus was relocated (the split flow changed to 43.7ml/min resulting in a 52:1 split), also resulting in good adjusted R² values. Table 3.3 details the values of the linear calibration fits for each VOC. Residuals from previous runs were checked for, and none were detected.

Table 3.3: Calculated values for the linear calibration curves for the 3 VOCs based on peak areas.

Compound	Slope value	Slope standard deviation	Adjusted R ²
Toluene	1.22141	0.01748	0.9945
(R)-(+)-limonene	1.04621	0.00411	0.9996
Dodecane	1.02666	0.00592	0.9991
For Mineral wool tests (post relocation of apparatus)			
Toluene	1.64557	0.01049	0.9989
(R)-(+)-limonene	1.51722	0.00539	0.9997
Dodecane	1.47314	0.00743	0.9993

An inter-laboratory check was done to compare results obtained on a similar thermal desorption / GC-FID which is present at Building Research Establishment (BRE), Watford, UK in collaboration with Bath University. A Tenax tube was injected with known amount of the 3 VOCs and analysed. The results are detailed in Table 3.4. Section 12 of ISO 16000-6:2001

(ISO, 2011a) gives the accepted analytical repeatability for various compounds to be 12% for non-polar hydrocarbons of 0.5L air samples. Although the sample was prepared using c.a. 1.5L nitrogen, the inter-laboratory repeatability was seen to result in good repeatability.

Table 3.4: Calculated mass obtained from analysing a Tenax tube using two thermal desorption / GC-FID systems present in different labs.

Compound	Injected mass (ng)	Calculated mass at Bangor (ng)	Calculated mass at BRE (ng)	Repeatability (based on ratio)
Toluene	639.25	688.62±16.49	614.04	12%
Limonene	619.72	628.05±9.73	684.89	8%
Dodecane	550.16	565.93±8.48	575.63	2%

3.3.3 Sample analysis

Each sample was weighed to 1.0000 ± 0.0001 g after being previously dried in a 50°C oven, and then was placed in the c.a. 60ml capacity sample holder. The same sample holder was used to enhance repeatability. The sample holder was fitted with a Tenax tube on top and connected to the gas flow setup at its bottom. A flow of 15.1 ± 0.2 ml/min of nitrogen passed through the VOC sources container, which was equilibrated at $30.3 \pm 2^\circ\text{C}$ and 2bar, was used to expose the sample for 30 ± 0.15 mins. The Tenax tube was subsequently analysed and the mass of each VOC that was not sorbed by the sample is calculated using the relevant linear calibration formula. Each sample type was tested in triplicates.

Blank runs were performed in triplicates or more under the same conditions, where the sample holder was left empty. Such runs were performed around and in between sets of the relevant sample runs, with the amounts detected corresponding to the total masses of the VOC the sample would have been exposed to. The amounts sorbed by the each type of sample were calculated, along with their standard deviations, as the averaged differences between the amounts detected from the sample runs and the amounts detected from their relevant blank runs. Statistical significance was calculated using IBM SPSS Statistics 22 software using one-way ANOVA. Calculations were based on the percentages sorbed rather on the exact masses, as the amount different samples were exposed to varied experimentally.

3.4 HPLC optimisation

3.4.1 Calibration and settings

The High Performance Liquid Chromatography (HPLC) apparatus was calibrated in accordance with ISO16000-3 (ISO, 2011b) using a 99.9% certified standard solution of 100µg/ml formaldehyde-DNPH in acetonitrile, which was successively diluted in acetonitrile resulting in 8 differing concentrations spanning from 2.5 to 0.0195µg/ml.

The HPLC, having a C-18 reverse phase column, was set to use the settings described in Table 3.5. Calibration runs were done in triplicates, resulting in a linear fit forced through an intercept of 0, having a slope of $23,400 \pm 53.3$ and an adjusted R^2 value of 0.9998.

Table 3.5: Optimum settings used for HPLC analysis.

Setting	Value
Injection volume	25 μ l
Flow	0.5ml/min
Column temperature	60°C, isocratic
Mobile phase	60% acetonitrile, 40% water
Detector wavelength	360nm
Run time	15min
Sampling rate	0.402sec (2251 data points)

3.4.2 Sample analysis

The same method used for sample analysis of toluene, limonene and dodecane was used for formaldehyde with the following exceptions. The flow originated from a cylinder containing formaldehyde in nitrogen as previously described, and was 15.2 ± 0.5 ml/min. DNPH cartridges were used to trap formaldehyde instead of Tenax tubes, since the latter only sorbs an undefined portion of the entire amount it is exposed to.

After the exposure experiment was complete, the DNPH cartridge's liquid contents were eluted using acetonitrile into a 10ml grade A volumetric flask by using a glass syringe (Figure 3.8). The same volumetric flask was used throughout all the experiments to enhance repeatability.



Figure 3.8: Elution of the liquid contents of a DNPH cartridge with acetonitrile using a glass syringe.

Each collected liquid sample was run on the HPLC with the above mentioned settings. For every sample run, it was made sure that the DNPH peak, which precedes the formaldehyde-DNPH peak in elution, was present in large amounts (Figure 3.9). This ensures that not all the DNPH was consumed, in which case excess formaldehyde would not form a formaldehyde-DNPH complex and escape detection.

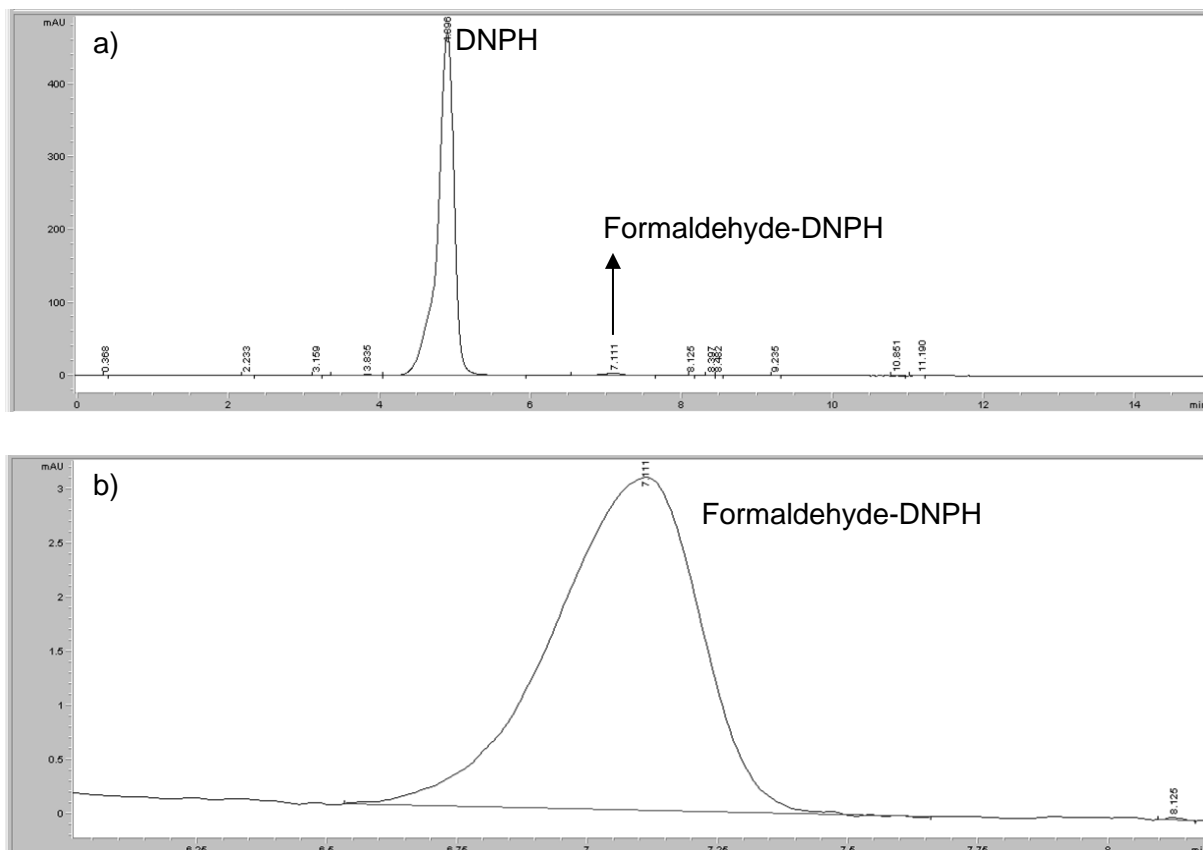


Figure 3.9: Chromatogram of sample run showing a) a large DNPH peak and a small formaldehyde DNPH peak and b) a close-up of the formaldehyde-DNPH peak.

The mass of actual formaldehyde, was calculated from the peak area of formaldehyde-DNPH using the following formula:

$$m_{FA} = \left(\frac{A_{FA-DNPH}}{Slope_{FA-DNPH}} \right) \left[\left(\frac{M_{FA}}{M_{FA-DNPH}} \right) \right] (V_{Elution})$$

Equation 3.1

Where:

- m_{FA} is the mass of formaldehyde calculated
- $A_{FA-DNPH}$ is the area of the formaldehyde-DNPH peak
- $Slope_{FA-DNPH}$ is the slope of the linear calibration fit of formaldehyde-DNPH

- M_{FA} is the molar mass of formaldehyde and $M_{FA-DNPH}$ is the molar mass of formaldehyde-DNPH complex, both in g/mol
- $V_{Injection}$ is the injection volume used by the HPLC, in ml
- $V_{Elution}$ is the volume of the volumetric flask used to elute the liquid contents of the DNPH cartridge into, in ml

The standard deviation was calculated for each sample set based on the difference in the results of the triplicate runs; however, if that standard deviation was less than the reported formaldehyde content declared by the DNPH cartridge supplier, the latter value was used in the results instead to ensure precision encompassing both the suppliers' and the used analytical equipment

Similar to the analysis of the other 3 VOCs by thermal desorption GC-FID, blank runs were performed in triplicate or more under the same conditions, where the sample holder was left empty. Such runs were performed before, after and in between sets of experiments, with the amounts detected corresponding to the total mass of formaldehyde the sample would have been exposed to. The amounts sorbed by the each type of sample were calculated, along with their standard deviations, as the averaged differences between the amounts detected from the sample runs and the amounts detected from their relevant blank runs. Statistical significance was calculated in the same manner described in section 3.3.3.

3.5 Dynamic vapour sorption

The previously described methods of using a constant flow containing small concentrations of v/VOCs passing through a sample emulates real life circumstances where building materials are subjected to such conditions. These calculations tell us the rate of sorption by the samples, but does not give a clear indication of the total capacity the sample is able to sorb. Such a description would give an idea of the real potential and longevity of a material to act as a v/VOC sorber.

In order to assess this, a Surface Measurement Systems Dynamic Vapour Sorption DVS system (Surface Measurement Systems Ltd. London, UK) was used. This method is able to assess the total physi- and chemi-sorption of a material, with the possibility of calculating each of those values (Curling et al., 2012). The system is able to weigh using a microscale a small sample exposed to a controlled temperature and relative humidity, which can be incrementally increased or decreased. The temperature during the entire experiment was kept constant at 20°C.

Formaldehyde can be added to the mixture to expose the sample to high concentrations of formaldehyde and weight the sorption. The method used by Curling et al showed good

repeatability; therefore, a modified version of the method was used: a flow of formaldehyde gas was produced by bubbling nitrogen into a 9.25% solution of formaldehyde and water. This flow can be adjusted to give differing partial pressures of the formaldehyde in the test chamber e.g. the amount of exposure to gaseous formaldehyde increases with increasing partial pressure. The micro-balance detects any uptake of moisture and formaldehyde by the fibre. The sample was subjected to the following cycles to calculate the weight of formaldehyde that the wool was able to chemically bind with (Figure 3.10):

- Specimen was left to equilibrate at 0% RH; i.e. it was not exposed to moisture or formaldehyde. This sets its baseline weight. Equilibration at all steps was based on a weight change (dm/dt) of less than 0.002% over 10 minutes.
- Specimen was left to equilibrate at 90% RH; i.e. it was exposed to high levels of moisture and formaldehyde where it sorbed both and gained weight.
- Specimen was again equilibrated at 0% RH; at this point it lost all the water it had sorbed. Any weight gain relative to the specimen's state at step 1 was therefore attributable to sorbed formaldehyde.
- Steps a to c were repeated several times to determine the total sorption capacity.

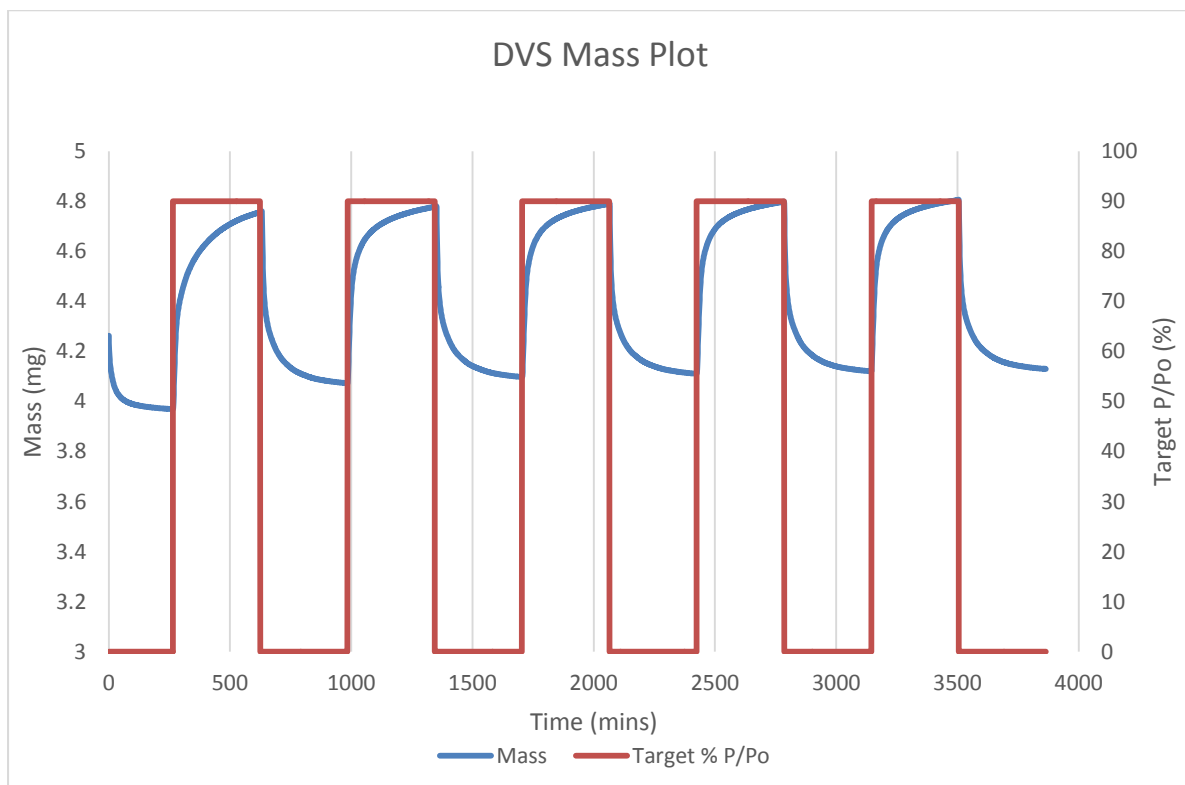


Figure 3.10: DVS sass plot of Swaledale wool exposed to formaldehyde gas.

Chapter 4: Characterising wool fibres' sorption capacities and profiles

4.1 Introduction

Studies concerning the physical and chemical properties of wool fibres are often published in textile related journals, but very little is discussed when it comes to wool fibres from different sheep breeds, with recent articles being almost non-existent (David, 1968; Demiruren and Burns, 1955; Mahal et al., 1951; Ryder, 1984). On the other hand, interest in building materials' ability to sorb v/VOCs has been recently increasing (Huang et al., 2006; Parida et al., 2006; Popa and Haghghat, 2002; Van Der Wal et al., 1998). However, limiting a literature search to wools' properties of gaseous sorption leaves a very limited number of journal papers and theses (Curling et al., 2012; Kinney, 2014; Lu, 2013b; Van Der Wal et al., 1998). A comparison of such properties between the wool of different sheep breeds has been non-existent. Therefore, it is of scientific interest to shed light on the sorptive patterns of different sheep wool types and discern the industrial and architectural opportunities that can be cultivated from the newly found differences.

To start with, a screening process of the sorptive capacity of formaldehyde was performed using a DVS system. Following on from that, three main wool types were further investigated concerning their sorption rates of formaldehyde, toluene, limonene, and dodecane at low concentration flows. In addition, some physical and chemical characteristics of these wool types, such as chemical functional groups, surface areas, pore size distributions and specific heat capacities, were studied in an effort to associate sorption profiles with defined properties.

4.2 Formaldehyde sorptive capacity by different wool types

4.2.1 Method

The method used to assess a wool sample's total capacity of sorption of formaldehyde is described in section 3.5. There was no need to pre-condition samples as conditioning takes place prior to the start and during the experiment inside the DVS system. Wool from different sheep breeds (British Wool Marketing Board, 2015a) were considered:

- Swaledale: A hardy United Kingdom (UK) hill sheep with a coarse durable wool predominately used for home furnishings and insulation. The fleece varies in pigmentation to give colours of white or grey (the latter referred to as Grey Swaledale).
- Welsh Mountain: A hardy UK hill breed and the wool has been commonly used for home furnishings.

- Herdwick: The hardest of all British breeds, having wools commonly used in carpet and rug manufacture. The lambs are born with a black fleece, and with age white brittle fibres appear giving an overall grey colour. Wools obtained are referred to as light or dark Herdwick depending on the colour.
- Drysdale: A New Zealand breed noted for its coarse wool that is used in home furnishings.
- Blackface: A UK mountain breed with the wool used mostly for home furnishing and tweed cloth.
- Romanian: The wool is a blend obtained from different sheep breeds of Romanian origin.
- Fawn: This sheep wool is of mixed batches of international origin, possibly originating from different sheep breeds, which are sorted and named after the characteristic colour resembling that of fawn hair.

In addition, non-sheep wools, from the Alpaca species, was also studied. Alpaca is a llama like camelid with the hair in this case obtained from domestic animals raised in the UK. Alpaca wool samples were taken from both the saddle of the animal and from other areas that yield lower quality wool, labelled as 'waste wool'.

Unless otherwise stated, the wools tested were in their scoured state. Wools that were only easily obtained in their scoured state were scoured using industrial techniques, and therefore not tested in their unscoured states. However, Swaledale and Light Herdwick wools were tested in both their raw, unscoured form and in their scoured form (see Section 2.2.7.1). The unscoured wools tested were scoured in the lab to ensure no excessive alterations or variations due to seasons or batch processing are included. Scouring was carried out following the simple method used by Parvinzadeh (Parvinzadeh, 2007a). First, the unscoured wool was dried at 50°C for a period of ≥ 2 days; drying at higher temperature was avoided as it leads to the partial and slow thermal degradation of the fibres. The wool was scoured in 100g batches using 3980ml distilled water and 20g (0.5%) Hostapal MRZ (a non-ionic surfactant) in a 5L flask at 50°C, mixed for 30min, after which the aqueous mixture was disposed of. To remove the excess surfactant and residues, the wool was subsequently rinsed at least twice with c.a. 5L of distilled water, and left to dry at 50°C for ≥ 3 days.

4.2.2 Results and discussion

All tested wool types showed a capacity to sorb formaldehyde gas, with a maximum sorption range between 40.59 and 97.92g of formaldehyde per kg of wool (Figure 4.1). Figure 4.2 shows the progression of mass increase of some wool types as they are exposed to cycles of

excess formaldehyde. The more rapid increase in mass occurs at the end of the first cycle, which is followed by a steady increase after each cycle, resulting in a logarithmic progression.

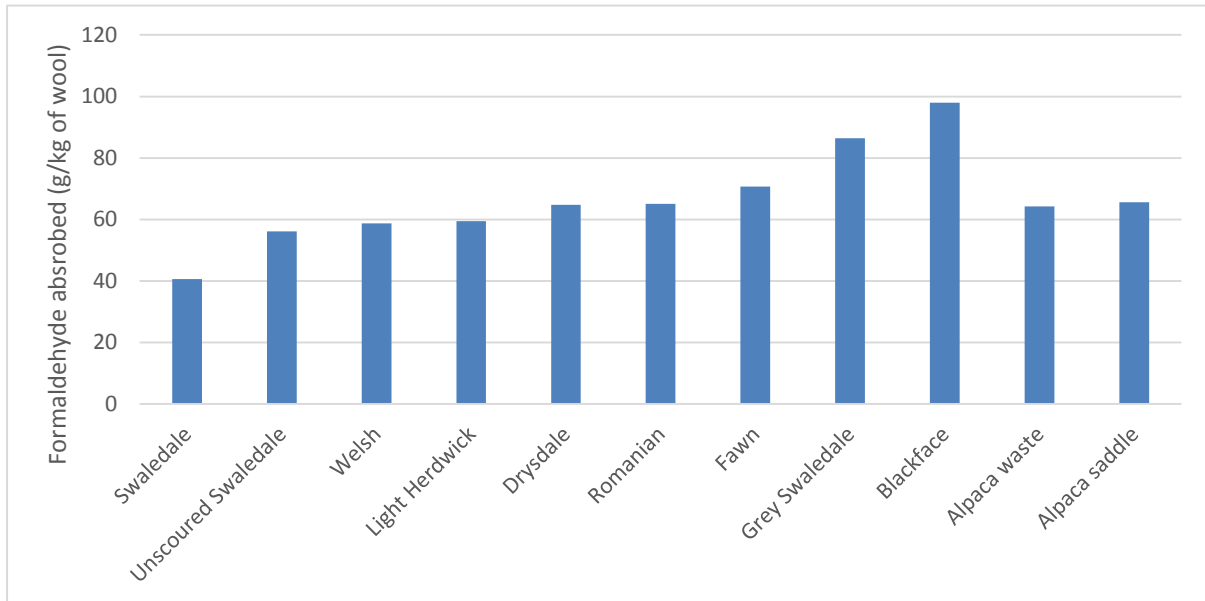


Figure 4.1: Maximum capacities of the sorption of formaldehyde gas by different wool types and conditions, determined by exposure to several cycles of excess levels of formaldehyde.

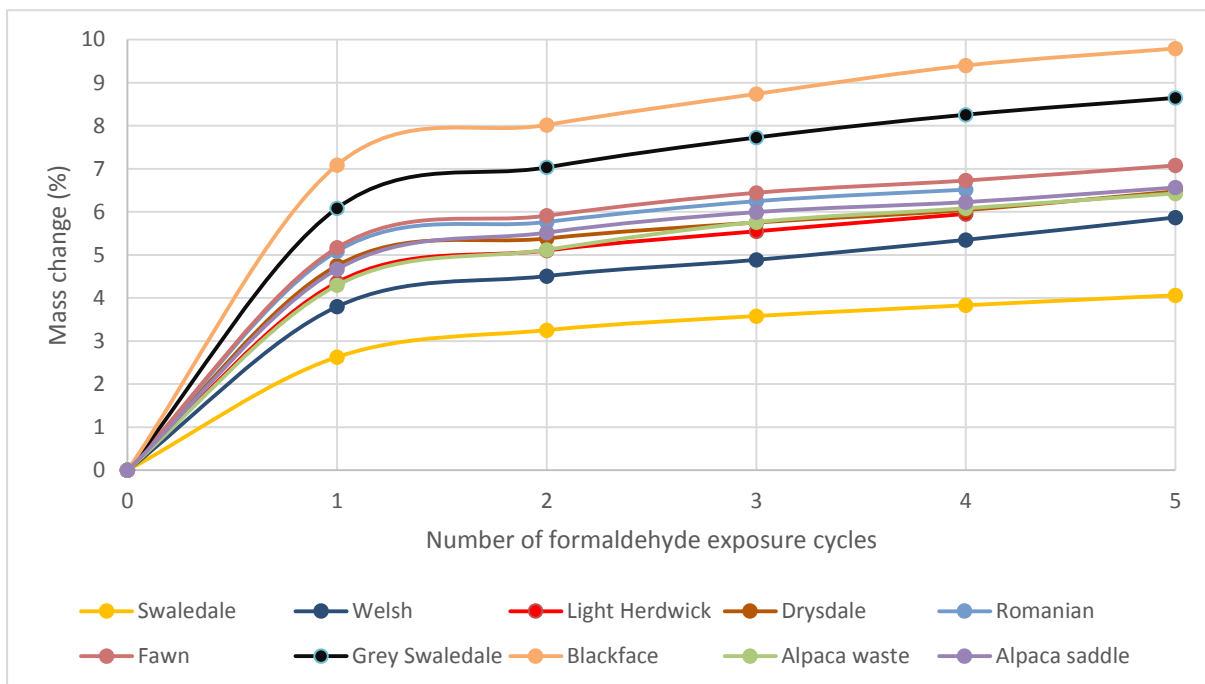


Figure 4.2: Increase in mass of wool types per each formaldehyde exposure cycle.

Sorption capacity differences between the wool types is noted. Although no experimental repeats were performed due to the length of time each experiment requires, the method is

based on one used by Curling et al which utilizes cyclic repeats of exposure (Curling et al., 2012).

Differences between wool types is considerable in most cases, with Swaledale wool showing the lowest maximum capacity of 40.6 g/kg of wool. Light Herdwick exceeds Swaledale by 18.9g/kg of wool whereas Blackface has the highest capacity, exceeding Swaledale by 57.3g/kg of wool. Unscoured Swaledale had greater maximum capacity than its scoured counterparts, exceeding it by 15.6g/kg of wool.

Wool from a different species, alpaca, showed a comparable average capacity compared to the tested sheep wools.

For further experiments, the number of wool types tested was limited to 3 different types and some of their unscoured counterparts. The types selected were based on the results above, with Swaledale being selected as having the lowest formaldehyde sorption capacity, Light Herdwick having an average formaldehyde sorption capacity, and Blackface having the highest formaldehyde sorption capacity.

4.3 v/VOCs sorption profiles by different wool types

4.3.1 Method

As explained in section 3.2, the v/VOC sorption rates of fibres were deduced using a gas flow setup that uses a constant flow containing small concentrations of v/VOCs fully interacting with a sample, emulating a real life scenario. This stands in contrast to the DVS method that gives an indication to the maximum sorptive capacity of the fibres. Statistical significance was calculated using IBM SPSS Statistics 22 software using one-way ANOVA.

4.3.1.1 Formaldehyde

The method used to assess a wool sample's sorption of a low concentration flow of formaldehyde is described in Section 3.2 and 3.4. All samples were dried in a 50°C oven for a period at least 2 days. Along with the use of dry air as a carrier gas in the gas flow set-up, the interaction of moisture with the fibres and VOCs was minimised to the lowest level possible without altering the fibre through thermal degradation.

Swaledale wool was tested both in raw unscoured form and in its scoured form (see Section 2.2.7.1 and 4.2.1). Mineral wool was also tested to compare the sorptive abilities of synthetic fibres to that of wool fibres. Mineral wool was exposed to a lower amount (ng) of formaldehyde compared to the wool fibres due to the experiments being performed at a different time, as the formaldehyde within the cylinder degrades with long period of time (i.e. over a few weeks).

Another set of experiments were performed on Light Herdwick fibres where the total amount of formaldehyde the fibres were exposed to differed. A high range ($565\pm 18\text{ng}/30\text{min}$) of formaldehyde was delivered to the fibres using the same procedure mentioned in section 3.4.2, using a 100% flow from the cylinder. A medium range ($370\pm 10\text{ng}/30\text{min}$) was delivered using a 50%/50% ratio of formaldehyde carrier and pure nitrogen gas. The low range ($150\pm 3\text{ng}/30\text{min}$) was achieved using a ratio of 33%/66% of formaldehyde carrier to pure nitrogen gas. Total flow volumes remained the same in all cases. For each range, blanks and samples were run in triplicate according to section 3.4 to deduce the standard variation.

4.3.1.2 Toluene, limonene and dodecane

The method used to assess a wool sample's sorption of a low concentration flow of toluene, limonene and dodecane is described in Section 3.2 and 3.3.

Similar to the formaldehyde setup mentioned above, the interaction of moisture with the fibres and VOCs was minimised to the lowest level possible through the use of nitrogen as a carrier gas in the gas flow set-up and drying all samples in a 50°C oven for a period ≥ 2 days. Also, Swaledale and Light Herdwick wools were tested both in raw unscoured form and in their scoured form (see Section 2.2.7.1 and 4.2.1). Mineral wool was also tested to compare the sorptive abilities of synthetic fibres to that of wool fibres. Mineral wool was exposed to a higher amount (ng) of VOCs compared to the wool fibres due to the experiments being performed at a different time, as the VOC amounts (ng) released from the sources vary with long period of time (i.e. over a few weeks). Considering the relatively low concentrations used, the total exposure is expected to be well below the max capacity of the material, posing no interference.

Another set of experiments were performed on Light Herdwick fibres where the total amount of each VOC the fibres were exposed to differed. Three different flow compositions were achieved by changing the temperature of the sources container or by removing some of the sources tubes used within it. Table 4.1 describes the changes between each range and the amounts delivered to the samples and blank runs. For each range, blanks and samples were run in triplicate in accord to section 3.3 to deduce the experimental standard variation.

Table 4.1: The different flow compositions of the three VOCs delivered to samples and blank runs.

Range	Temperature of sources ($^\circ\text{C}$)	Number of sources tubes used	Amount of toluene (ng/30min)	Amount of limonene (ng/30min)	Amount of dodecane (ng/30min)
High	30.3 ± 2	3	401 ± 81	807 ± 42	$1,310\pm 46$
Medium	20.3 ± 2	3	410 ± 44	516 ± 14	489 ± 10
Low	20.3 ± 2	1	304 ± 41	174 ± 4	150 ± 8

4.3.2 Results and discussion

4.3.2.1 Formaldehyde

Contrary to the study of formaldehyde sorption capacity, these sets of experiments showed no significant difference ($F(2,6) = 2.091$, $p = 0.205$) in the sorption of a low concentration of formaldehyde between different scoured wool types, which was $40-47 \pm 4-7\%$ of the total amount of formaldehyde the fibres were exposed to. However, unscoured Swaledale sorbed $26 \pm 8\%$ more compared to scoured Swaledale, a statistically significant increase ($F(1,4) = 18.332$, $p = 0.013$). Mineral wool on the other hand sorbed much less than any of the wool fibres, only absorbing $21 \pm 10\%$ of the formaldehyde it was exposed to.

Results are summarised in Figure 4.3.

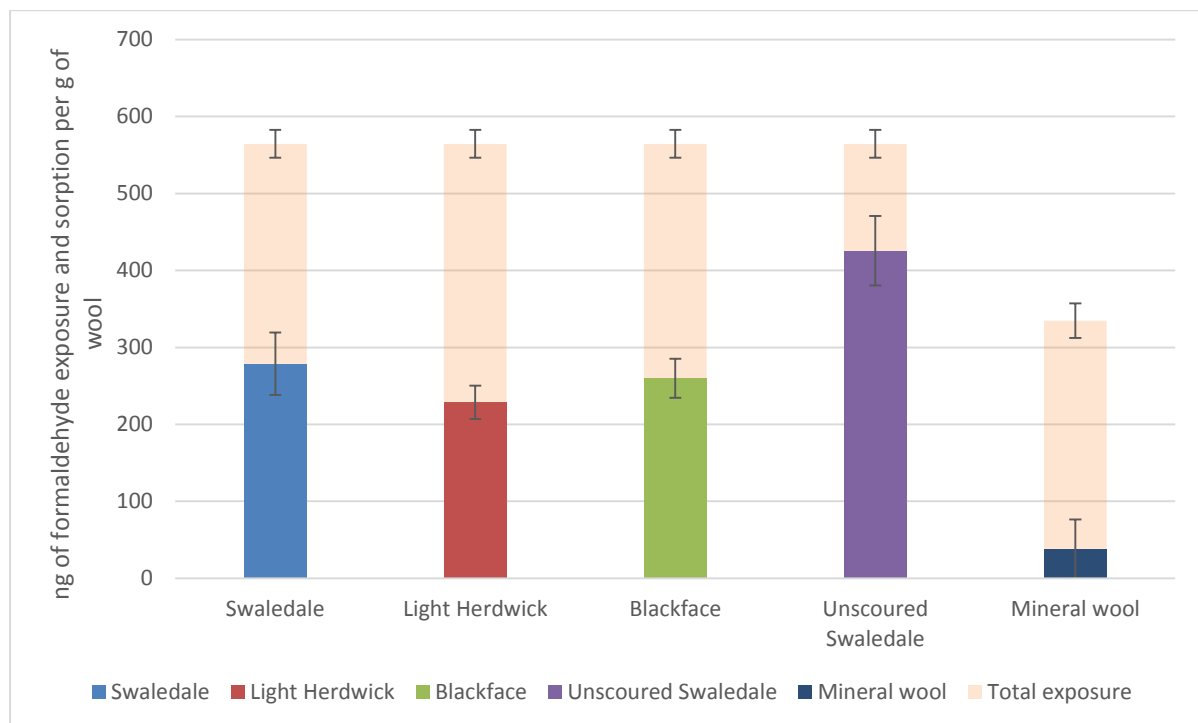


Figure 4.3: Sorption of a low concentration flow of formaldehyde by different wool types.

When studying the effect the amount of formaldehyde a fibre is exposed to has on its sorption profile, decreases in the amounts sorbed are seen with decreasing exposure (Figure 4.4a). However, when the same data are reorganised as percentages of the amounts sorbed relative to the amounts of exposure, the percentage sorbed significantly increases with decreasing exposure ($F(2,6) = 67.898$, $p = 0.000$; Figure 4.4b). Decreasing the exposure amount from 565 ± 18 ng (high range) to 370 ± 10 ng (mid range) was accompanied by a $20 \pm 4\%$ sorption increase ($F(1,4) = 36.668$, $p = 0.004$), and furthering the decrease from the mid range to 150 ± 3 ng (low range) was accompanied by an additional $22 \pm 5\%$ sorption increase ($F(1,4) = 34.314$, $p = 0.004$). Hence it is concluded that the percentage sorbed decreases with

increasing exposure levels, as the actual increase in the mass sorbed grows smaller with increasing exposure levels. The mass sorbed remains the same as long as there is excess formaldehyde nearby, but decreases when the limit is reached.

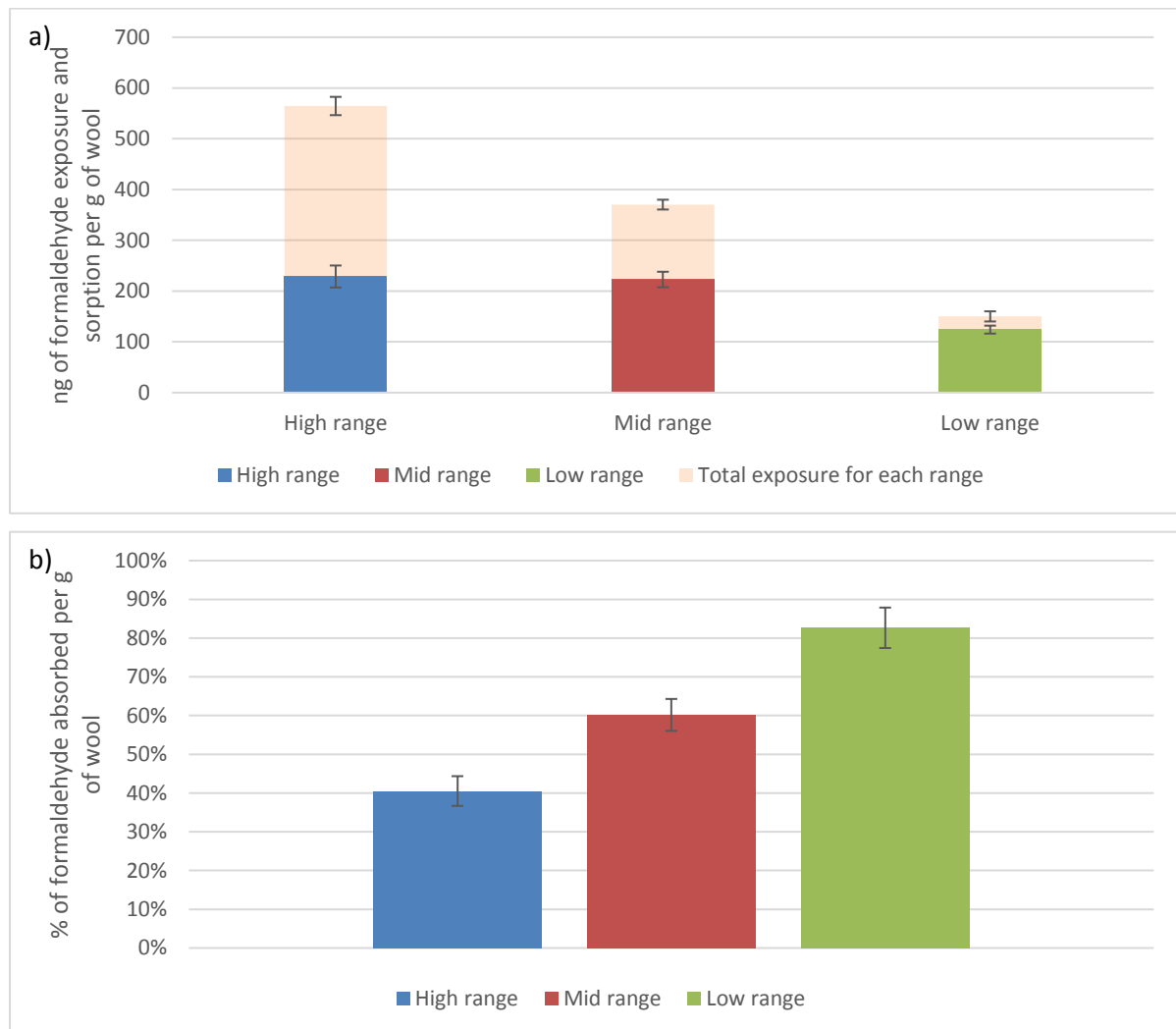


Figure 4.4: Sorption of formaldehyde by Light Herdwick when different exposure quantities are introduced: a) Mass (ng) of formaldehyde sorbed and used to expose fibres to; b) Percentage of formaldehyde sorbed relative to the total amount of formaldehyde each set of fibres was exposed to.

To further analyse these profiles, when the exposure concentration is compared graphically to the percentage absorbed, it is seen that an increase in formaldehyde exposure is accompanied by a linear decrease in sorption of amounts exposed to. Figure 4.5 shows the linearly inverse relationship between exposure and sorption percentage at such exposure levels. It is expected that at a certain high level of exposure, the increase in mass sorbed would have reached its maximum and further increases in exposure would lead to no more further significant increase in sorption. Therefore it is logical to conclude that, at higher levels of exposure, this linear relationship starts changing into a logarithmic one, plateauing at the fibre's maximum capacity of sorption. These levels are not reached under these experimental

conditions, but when fibres are exposed to excess formaldehyde gas as previously shown under section 4.2, sorbing tens of mg of formaldehyde per g of wool (Figure 4.1).

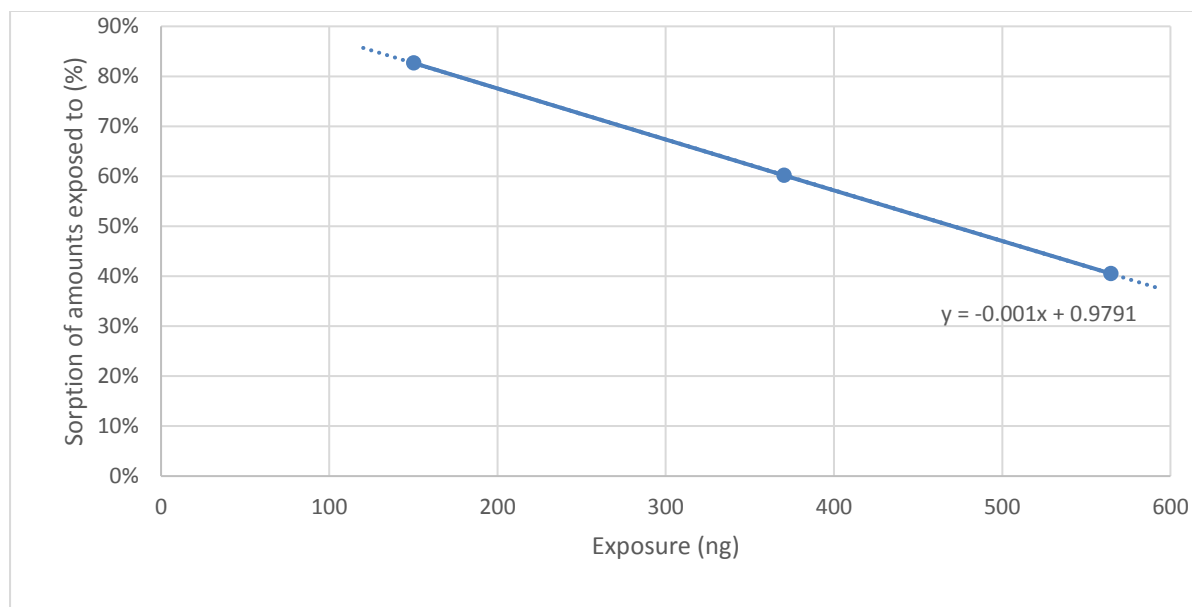


Figure 4.5: Percentages sorbed as a function of total formaldehyde exposure amounts.

4.3.2.2 Toluene, limonene and dodecane

When comparing the sorption profile of toluene by the different wool types and mineral wool, there seems to be very small to insignificant percentage of toluene sorbed across the whole range of fibres ($F(5,12) = 1.030$, $p = 0.443$). Although insignificant, sorption values between different wool types were highest for Swaledale, followed by Light Herdwick, and lowest for Blackface. The highest sorption of toluene is observed in the case of unscoured wools, being 33 to $37 \pm 20\%$ of the amount of VOCs the fibres were exposed to.

Sorption of limonene on the other hand was more pronounced (for scoured wools, ($F(2,6) = 8.537$, $p = 0.018$), with a maximum of $46 \pm 5\%$ for Swaledale. Light Herdwick similarly sorbed $44 \pm 9\%$ and sorption by Blackface decreased significantly to $28 \pm 5\%$. However, a dramatic increase is again noted in the case of unscoured wools which sorbed the whole amount they were exposed to ($F(1,4) = 493.143$, $p = 0.000$ for Swaledale and $F(1,4) = 121.878$, $p = 0.000$ for Light Herdwick). Mineral wool in comparison sorbed considerably less of a percentage than any of the wool fibres, reaching $20 \pm 9\%$ of the amount it was exposed to.

Dodecane was sorbed in high quantities by all fibres, the sorption profile following a similar pattern as limonene. Sorption levels varied from $94 \pm 4\%$ for Swaledale and $91 \pm 4\%$ for Light Herdwick to a lower value of $81 \pm 4\%$ for Blackface (for unscoured wools, ($F(2,6) = 18.348$, $p = 0.003$). Again, in the case of unscoured wools, the VOC is completely sorbed ($F(1,4) = 22.929$, $p = 0.009$ for Swaledale and $F(1,4) = 24.911$, $p = 0.008$ for Light Herdwick). In the case of mineral wool, a sorption of $81 \pm 5\%$, similar to that of Blackface, is noted.

Results are summarised in Figure 4.6.

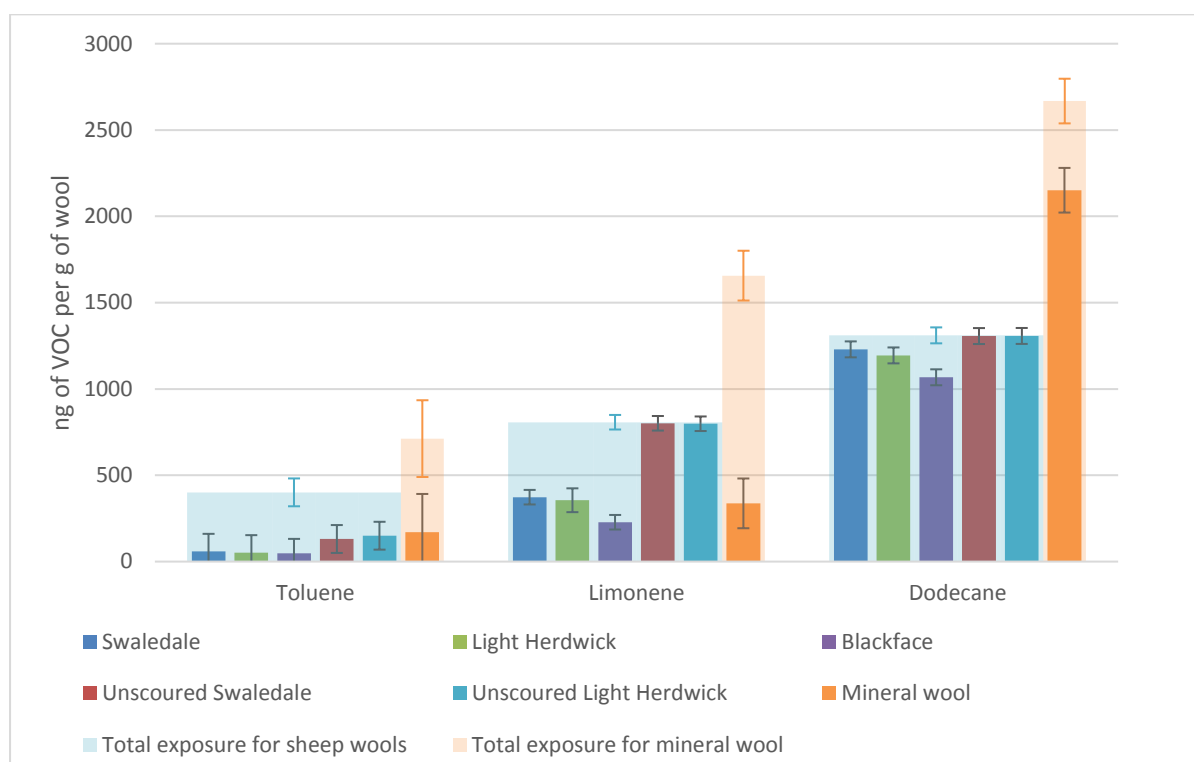


Figure 4.6: Sorption of a low concentration flow of toluene, limonene and dodecane by different wool types.

The difference in the profiles of sorption between the scoured wool types is consistent for VOCs that result in statistically significant sorption differences. Swaledale seems to sorb slightly more than Light Herdwick, and both sorb more than Blackface does. Comparing these results with the total sorption capacity of formaldehyde (as determined using DVS method), this profile for the non-polar VOCs (limonene and dodecane) is the reverse of the profile observed in the case of the polar vVOC (formaldehyde). This change in profiles is logical and implies that the surface polarity of different wool fibre types is not the same. The more polar the surface of the fibre is, as noted in the case of Blackface, the more it can sorb polar vVOCs such as formaldehyde, but would have less affinity towards the non-polar VOCs such as limonene and dodecane; the reverse is also true, as noted in the case of Swaledale.

When studying the effect the amount of VOCs a fibre is exposed to has on its sorption profile, differences in the amounts observed are clearly seen. However, when these amounts are converted to percentages of total exposure, these differences in sorption are very small. In the case of toluene, the change in the amounts (ng) of exposure did not vary much experimentally ($F(2,6) = 0.296$, $p = 0.773$) as it was difficult to control due to the high volatility of the chemical. In the case of limonene, increasing the amount of exposure from 173 ± 4 ng (low range) to 516 ± 14 ng (mid range) was accompanied by a $6 \pm 4\%$ sorption increase, and furthering the increase from the mid range to 807 ± 42 ng (high range) was accompanied by an additional

11±9% sorption increase ($F(2,6) = 1.937$, $p = 0.224$). For dodecane, increasing the amount of exposure from 132±2ng (low range) to 438±2ng (mid range) and furthering the increase from the mid range to 1310±46ng (high range) were both accompanied by small but statistically insignificant sorption percentage increases ($F(2,6) = 2.261$, $p = 0.185$).

Results are summarised in Figure 4.7.

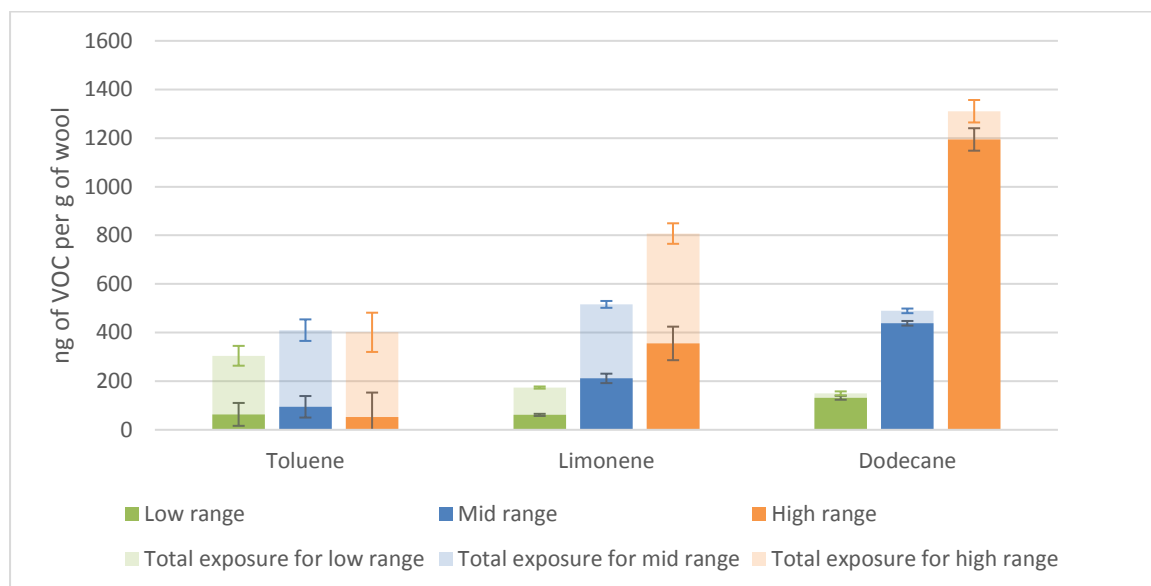


Figure 4.7: Sorption of toluene, limonene and dodecane by Light Herdwick when different exposure quantities are introduced

In a similar comparison to that made for formaldehyde sorption (Figure 4.5), the percentage of the amounts of limonene and dodecane sorbed seem to both follow a linear trend with increasing exposure levels (Figure 4.8), indicating a direct relationship between exposure and sorption. The gradient for limonene is higher than that of dodecane, both being positive – unlike the case of formaldehyde. This observation is of interest since it shows that when higher quantities of non-polar VOCs are exposed to wool fibres, the percentage sorbed escalates in a linear fashion at low levels. However, as seen in the case of the polar vVOC formaldehyde, increasing the quantities of exposure leads to a linear decrease in the percentage sorbed. Thus, it can be concluded that although the surface of wool fibre (Light Herdwick in this case) has both polar and non-polar regions, the average polarity of the fibre surface seems to favour the non-polar attractions of VOCs. According to previous results, this preferential sorption of non-polar VOCs is expected to be enhanced for certain wool fibres such as Swaledale, or it may be reduced or even reversed for other wool fibres such as Blackface. It all appears to be a functionality of the polarity of the surface of the fibre in question.

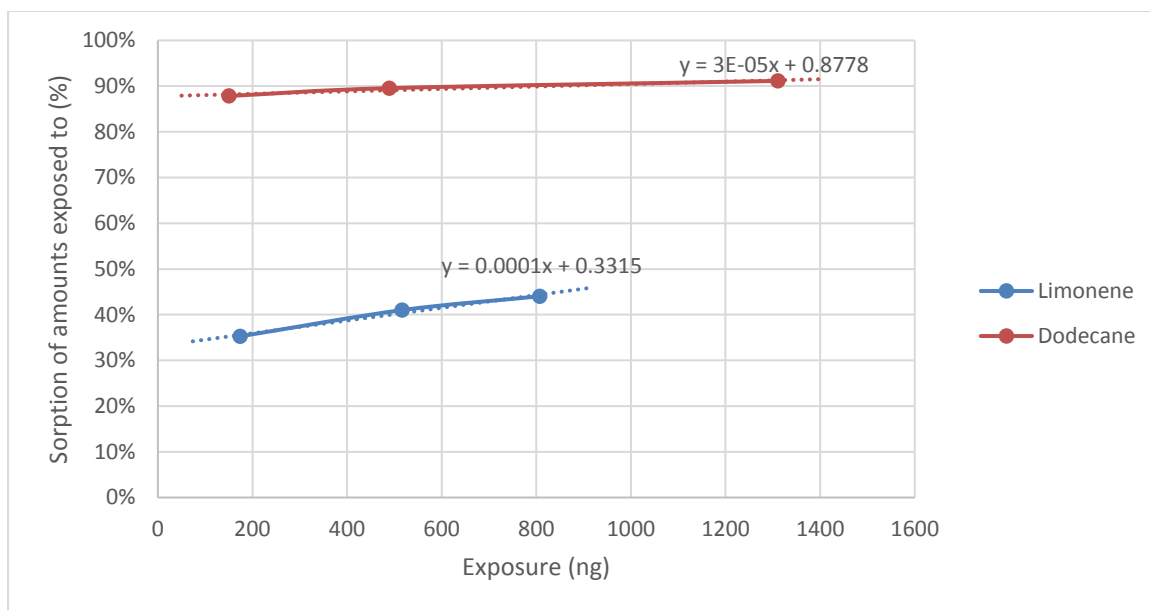


Figure 4.8: Percentages sorbed as a function of total limonene and dodecane exposure amounts.

The differing slopes observed for the 3v/VOCs in Figure 4.5 and Figure 4.8 are further investigated. Replacing the exposure amounts with successive increases in exposure (differences in exposure amounts) and replacing the percentages sorbed with successive changes in sorption percentage (differences in percentages sorbed) gives a graph showing how the acceleration/deceleration of sorption percentage (as opposed to sorption percentage itself) changes with changing exposure. With increasing exposure concentrations, the percentages sorbed decelerates linearly for formaldehyde, accelerates exponentially for limonene and accelerates logarithmically in dodecane's case (Figure 4.9).

Considering that the exposure levels used for testing are relatively low, I can conclude that the fibres (Light Herdwick in this case) reach almost full dodecane sorption efficiency starting from very low levels, but are intensely more efficient at sorbing limonene at higher concentrations. In the case of formaldehyde, the fibre's efficiency in sorption declines at higher concentrations. Relating these observations to the surface chemistry of the fibre (see section 1.3.5) can be used to predict that the outermost surface, which is the first point of contact with surrounding gases, must be very non-polar in nature. This is in agreement with the literature reporting an integral structural layer of lipids as the outermost layer, more so when the surrounding environment is dry (see section 1.3.5) – which was the experimental condition (see section 2.2.5). Hence, dodecane will be instantly and efficiently sorbed by this layer. In case of the slightly less polar limonene which is marginally deterred to start with, higher concentrations will further its penetration of the surface to underlying or mixed-in chemical functionalities having similar polarities, resulting in the exponential increase in sorption. However, in the case of formaldehyde, increasing the concentration causes the lipid layer to

deter more of the v/VOC it is exposed to, resulting in a deceleration of sorption (although in mere quantities, more is sorbed). Any patches of polar regions on the surface therefore must be severely outnumbered by the non-polar regions caused by the outer lipid layer. The peculiar linearity of the decrease in sorption rates of formaldehyde may be explained by Maxwell and Huson's explanation of how the lipid layer dynamically reorients itself upon exposure to a polar environment so that the non-polar chains of the lipid layer are orientated inward the fibre surface rather than outward (Huson et al., 2008; Maxwell and Huson, 2005).

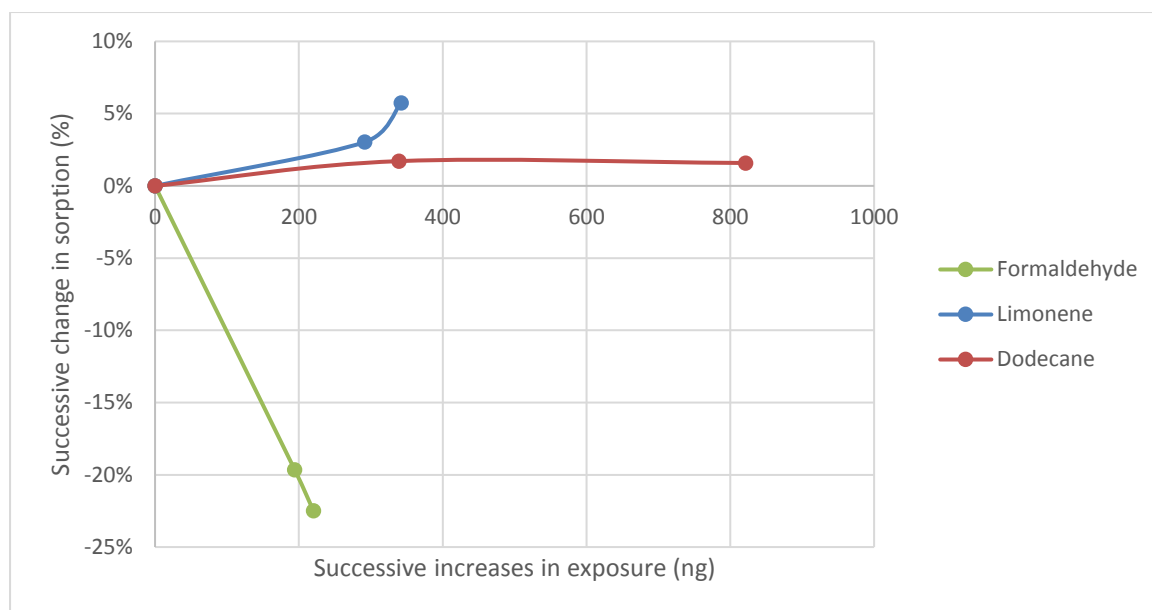


Figure 4.9: Successive changes in sorption percentages as a function of successive increases in exposure for 3 different v/VOCs with Light Herdwick wool fibre.

Maxwell and Huson's explanation of the dynamic outer lipid layer of the fibre also fits in the fact that the maximum potential of formaldehyde sorption is not reached until several cycles of high-formaldehyde-concentrations and no-formaldehyde-concentrations (pure N₂) are alternated (see section 4.2). In one sudden exposure to formaldehyde gas, the lipid layer dynamically moves inwards into the fibre, exposing the more polar regions and allowing the sorption of some of the gas; however, reverting back to a non-polar formaldehyde free environment of N₂ gas reverts the lipid layer back to the outer surface. Repeating the exposure to formaldehyde gas would allow the sorption of more formaldehyde whilst the formaldehyde already sorbed in the previous cycle is slow at desorption, resulting in increased sorption. Adding to that, with several cycles of formaldehyde/no-formaldehyde exposures, the mechanical motion of the lipid layer may cause the sorbed formaldehyde to be progressively pushed into the fibre and to be potentially 'locked-in' the inner polar structure of the fibre. This is coherent with the observation of Curling *et al.* of the presence physi- and chemi-bound formaldehyde by wool fibres (Curling et al., 2012).

4.4 Characterisation of different wool types

In order to understand the underlying properties of different wool types that leads to their different sorptive behaviour, some of the chemical and physical properties were examined. This is in an effort to clarify which of the main properties of wool has the most pronounced effect on sorption patterns.

4.4.1 Fourier transform infrared spectroscopy (FTIR)

4.4.1.1 Method

Samples were directly scanned using attenuated total reflectance (Thermo scientific Nicolet 8700 FTIR with Pike GladiATR) technique after they have been dried in a 50°C oven for over a week. Each sample was scanned after a background spectrum has been acquired.

4.4.1.2 Results and discussion

Results were interpreted according to the literature (Aluigi et al., 2007; Krimm, 1960; Li et al., 2009; Wojciechowska et al., 1999; Xiao and Hu, 2016; Xu et al., 2006). The common features observed in all wool types are (Figure 4.10):

- OH stretching along with the Amide A band (NH stretching) at 3600 to 3100cm⁻¹
- Amide B band (NH stretching) at 3075 to 3056cm⁻¹
- CH₂ stretching at 2930cm⁻¹ and 2850cm⁻¹, observed to be more intense for the unscored wools
- Amide I band (C=O stretching) at 1600 to 1690cm⁻¹, sensitive to secondary structure of proteins, also observed to be more intense for the unscored wools
- Amide II band (NH bending and CN stretching; bending deformation peak of C–N–H) at 1480 to 1580cm⁻¹
- Peak at 1448 to 1455 cm⁻¹ are due to stretching vibration of carboxyl (C-O) groups
- Peak at 1390cm⁻¹, seen at higher intensity for unscoured wools, is due to the stretching vibration of C-C backbone
- Amide III band (phase combination of CN stretching and NH bending, plus CC stretching and C=O bending) at 1220 to 1300cm⁻¹, depending on conformation of keratin molecule
- Disulphide bonds at 1300 to 1000cm⁻¹

Relatively few differences in the spectra exist between the wool types. Some minor shifts in the wavenumber of peaks between one wool type/condition and another are seen, and is attributed to the differences in the structure (α and β) of the wools and to physical treatments they have been subjected to, such as stretching (Yao et al., 2008). The differences seen for

the unscoured wools can be attributed to the presence of lanolin; lanolin is mostly composed of sterol esters and therefore would logically result in more intense CH₂, C=O and C-C stretching as it is present on the surface and an ATR technique was utilised. Some other peaks are seen for some wools but not others. They are:

- Peak at 1720cm⁻¹, typical of a C=O carbonyl group, seen mostly with unscoured Swaledale and to small extents for the other wools except for Blackface.
- Peak at 1160cm⁻¹, seen only for Light Herdwick, is associated with stretching of the C-O-C bridge of ester functions

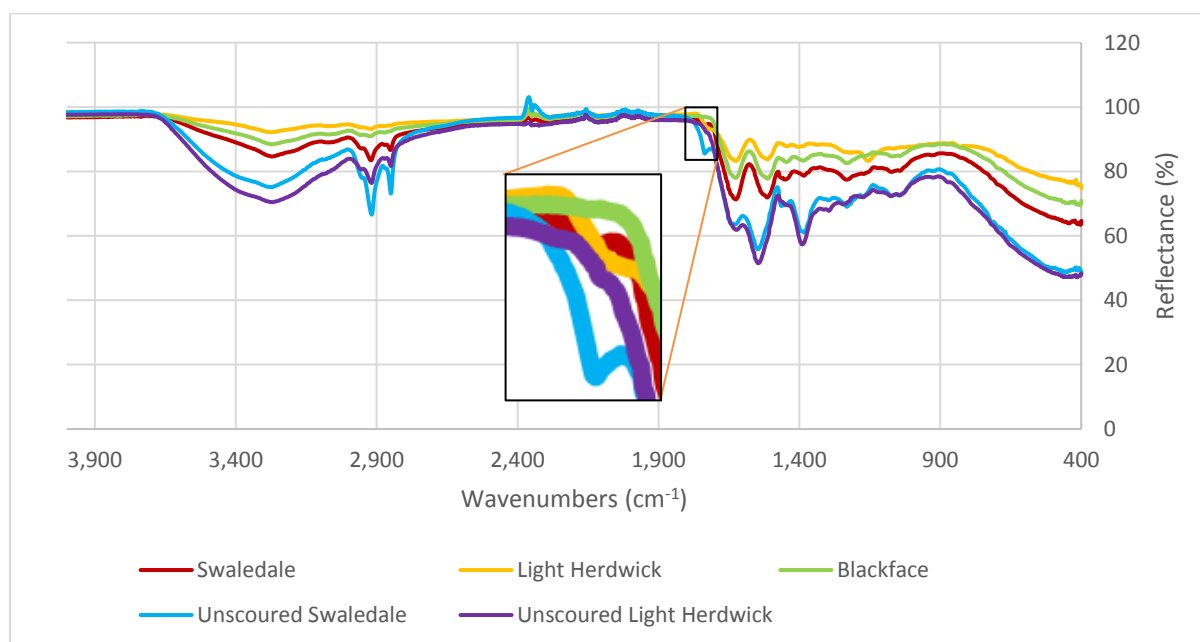


Figure 4.10: FTIR spectra of different wool types and conditions, with a zoom-in at the peaks at 1720cm⁻¹.

Associating the presence of C=O groups in all wools except Blackface may explain some sorption profiles. It is proposed that the surface lipid layer is covalently bound on wool fibres via thioester linkages with the amino acid cysteine (see section 2.2.5). Therefore, the more C=O groups are present, the more likely that lipids exist on the outer surface. This alludes to the fact that Blackface has less lipids than other wools on its surface, whereas unscoured Swaledale has the most. Such a conclusion is consistent with the sorption profiles observed for the tested v/VOCs and reinforces the surface polarity effect on sorption.

4.4.2 Surface area and pore size distribution

4.4.2.1 Method

Surface area and pore distribution of the samples was determined using nitrogen adsorbance as follows. Analysis was carried out on dried degassed samples using a Micromeritics Gemini surface area analyser with nitrogen as the adsorbate, and liquid nitrogen as the sample

coolant (to ensure temperature stability). The machine was calibrated using a Kaolinite calibration standard. Surface area was calculated by the Micromeritics Stardriver software using the Brunauer, Emmett and Teller (BET) theory (Brunauer et al., 1938), based on volume of nitrogen adsorbed at different partial pressures (zeroed for background pressure). Pore size and distribution was determined using the Barrett, Joyner and Halenda (BJH) theory (Barrett et al., 1951a).

Mineral wool was tested as a reference material. Each sample was run in triplicate after being dried for 7 to 10 days in a 50°C oven. Each sample run was preceded with zeroing the volume of nitrogen adsorbed at background pressure. Pore distribution and cumulative pore volume graphs are presented with the standard deviation as semi-transparent bars across all graph values. Statistical significance was calculated using IBM SPSS Statistics 22 software using one-way ANOVA.

4.4.2.2 Results and discussion

Surface area measurements (Figure 4.11) show a trend for wool fibres to have a higher surface area than mineral wool, with Light Herdwick having the highest value, followed by Blackface and then Swaledale (for mineral wool and unscoured wools, $F(3,8) = 1.417$, $p = 0.307$). Unscoured wools also seem to have slightly higher surface areas compared to their counterparts ($F(1,4) = 7.979$, $p = 0.048$ for Swaledale and $F(1,4) = 0.219$, $p = 0.664$ for Light Herdwick).

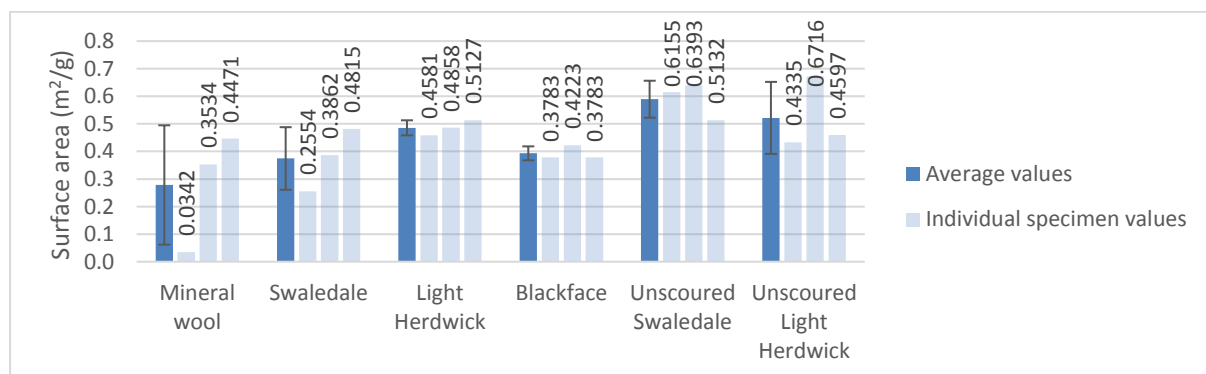


Figure 4.11: Surface area measurements for different wool types and conditions (scoured and unscoured), in addition to mineral wool.

Pore size can be classified into:

- Microporus: <2nm
- Mesoporus: Between 2nm and 50nm
- Macroporus: >50nm

Pore size distribution was assessed for mesopores, and for macropores where possible. No noteworthy differences can be observed throughout the whole pore size range; however, the distribution indicates that the mesopores present are in the smaller range for all wool types -

in the 2 to 10nm range. Mineral wool's distribution compared to all other wools is lower. Between 10 and 30nm, the distribution appears identical, only increasing for Blackface and decreasing for mineral wool beyond 30nm (Figure 4.12a). The increased distribution of pores greater than 30nm for Blackface could be a result of patches where there are no lipids surrounding the surface compared to other wools.

When comparing scoured wools with their unscoured counterparts, the only notable difference is seen in the case of Swaledale, where scouring seems to have lowered the distribution of pores sized between 12 and 18nm, and increased the distribution of pores sized over 47nm (Figure 4.12b). Again, this increase in distribution of larger mesopores is likely to be the result of the patchy removal of some of the surface lipids due to scouring.

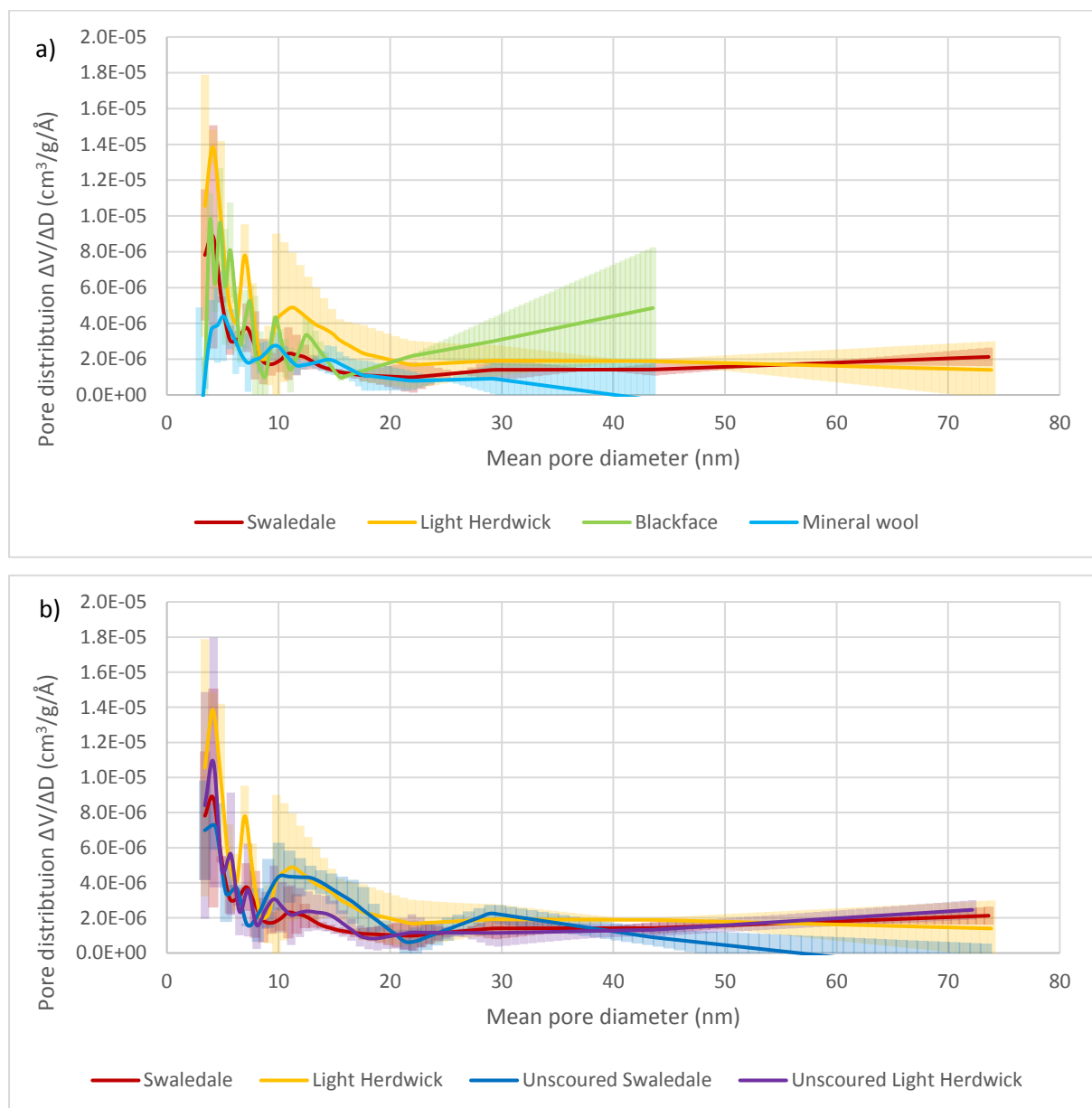


Figure 4.12: Pore size distribution for a) different wool types and mineral wool and b) scoured and unscoured wool types. The shaded areas represent the standard deviation for all pore distribution values.

Cumulative pore volumes (Figure 4.13a) are distinctively different for wool types, showing the most adsorbant of N₂ to be Light Herdwick followed by Blackface and then Swaledale. This trend is not different than that seen for surface area measurements (Figure 4.11) and in the microporous section of pore size distribution (Figure 4.12a). It shows that most of the volume is provided by the smaller pores, as the cumulative volume increases the most at the beginning of the curve. Extrapolating the graphs towards the larger pores (greater than 43nm) using a linear fit shows that the larger pores contribute a greater proportion of the volume in blackface than in the others. This again follows the same trend seen for pore size distribution of Blackface. Mineral wool is less adsorbant than any wool types, which can be easily explained by its reduced number of pores it possesses.

Scouring has the effect of increasing the cumulative pore volume considerably. This is reasonable since the wax-like lanolin and other sediments are washed out of the pores during the scouring processes, increasing their free volume. This may seem at first glance contradictory to surface area measurements, but the fact that lanolin may create a barrier on the fibre surface that prevents the detection of underlying pores explains this observation.

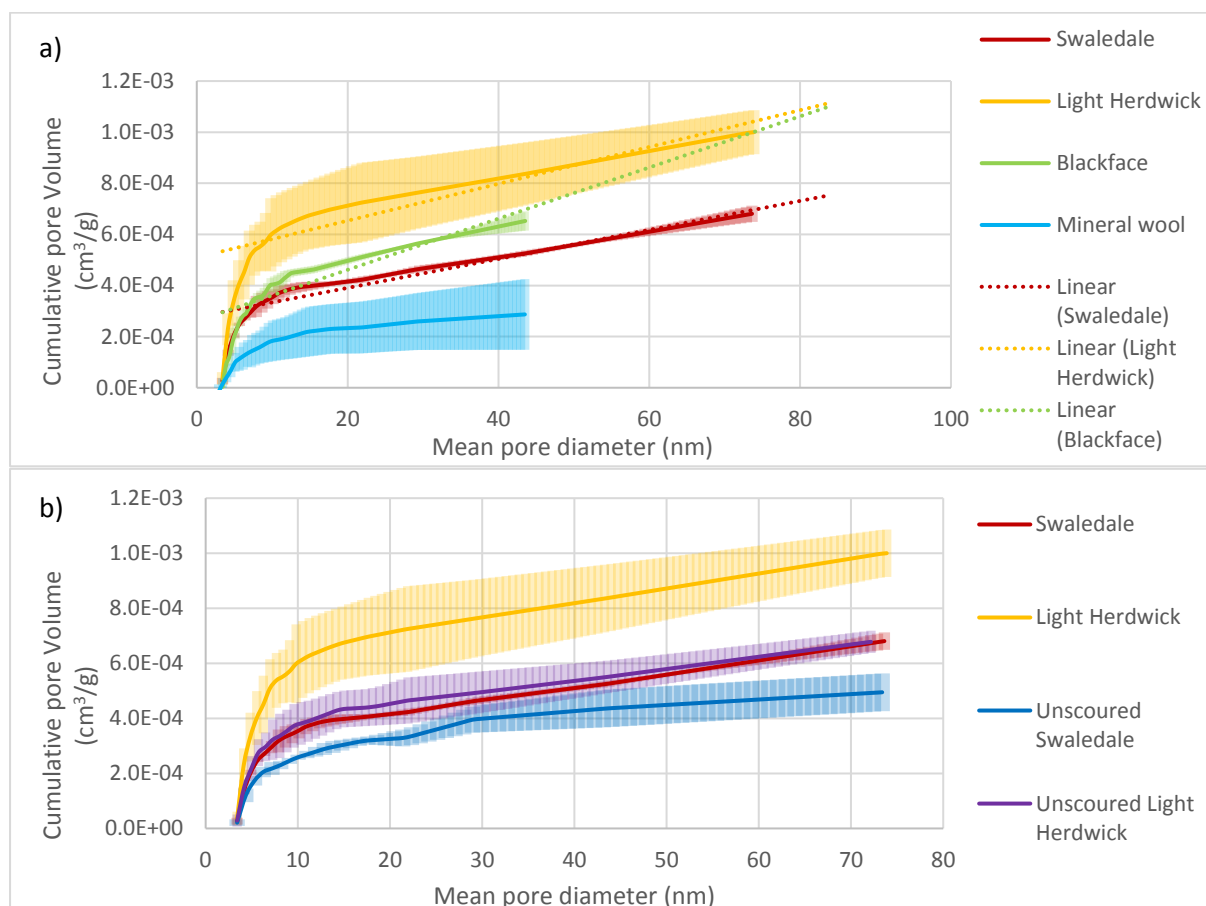


Figure 4.13: Cumulative pore volume for a) different wool types and mineral wool and b) scoured and unscoured wool types. The shaded areas represent the standard deviation for all cumulative pore volume values.

Relating this information back to the sorption of v/VOCs by the different wool types, it seems that surface area plays a part in their sorption as indicated by the cases of unscoured wools; although other factors may have a larger roles such as chemical functionalities offered by lanolin and contaminants present on unscoured wools. Examining the case of formaldehyde sorption capacity, it seems that increasing mesopores especially those between 30 and 50nm may contribute to their enhanced sorption as seen in the case of Blackface. In the case of less polar VOCs, which also happen to be larger molecules, pore size is no longer an important factor; however, the size of these v/VOC molecules is much less than 30nm – toluene for example has a critical diameter of $6.7\text{\AA}=0.67\text{nm}$ (Sigma-Aldrich, 2017).

4.4.3 Specific heat capacity

4.4.3.1 Method

A Thermogravimetric Analysis (TGA) system (Mettler) was used to quantify the specific heat capacities of the different wool types, mineral wool, and unscoured wools at different temperatures ranging from 25 to 185°C. Only one platinum 150 μm crucible with a loose lid was used for all runs to reduce the error margin as much as possible, with a similar crucible being used as a reference. The instrument was calibrated against sapphire using the same temperature program as the samples underwent:

- 25°C for 10min to allow equilibrate
- Ramp up to 105°C at 10°C/min
- Hold at 105°C for 10min to remove moisture
- Ramp up to 185°C at 10°C/min
- Hold at 185°C for 8 min to equilibrate

All samples were run in triplicate, with each run using 5-40mg of material. Wool samples were rolled and compressed by hand to condense as much as possible, fitting as much as possible into the crucible. Statistical significance was calculated using IBM SPSS Statistics 22 software using one-way ANOVA.

4.4.3.2 Results and discussion

Figure 4.14 shows the results for different wool types and mineral wool. No considerable difference was observed between different wool types; however, mineral wool showed a contrasting reduced specific heat capacity, especially in the range of 25 to 100°C. In that range, the wool samples are expected to contain bound water, which is later driven off by the temperature going above its boiling point. Specific heat capacity graphs are presented with the standard deviation as semi-transparent bars across all graph values.

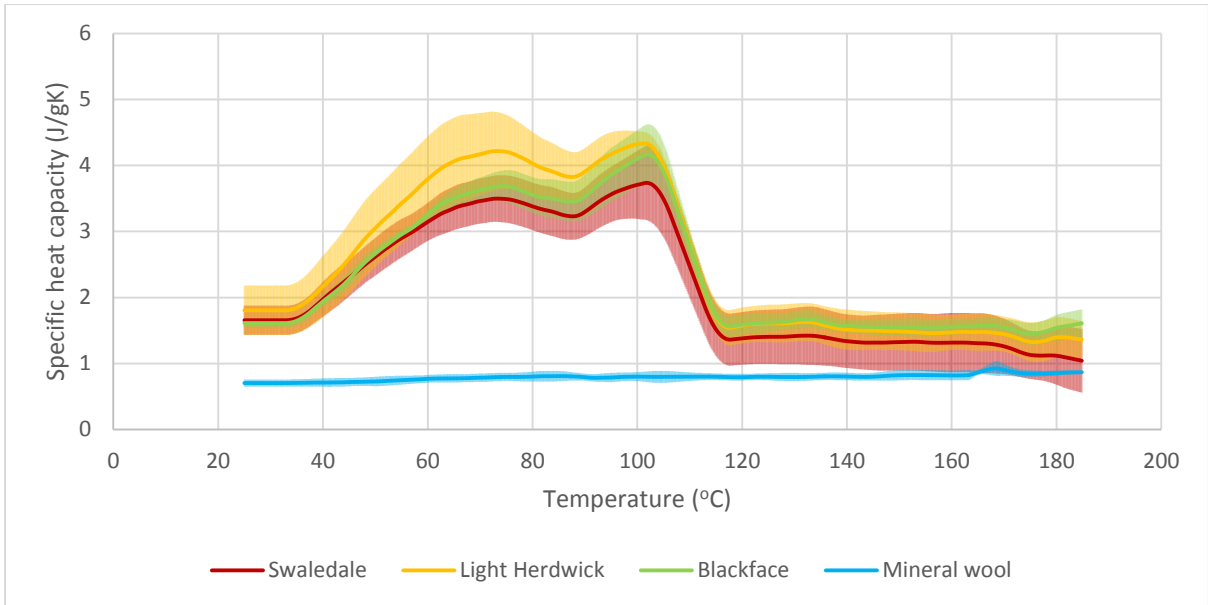


Figure 4.14: Specific heat capacity results for different wool types and mineral wool. The shaded areas represent the standard deviation for all specific heat capacity values.

Figure 4.15 shows the results of scoured and unscoured wools. The only difference observed is a slight rise at 100°C for unscoured wools compared to their scoured counterparts, explained by the water driven off at this temperature from the scoured wools, which have lost some of their hydrophobic layer (see section 2.2.5).

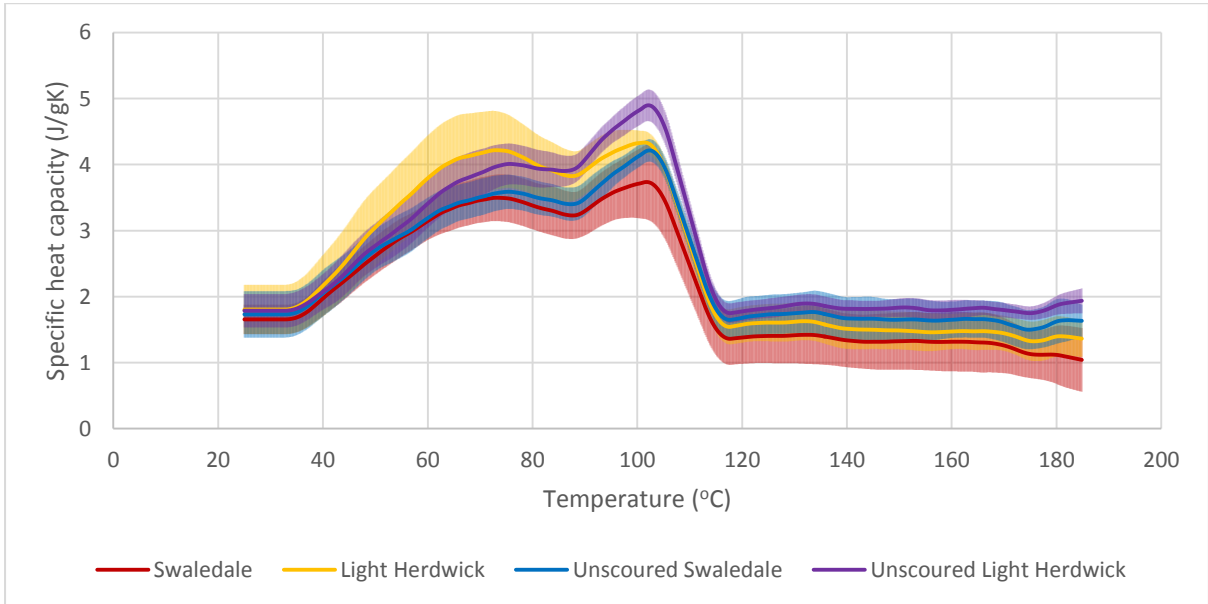


Figure 4.15: Specific heat capacity results for scoured wools and their unscoured counterparts. The shaded areas represent the standard deviation for all specific heat capacity values.

4.4.4 Thermal conductivity

4.4.4.1 Method

FOX 314 (LaserComp, Inc. of Massachusetts USA) was used to measure thermal conductivity. Samples of industrially manufactured insulation matts were composed of a blend of different

wool types, all scoured industrially and carded (Figure 4.16a). Measurements were done on 5 different specimens for each temperature range. The specimens were loaded between the instruments two metal plates (upper and lower), which were controlled between 0 and 10°C for one set of runs, 10 and 20°C for another, and 0 and 20°C for another.

Other samples of loose, uncarded Swaledale wool (Figure 4.16b) were also tested, although tests were done on one specimen only per wool type, which were wrapped with a thin plastic layer, and only in the temperature range of 10 and 30°C using a FOX600 – similar to a FOX314 but able to fit larger specimens (another instrument was used due to a malfunction). Table 4.2 lists the dimensions and densities of the samples tested.

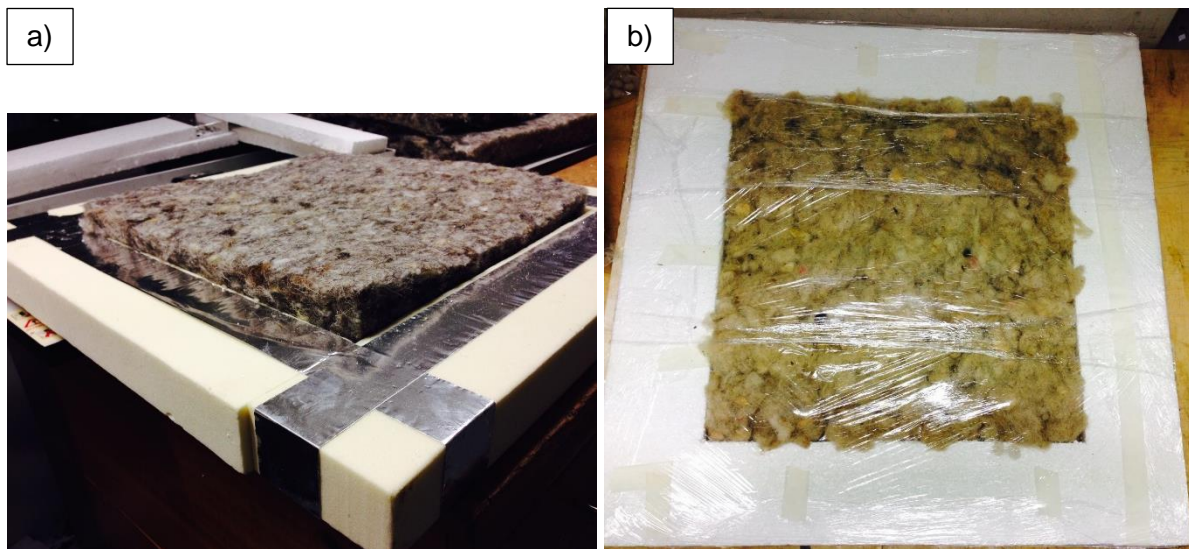


Figure 4.16: a) An industrial wool insulation specimen and b) a loose wool sample specimen used for thermal conductivity measurements.

Table 4.2: Dimensions and densities of the samples tested for thermal conductivity.

Sample	Length (mm)	Width (mm)	Thickness (mm)	Density (kg/m ³)
Mineral wool insulation	305±6	305±6	44±4	44.0±4.3
Wool insulation	310±6	310±6	56±12	22.6±0.7
Loose Swaledale	400	400	25.4	59.1
Loose unscoured Swaledale	400	400	25.4	59.1

4.4.4.2 Results and discussion

The results (Figure 4.17) show that thermal conductivity values do not alter much between the different temperature ranges used for either mineral wool or wool. A slight decrease in thermal performance (i.e. increase in thermal conductivity) is noted for wool compared to mineral wool, but the difference is quite minimal in terms for real-life performance.

With regards to the loose wools, there is no apparent difference between values for scoured or unscoured wools. Even though their measurements are comparable to those of the wool insulation's, it must be noted that the specimens' densities are vastly different – over 2.5 times more than the wool insulation.

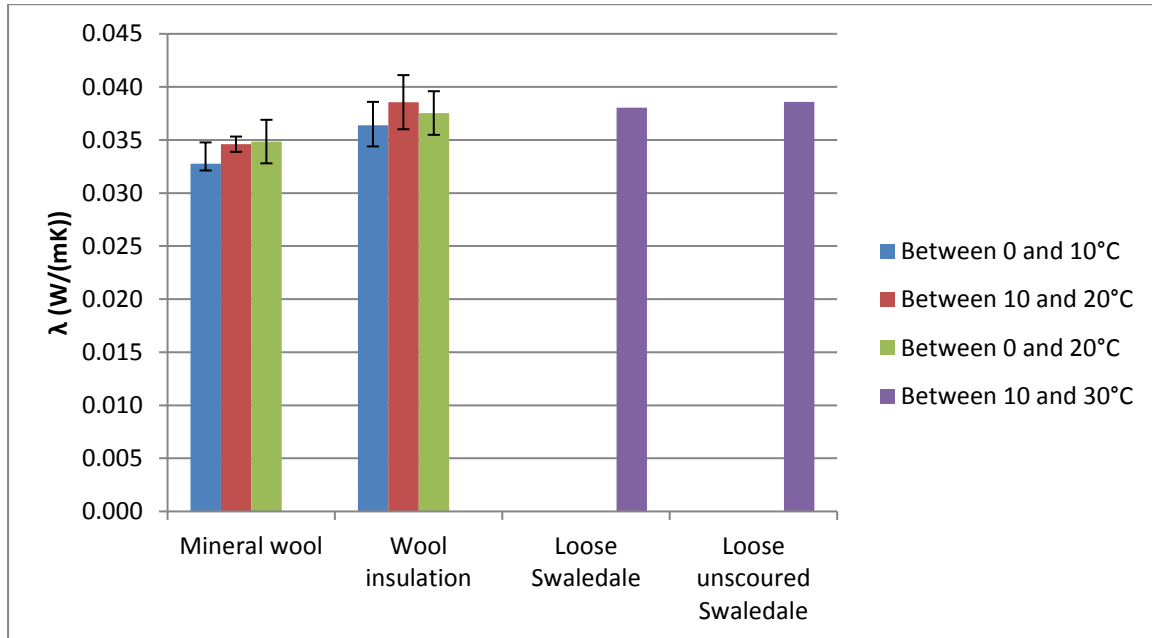


Figure 4.17: Thermal conductivity results for mineral wool and wool insulation products at different temperature ranges.

4.5 Conclusions

- Maximum sorption potential of excess formaldehyde by wool fibres differ according to wool type and condition: the least value was observed for Swaledale whilst the most was observed for Blackface, and unscoured wools have higher values than their scoured counterparts.
- Sorption of low levels of v/VOCs varied according to the type of v/VOC, the amounts of v/VOCs the fibres were exposed to, fibre type and fibre condition:
- Mineral wool always sorbed significantly less than any wool fibre for any v/VOC tested.
- When low concentration levels were used, formaldehyde was sorbed equally between wool types and more so by unscoured wools. Increasing exposure concentrations leads to an increase in sorption, but the percentage sorbed decreases with increasing exposure levels in a linear fashion and is expected to eventually plateau at very high levels.
- For different wool types: toluene was sorbed in small to negligible quantities, limonene exhibited mediocre sorption, and dodecane was sorbed in high quantities. Higher quantities were always sorbed by unscoured wool fibres.

- The profile of sorption for the 3 non-polar VOCs, although almost insignificant at some times, was highest in the case of Swaledale and lowest in the case of Blackface. This is in opposition to the capacity observed for polar formaldehyde sorption using DVS, and is to be expected considering the polarities of the v/VOCs tested.
- Increasing exposure concentrations for the three non-polar VOCs at low levels leads to increase in their sorption. As percentages, sorption increases but by small values, unlike formaldehyde which sorption percentage decreases with increasing exposure. This shows that although the surface of wool fibre (Light Herdwick in the tested case) has both polar and non-polar regions, the average polarity of the fibre surface seems to favour the non-polar attractions of VOCs. This partiality may change or even reverse in the case of other wool fibres depending on their surface polarity.
- The dynamic outer lipid layer of wool fibres explains the trend of increasing sorption percentage change with increased exposure concentrations of non-polar VOCs and the decreasing trend of the polar formaldehyde. It also explains why several cycles of polar and non-polar environments are required to reach the maximum sorption capacity of formaldehyde, as the some of the sorbed formaldehyde may be mechanically pushed and potentially locked into the inner structure of the fibre.
- FTIR does not show major chemical differences between different wool types or conditions (scoured vs unscoured), except in the case of C=O groups. The presence of lower amounts of bound lipids via thioester linkages on the surface of Blackface, and higher amounts in unscoured Swaledale, complements sorption observations and surface polarity explanations.
- Although surface area plays a part in sorption potential (as indicated by the cases of unscoured wools), other factors may have a larger roles such as chemical functionalities offered by lanolin and contaminants present on unscoured wools. The higher distribution and cumulative volume of pores greater than 30nm for Blackface could be a result of patches where there are no lipids surrounding the surface compared to other wools. Similarly, scouring seems to be able to increase the distribution of larger mesopores due to the partial and non-uniform removal of some of the surface lipids (although this was seen for Swaledale but not Light Herdwick). In the case of formaldehyde, it seems mesopores between 30 and 50nm enhance sorption (as seen in the case of Blackface). However, in the case of less polar VOCs, which also happen to be larger molecules, pore size is no longer an important factor. Wool insulation has thermal conductivity values comparable to those of mineral wool insulation. As loose wool, no apparent difference is seen for the thermal performance of scoured wool compared to its unscoured counterpart.

Chapter 5: Moisture sorption and kinetics modelling

5.1 Introduction

In order to better understand the interactions involved with sorption by wool fibre, an explanation is presented on the modelling of moisture sorption kinetics using different wool types (Ormondroyd et al., 2016). Mathematical modelling of moisture sorption profiles of different wool types across different relative humidities is undertaken by taking into account the properties of the polymeric materials and the clustering effect of water. Moisture was selected as the sorbate since it would not involve the permanent chemi-sorption by wool fibres (Curling et al., 2012). The use of wool in garments is partly due to the ability to sorb and desorb water vapour providing moisture buffering behaviour; these properties are also of increasing interest for the use of natural wool as insulation materials in buildings (Papadopoulos, 2005). Understanding the interactions involved in the sorption of v/VOCs by wool is logically expected to be far more complex since they include both physical and chemical interactions. This modelling work can be further built for other sorbates in future work.

Very early work on the water sorption behaviour of wool was conducted in the University of Leeds, UK by Speakman (1929), who reported comprehensive data on the change in the rigidity (modulus of elasticity) of wool with moisture content (MC). He found that the rigidity was dependent upon the MC only and did not depend upon whether the measurements were made under conditions of sorption or desorption. King and Cassie (1940) concluded that due to the very high surface to volume ratio the sorption behaviour of wool fibres was solely governed by the heat evolved during sorption and the consequent rise in the temperature of the fibres and that the composition of the fibres was of no importance. However, the apparatus involved a static sorption experiment, with no air flow over the fibres.

The composition of the sorbed water within the amorphous matrix of the wool fibres was also the subject of early research studies. Speakman (1944) analysed earlier sorption data for Cotswold wool and separated the sorbed water into two forms (termed α -water and β -water). The α -water was assumed to be directly associated with the polymers, whereas the β -water was considered to be filling the micro-pore spaces within the internal structure, but not directly associated with the polymers and therefore less bound.

Cassie (1945) examined the sorption isotherm of wool, taking into account the effect of the elastic strain exerted within the wool structure as a result of the presence of sorbed water molecules, coming to the conclusion that the sigmoidal shape of the isotherm was no longer present under these conditions. The inflexion in the isotherm observed at higher levels of equilibrium moisture content, EMC (also termed moisture regain) was attributed to a decrease

in elastic modulus caused by plasticisation of the polymeric gel structure by the sorbed water molecules.

It is known that the sample history can have an important influence on the sorption properties of wool. Speakman and Stott (1936) showed that as the temperature used for drying wool (from regains below saturation) increased, the subsequent sorption of water at 25°C was reduced, although the regains on desorption from saturation were unaffected.

The phenomenon of sorption hysteresis is a well-established phenomenon in wool and many other natural materials. Although studies by Watt (1980) and Watt and D'Arcy (1976) reported that the magnitude of the hysteresis was a function of the rapidity with which water was desorbed from the substrate, this can only be because of the failure to establish true equilibrium conditions, since the existence of hysteresis is established beyond doubt. Jeffries reported a reduction in sorption hysteresis as the temperature of sorption and desorption is increased (Jeffries, 1960).

It was shown by Le Roux and Speakman that there was a relationship between the accessibility of the wool internal surface to water and the plasticity of the wool fibre (Roux and Speakman, 1957). Fibres showing the highest degree of plasticity and swelling also exhibited the highest level of accessibility (determined using deuterium exchange). The purpose of their study was to examine the effect of variations of cysteine content and of amorphous/crystalline content of the fibres upon the mechanical properties. Fibres with a higher cysteine content also exhibited the higher amorphous content, suggesting that the bulky side chains of tyrosine were responsible for disrupting chain order.

In a study of the sorption kinetics of wool fibres, it was reported that for water sorption at 35°C associated with fibres with a low water content (0-20% regain), Fick's law was obeyed, but with increasing deviation thereafter as water content increased. A distinct two-stage nature of the sorption was noted (Watt, 1960a). These experiments were carried out to eliminate the effect of heat of sorption on the isotherm experiment, by ensuring a large separation of fibres. Polymers in a glassy state (i.e., at temperatures below the second order transition temperature) invariably exhibit non-Fickian sorption behaviour (Watt, 1960b). In this further study of the two stage sorption kinetic behaviour of wool, it was found that the results were influenced by the previous history of the sample. It was considered that the properties of the second-stage sorption were consistent with the concept of an osmotic balance between the expansion pressure of the sorbed water molecules and the cohesive forces of the fibre. The first-stage sorption was equated with a Fickian, diffusive, process. Nordon et al. (1960) stated that the sorption process consisted of a Fickian process and a second process where the rate is controlled by molecular relaxation of the substrate. Although not fully understood at the time,

the second process was thought to be due to relaxation of the elastic strain imposed on the polymer network due to volume swelling caused by the sorbed water molecules. Watt and Algie (1961) also noted deviations from Fickian behaviour with sorption onto wool. Downes and Mackay (1958) observed two stage sorption for wool and concluded that wool behaved as a polymer below its second order transition temperature. A coupled diffusion-relaxation mechanism has been put forward by Newns (1956) as an explanation of anomalous sorption by polymers below their second order transition temperature. Barba et al. (2013) used a dynamic vapour sorption apparatus to study the sorption isotherm and sorption kinetic behaviour of wool and human hair. The kinetic parameters were obtained by applying Fick's diffusion equation to a cylinder. Although early studies had claimed that wool attained very rapid equilibrium in sorption experiments, subsequent experiments clearly showed that it took an appreciable time for wool to achieve equilibrium in an air flow using 1g samples (Finnimore and Wortmann, 1980).

5.2 Sorption model for gel-like polymers

Although sorption models such as Brunauer-Emmett-Teller and Guggenheim-Anerson-de Boer are very widely used in the literature to describe the interaction of water vapour with materials, they are based on assumptions that do not reflect the physical reality of the sorption interaction of water with gel-like materials, such as wool. Multilayer models, such as BET, were developed to explain the sorption of gases on surfaces and do not take into account the geometry of the internal micro-pore environment which exists within the amorphous matrix of the wool structure (Martí et al., 2007). Furthermore, such models are unable to explain the phenomenon of sorption hysteresis, which is observed with a large number of materials. They are also unable to take account of the dimensional changes taking place in the substrate during the sorption process. It is quite possible to fit such models to both the sorption and desorption branches of the isotherm, but the validity of doing so for the desorption branch, which is composed of combination of a scanning isotherm and a boundary isotherm is questionable. Models for explaining hysteresis in rigid porous materials (e.g., the Barrett Joyner Halenda model) (Barrett et al., 1951b), are also not appropriate for swelling gel-like materials, such as wool and where the water in wool acts as a plasticiser affecting the viscoelastic properties of the fibre (Wortmann and Jong, 1985).

Pierlot considered that for wool it was more appropriate to adopt the approach of Vrentas and Vrentas, which is a modification of the Flory-Huggins model (Pierlot, 1999). The Flory-Huggins solution theory has been used to describe sorption isotherms for rubbery polymers. Isotherms of this category exhibit IUPAC Type III behaviour. The Flory-Huggins isotherm has the mathematical form:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2)$$

Equation 5.1

Where p_1 is the pressure of the penetrant, p_1^0 the saturation pressure of the penetrant, ϕ_1 is the volume fraction of the penetrant and ϕ_2 is the volume fraction of the polymer. The term χ is the Flory-Huggins interaction parameter from the solution theory, which is related to the difference in energy between a solvent molecule in pure solvent (in this case water) compared to the energy of the solvent molecule in the polymer. Although in principle the value of χ can be calculated, it is invariably obtained from the experimental isotherm.

However, the sorption isotherms of wool are sigmoidal and exhibit IUPAC Type II behaviour, which is typical of glassy polymers changing to a rubbery behaviour at higher penetrant concentrations. This type of behaviour has been explained by a model developed by Vrentas and Vrentas (1991) who modified The Flory-Huggins model to describe sorption in glassy polymers:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2 + F)$$

Equation 5.2

The new term F can be calculated from:

$$F = M_1 w_2^2 (c_{pg} - c_p) \left(\frac{dT_{gm}}{dw_1} \right) \left(\frac{T}{T_{gm}} - 1 \right) / RT$$

Equation 5.3

Where M_1 the molecular weight of the penetrant, w_2 is the weight fraction of the polymer ($w_2 = 1 - w_1$), w_1 is the weight fraction of the penetrant, c_p and c_{pg} are the specific heat capacities at constant pressure for the equilibrium rubbery and glassy polymers respectively, T_{gm} is the glass transition temperature of the polymer/penetrant mixture, R the gas constant and T the absolute temperature.

It can be seen that $F=0$ at $T=T_{gm}$ and that consequently the Vrentas equation reduces to the Flory-Huggins equation at the glass transition temperature, which becomes valid at $T > T_{gm}$. For $T < T_{gm}$, F is negative. The F parameter takes account of the elastic energy stored in the polymer, which no longer occurs when the polymer is in a rubbery state.

This model was further extended by Vrentas and Vrentas to describe desorption in glassy polymers (Vrentas and Vrentas, 1996).

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2 + kF)$$

Equation 5.4

Where the quantity k is derived in the following manner:

$$k = \frac{[(T_D - T_{g2}) - T_D \ln(T_D / T_{g2})]}{[(T - T_{g2}) - T \ln(T / T_{g2})]}$$

Equation 5.5

T_{g2} is the glass transition temperature of the pure polymer and T_D is a parameter defined in the Vrentas model. One of the assumptions of the Vrentas model is that removal of penetrant from the polymer-penetrant mixture forms a glassy structure and this structure is equivalent to cooling the polymer in a sorption experiment by a temperature T_D .

In consequence, both the sorption and desorption isotherms (in principle) can be predicted and do not require any adjustable constants. The methodology developed by Vrentas and Vrentas was originally formulated to explain the sorption behaviour of non-polar polymers interacting with organic vapour and it would not necessarily be expected to work with polar systems experiencing extensive hydrogen bonding. However, it has been successfully applied to the sorption of water vapour by hydrophilic polymers (Shamblin et al., 1998). The Vrentas model was used by Pierlot (1999) to fit to the experimental data of Watt and D'Arcy (1979). Satisfactory fits were obtained, using a value of $k=2.5$, to sorption data. This is the only study reported in the scientific literature where the Vrentas model has been applied to wool.

5.3 Penetrant clustering effect

According to the classical monolayer-multilayer sorption models, on entering the wool fibre, water molecules will diffuse through the matrix until they encounter a sorption site. It is assumed that this process will continue until all of the sorption sites are occupied and then further layers of water will form within the matrix. It is thought that the water associated with the sorption sites is somewhat less mobile than the water of the multilayers. This view of sorption is the basis for the BET and GAB models often used in the literature. These gas models of sorption assume that the attractive forces between water molecules are unimportant, which is clearly not a realistic view. Given that water molecules are strongly attracted to one another by hydrogen bonding interactions, it is very likely that water molecules will tend to form clusters around specific sorption sites, rather than a neat building up of a monolayer and then multilayers. As the sorption process continues, the likelihood of newly sorbed water molecules encountering previously sorbed water molecules will increase and clustering of the water molecules is increasingly likely to occur if this is energetically favourable. The Zimm-Lundberg (Z-L) clustering function provides information regarding the state of the sorbed water molecules in the cell wall matrix (Zimm, 1953; Zimm and Lundberg, 1956). The Z-L function has the advantage that it is possible to use sorption isotherm data for inputs. The function has the form:

$$\frac{G_{11}}{v_1} = -(1 - \phi_1) \left[\frac{\partial(\frac{a_1}{\phi_1})}{\partial a_1} \right]_{P,T} - 1$$

Equation 5.6

Where G_{11} is the cluster integral and v_1 the molar volume, a_1 the activity (RH/100) and the ϕ_1 volume fraction of the water. For ideal solutions (sorption isotherms obeying Henry's Law) the cluster function $G_{11}/v_1 = -1$, meaning that a water molecule excludes its own volume to other sorbed water molecules but does not affect their distribution. Values of the cluster function greater than -1 indicate that the water molecules are forming clusters. The expression $\phi_1(G_{11}/v_1)$ represents the mean number of penetrant molecules that exceeds the local concentration and the quantity $1 + \phi_1(G_{11}/v_1)$ is an estimate of the mean number of molecules in a cluster, otherwise known as the mean cluster size (MCS) (Davis and Elabd, 2013; Li et al., 2014; Metz et al., 2005). The Z-L clustering function has found wide applicability in the study of polymer sorption phenomena (Du et al., 2012; Kilburn et al., 2004; Yang et al., 1985).

Although potentially a useful analytical tool, the Z-L function has been criticised when applied to sorption on glassy polymers because the theoretical basis for the function assumes thermodynamic equilibrium. According to Davis and Elabd (Elabd, 2013) when sorption behaviour of glassy polymers is investigated below the glass transition temperature (T_g), difficulties can arise due to the polymer matrix being in a non-equilibrium state. In order to determine the applicability of the Z-L approach, they used Fourier-Transform Infra-Red (FTIR) spectroscopy to directly determine water association in several glassy polymers. They concluded that the Z-L function tends to under-estimate the extent of water clustering in the sorbent. It is clear from that study that the results of the Z-L function need to be treated with caution when dealing with glassy polymers below T_g .

5.4 Sorption kinetics across different relative humidities

It has been shown the water vapour sorption kinetics of natural fibres are not Fickian, but follow the Parallel Exponential Kinetic (PEK) model which gives very precise fits of the sorption kinetics data (Hill and Xie, 2011; Kohler et al., 2003). This model has a double exponential form, representing fast and slow kinetic processes, taking place simultaneously, as described in the equation below:

$$MC = MC_0 + MC_a \left[1 - e^{-t/t_a} \right] + MC_b \left[1 - e^{-t/t_b} \right]$$

Equation 5.7

Where: MC is the moisture content at time t of the sample exposed to a constant RH, MC_0 is the moisture content of the sample at the time 0 of each RH change. The two exponential terms with the characteristic times t_a and t_b and the moisture contents at infinite time MC_a and

MC_b , are associated with the fast and slow processes, respectively. A summation of MC_0 , MC_a and MC_b gives the equilibrium moisture content (EMC), also known as moisture regain in the textile literature.

The form of the fast and slow component of the PEK equation is identical with that describing the dynamic response of a Kelvin-Voigt element when subjected to an instantaneous stress increase (σ_0):

$$\varepsilon = \sigma_0/E [1 - e^{-t/\varphi}]$$

Equation 5.8

Where ε is the strain at time t , E is the elastic modulus and φ is a time constant which is defined as the ratio η/E , where η is the viscosity (H. A. Barnes et al., 1989). In the present case, there is a change in atmospheric relative humidity (RH) which leads to a response in the wool cell wall. The maximum swelling pressure (Π – which is here equivalent to σ_0) that is exerted on an elastic gel when the surrounding water vapour pressure is raised from an initial value p_i to final value p_f is given by the following equation (Krabbenhoft and Damkilde, 2004):

$$\Pi = -\left(\frac{\rho}{M}\right)RT \times \ln(p_i/p_f)$$

Equation 5.9

Where ρ is the density and M is the molecular weight of water, R is the gas constant and T is the isotherm temperature in Kelvin. In the present situation, the strain of the system is assumed to be equivalent to the volume change of the cell wall as a result of water vapour sorption or desorption. This volume change is assumed to be linearly related to the change in the mass fraction of the water present in the cell wall.

The sorbed water vapour molecules exert a pressure within the cell wall leading to dimensional change, which is equivalent to the extension of the spring in the Kelvin-Voigt model. This expansion/extension results in an increase in the free energy of the system (Matsuoka, 1992). Expansion will continue until the free energy of the system is equal to the free energy of the water vapour molecules in the atmosphere. The spring modulus therefore defines the water content of the system at infinite time (MC_a , MC_b).

$$MC_a = \frac{\sigma_0}{E_a} \text{ and } MC_b = \frac{\sigma_0}{E_b}$$

Equation 5.10 and Equation 5.11

The rate at which water molecules are sorbed or desorbed by the system is a function of the viscosity of the dashpot in the model. This viscosity is in turn related to the micro-Brownian motion of the cell wall macromolecular network. The more rapidly the matrix is able to deform, the faster the rate of water ingress or egress into or out of the cell wall. The rate of local

deformation is related to the energy barrier associated with the local relaxation process and whether there is sufficient free volume to allow the relaxation process to take place. In glassy solids below the glass transition temperature (T_g) there is insufficient free volume to allow a local relaxation to take place without the cooperative motion of adjacent relaxors (a relaxor is defined as the smallest molecular segment of relaxation in each polymeric unit). This gives rise to the concept of cooperative domains within the matrix (Bartolotta et al., 2010; Matsuoka, 1992; Matsuoka and Hale, 1997). As the glass transition temperature is approached, the domain size decreases until T_g is reached. At this point the domain contains only one relaxor and there is sufficient free volume to allow for relaxation without the cooperation of neighbours.

As it was found to be lacking in the literature, a PEK model is applied to the investigation of the sorption kinetics of wool, along with the clustering of water in wool fibres using the Z-L approach. The Vrentas sorption model is also applied to water vapour sorption isotherms in wool.

5.5 Method

Wool from a number of differing sheep breeds were selected for testing, as well as wool from Alpaca. All samples were obtained from commercially available sources (British Wool Marketing Board, 2015b). These comprised sheep wool from the following breeds: Swaledale, Welsh Mountain, Drysdale, Blackface, as well as wool from the Alpaca species (see section 4.2.1 for details).

The water vapour analysis of the wool samples was performed using a Surface Measurement Systems DVS (Surface Measurement Systems Ltd. London, UK). The samples (2.5 ± 0.25 mg) were placed on the sample holder connected to the micro-balance, which is located in a thermostatically controlled chamber in which the humidity can be varied by altering the flows of dry nitrogen and water vapour containing nitrogen.

The sorption/desorption isotherms were obtained by determining the EMC at the following relative humidity (RH) values: 5, 10, 20, 30, 40, 50, 60, 70, 80, 85, 90, 95% RH and then in reverse order to zero RH. The temperature during the entire experiment was kept constant at 20°C. The instrument maintained the sample at a constant RH until the rate change in mass (dm/dt) was less than 0.002% per minute over a period of 600s. Mass change data were acquired every 60s. The running time, target RH, actual RH, and the sample weight were recorded throughout the isotherm run. The data were recorded as percentage equilibrium moisture content, which is $(\text{mass of sorbed water/dry mass of sample}) \times 100$.

By plotting percentage mass gain or loss against time, with time zero theoretically corresponding to the point at which a RH step change occurs, the kinetic curves were

obtained. The sorption/desorption curves were fitted with the Exponential Association function in Origin 9.1 software (OriginLab Corporation, Northampton, MA). Because the RH for each step (i.e. from 0 to 5%) does not take place instantly, there is a finite time during which the RH is moving from one stable value to the next; during this period, the moisture content (MC) of the sample is not initially moving towards a static equilibrium point. Therefore the first data point was eliminated from the fit (if data are captured every 20 seconds then the first three data points are removed). This has been found to yield reproducible data, provided the sample mass is not allowed to vary by more than $\pm 10\%$. During the fitting procedure, no parameters were fixed. This procedure is described in detail by previous references (Hill and Xie, 2011; Popescu and Hill, 2013; Sharratt et al., 2010; Xie et al., 2010).

5.6 Results and discussion

The sorption isotherms for the different wool types are shown in Figure 5.1. There are differences in behaviour, most notably between the alpaca and the sheep wool. There are also differences in behaviour between the various wool breeds, which is also seen in the graphs of the absolute hysteresis versus moisture content in Figure 5.2. Since the history and treatments of the different fibre types is not known, it is not possible to assign the differences between them to variation in fibre composition with any certainty. In all cases, a sigmoidal isotherm (IUPAC Type II) is obtained, with an increase in the EMC observed at the upper end of the hygroscopic range; attributed to the onset of the glass transition temperature (T_{g2}) at 20°C and an EMC of approximately 20%. The sorption and desorption branches of the isotherm also closely approach each other at the top end of the hygroscopic range with the sheep wool samples, indicative of the onset of the glass transition temperature, resulting in the collapse of hysteresis. This is consistent with values of T_{g2} for sheep wool given in the literature (Pierlot, 1999). Empirical observation of the data reproduced here indicates that the glass transition temperature of the Alpaca wool is higher than that of the sheep wool.

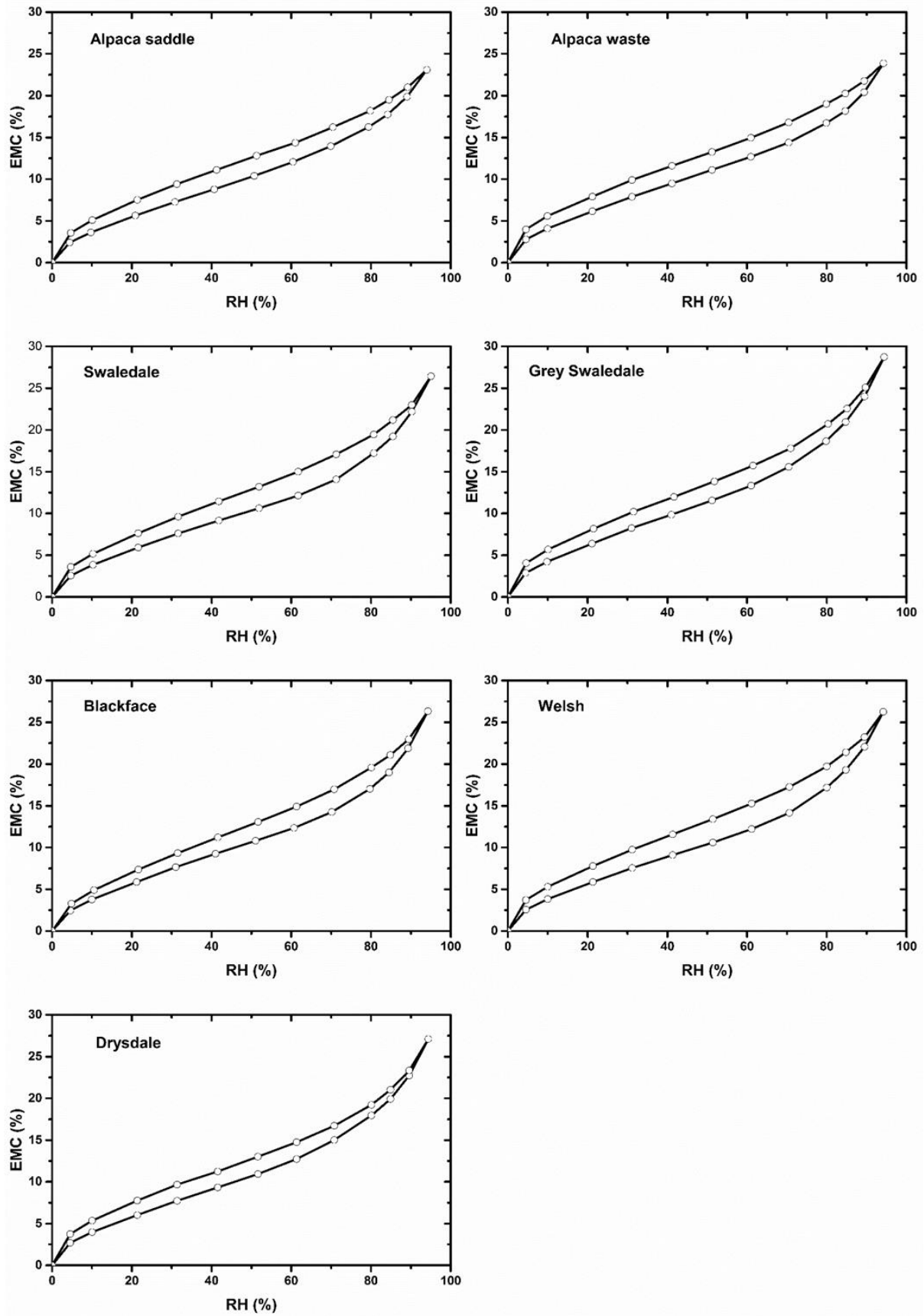


Figure 5.1: Sorption isotherms for the different wool types.

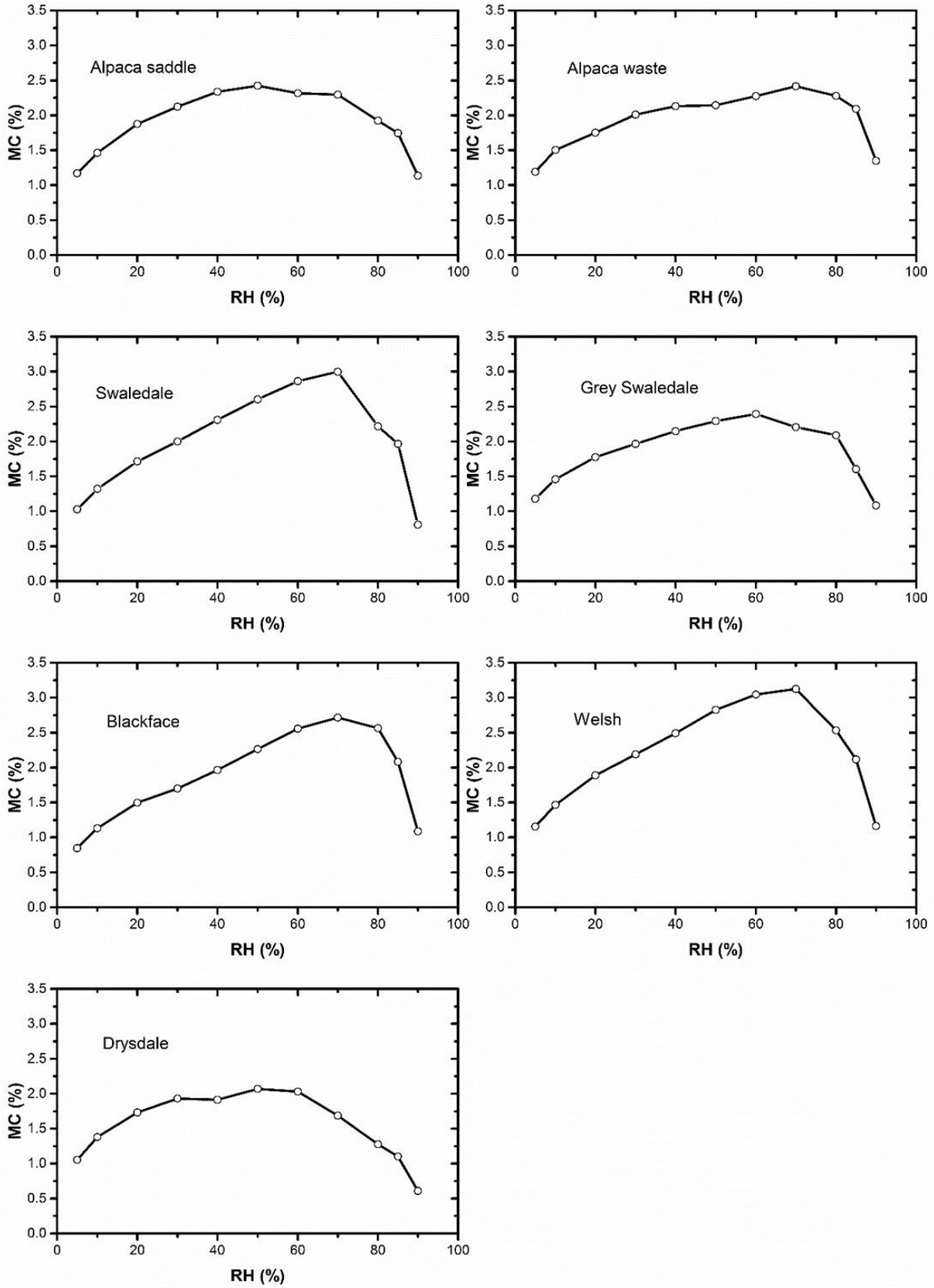


Figure 5.2: Absolute hysteresis versus moisture content of the different wool types.

The fitting of the sorption isotherm data to the Vrentas-Vrentas model and to the Flory-Huggins model is shown in Figure 5.3 and the fitting parameters are given in Table 5.1, along with the fitting parameters used by Pierlot (1999). The sorption data used by Pierlot (Pierlot, 1999; Watt and D'Arcy, 1979) are reproduced in Figure 5.4, along with the sorption isotherm data from the present study (all isotherms at 20°C). Although satisfactory fits were obtained for both the sorption and desorption loops of the isotherms in the present study, this required adjustment of more than the k parameter (Table 5.1). Good fits to the data required much lower values of T_{g1} (the glass transition temperature of water) than that used by Pierlot. Although the glass transition temperature of water is not known with certainty, it is probable that the values used herein are unrealistically low (Velikov et al., 2001). Furthermore, there is no justification in the theory of Vrentas and Vrentas to allow for the use of different T_{g1} values for sorption and desorption. The values of $C_{pg}-C_p$ (where C_{pg} is the specific heat capacity of glassy polymer and C_p the specific heat capacity of the rubbery polymer) are also rather higher than those used by Pierlot (1999). Nonetheless, the magnitude of the difference in specific heat capacity used in the Pierlot study was an estimate and the values used herein do not appear to be unrealistic by comparison.

It is also important to note that Pierlot used a k value greater than unity for fitting to sorption data, which is not appropriate (a k value of unity should be used for sorption). Finally, the T_{g2} (glass transition temperature of dry wool) used by Pierlot was 475K, which was the offset glass transition temperature of wool measured from a heating scan using differential scanning calorimetry. This value was also used in the present study. Thus, although satisfactory fits to the data were obtained, this did require some adjustment of the T_{g1} parameter, which may point to the theory not adequately describing the physical background. It is known that the Flory-Huggins theoretical approach can be problematical under circumstances where clustering of the sorbate molecules occurs; a highly likely situation for polar water molecules (Beck and Tomka, 1997; Favre et al., 1993). An examination of water clustering was therefore undertaken using the Zimm-Lundberg model.

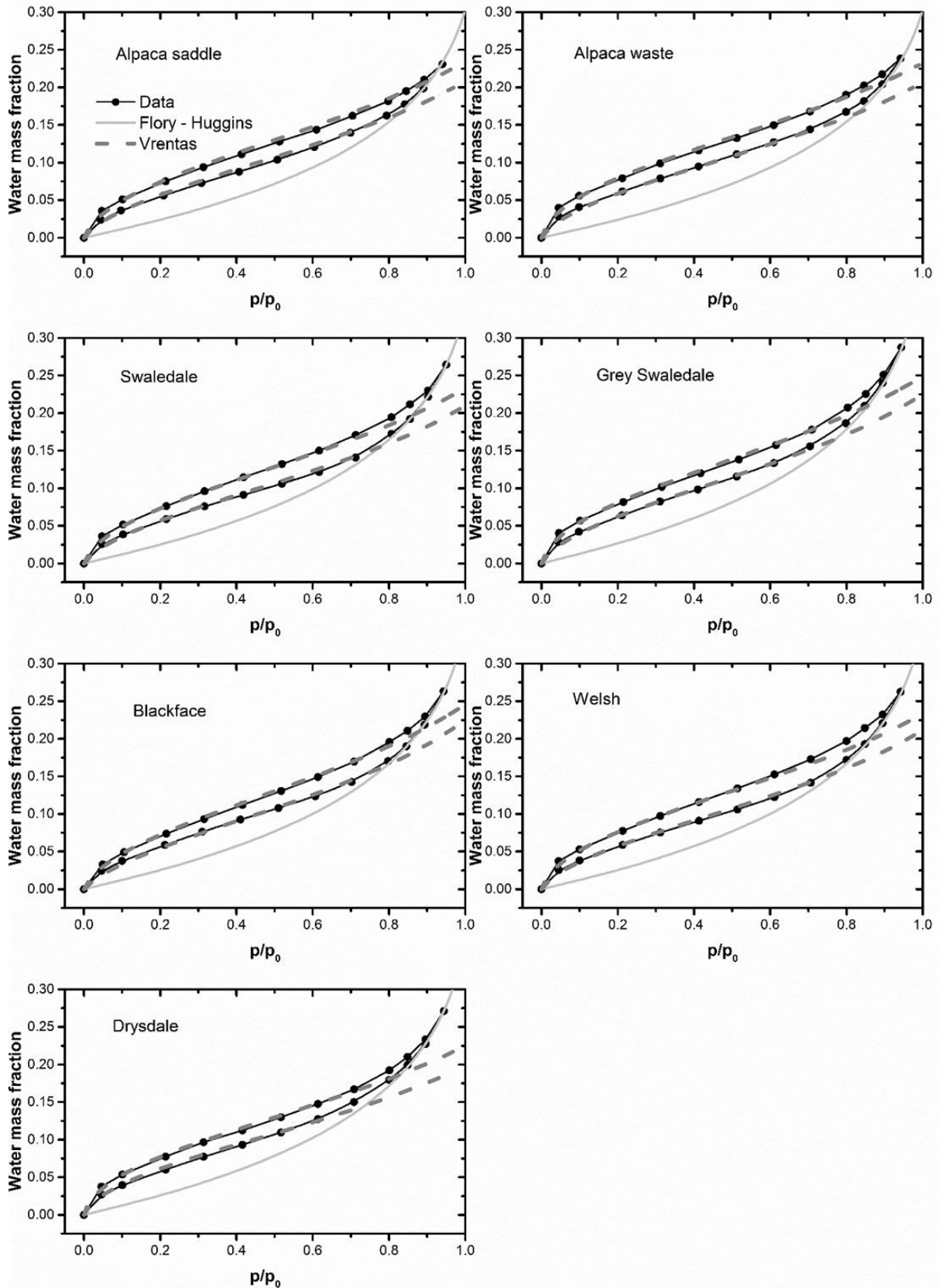


Figure 5.3: Fitting of the sorption isotherm data to the Vrentas-Vrentas model and to the Flory-Huggins model of the different wool types

Table 5.1: The fitting parameters of the sorption isotherm data to the Vrentas-Vrentas model and to the Flory-Huggins model. a-b refer to the graphs in Figure 5.3 and (x) refers to Pierlot's data (1999)

Sorption	a	b	c	d	e	f	g	(x)*
T_{g1} (K)	100	100	95	100	100	95	90	148
$C_{pg}-C_p$ (J/gK)	-0.375	-0.400	-0.350	-0.400	-0.320	-0.350	-0.400	-0.250
T_{g2} (K)	475	475	475	475	475	475	475	475
χ	0.94	0.94	0.89	0.83	0.88	0.88	0.86	0.93
Desorption								
T_{g1} (K)	120	120	115	120	120	115	110	
$C_{pg}-C_p$ (J/gK)	-0.375	-0.400	-0.350	-0.400	-0.320	-0.350	-0.400	
T_{g2} (K)	475	475	475	475	475	475	475	
χ	0.94	0.94	0.89	0.83	0.88	0.88	0.86	
k	1.7	1.8	1.7	1.7	1.8	1.8	1.6	

*n.b. Pierlot used a k value of 2.5 for sorption

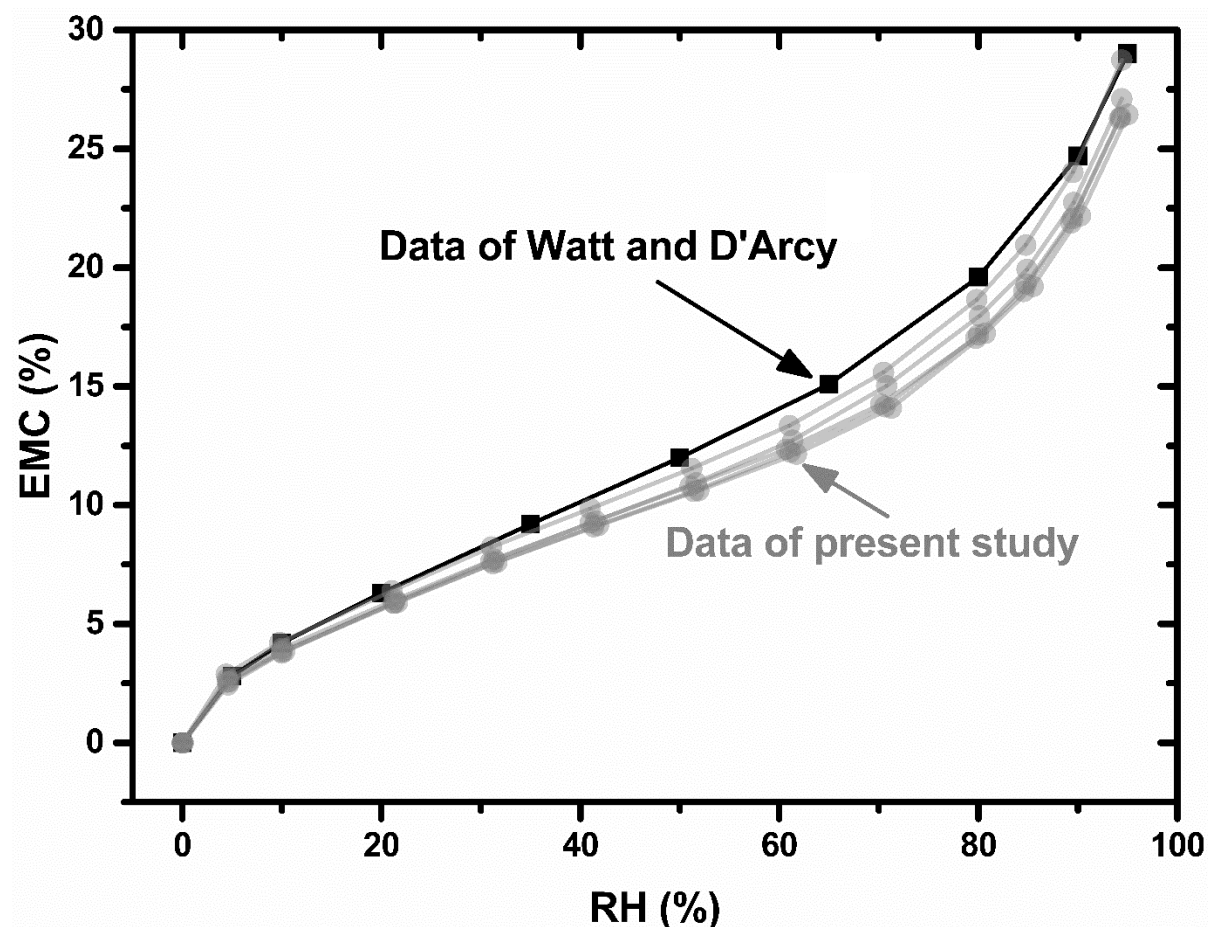


Figure 5.4: Sorption data used by Pierlot (Pierlot, 1999; Watt and D'Arcy, 1979) along with the sorption isotherm data from the present study.

The mean cluster size (MCS) of water molecules in the wool fibres is compared in Figure 5.5. The sheep wool (solid lines) and alpaca fibres (dashed lines) show similar behaviour, although the onset of water clustering occurs at a slightly higher relative humidity for the alpaca wool (Figure 5.5a). However, when the mean cluster size is plotted against the equilibrium moisture content (regain) of the wool fibres, as shown in Figure 5.5b, this distinction between fibre origins is no longer observed. Onset of clustering can be seen to occur in the EMC range of 15-18%, which is somewhat lower than the threshold moisture content determined from specific heat measurements (Haly and Snaith, 1968). Cluster formation undoubtedly occurs in the wool fibres at the upper end of the hygroscopic range, which casts some doubt on the applicability of the Flory-Huggins approach to modelling the sorption isotherm in this case.

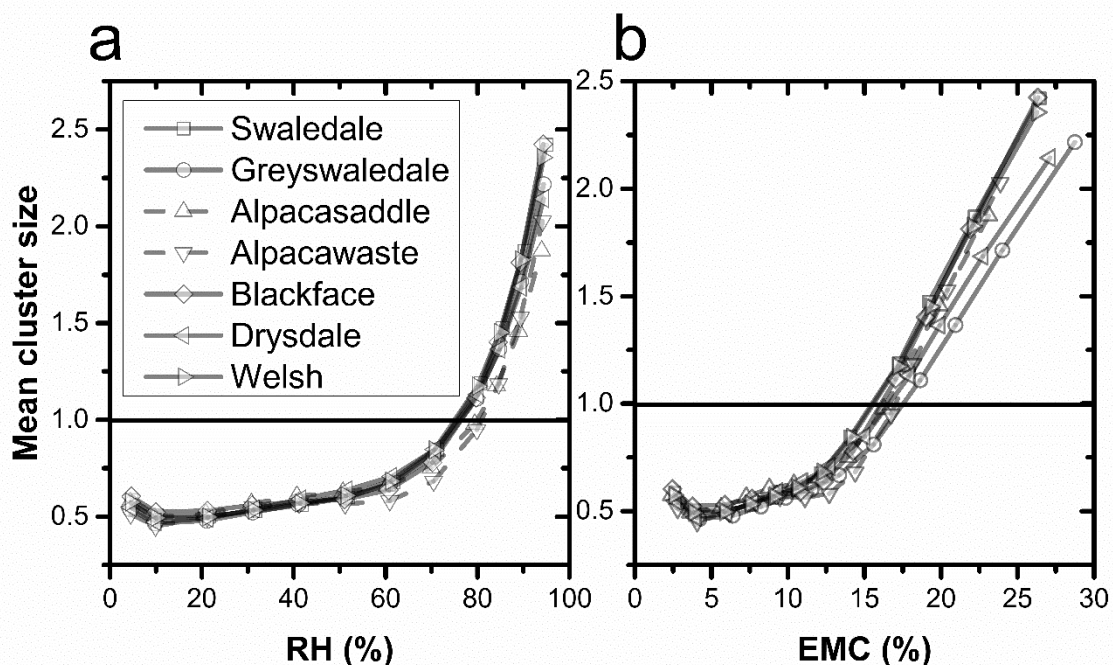


Figure 5.5: Mean cluster size (MCS) of water molecules in the wool fibres of the different wool types plotted against (a) relative humidity and (b) equilibrium moisture content/regain.

The sorption kinetic behaviour of the wool fibres was also studied. A typical PEK analysis of the sorption and desorption curves of Welsh wool is shown in Figure 5.6. The contribution of the fast (MC_a) and slow (MC_b) sorption kinetic processes is also shown in the plot. By cumulatively adding the MC_a or MC_b values for each incremental RH step and subtracting them for the corresponding RH decrements, it is possible to construct pseudo-isotherms, showing how the sorbed water is distributed between the fast and slow sorption processes. Kohler and co-workers did this analysis for their study of the sorption behaviour of flax fibres, noting that the resulting pseudo-isotherms did not form closed loops (called 'extra water' in

their study) (Kohler et al., 2003). This has been subsequently verified in two separate sorption experiments with flax fibres (Hill et al., 2010; Xie et al., 2010).

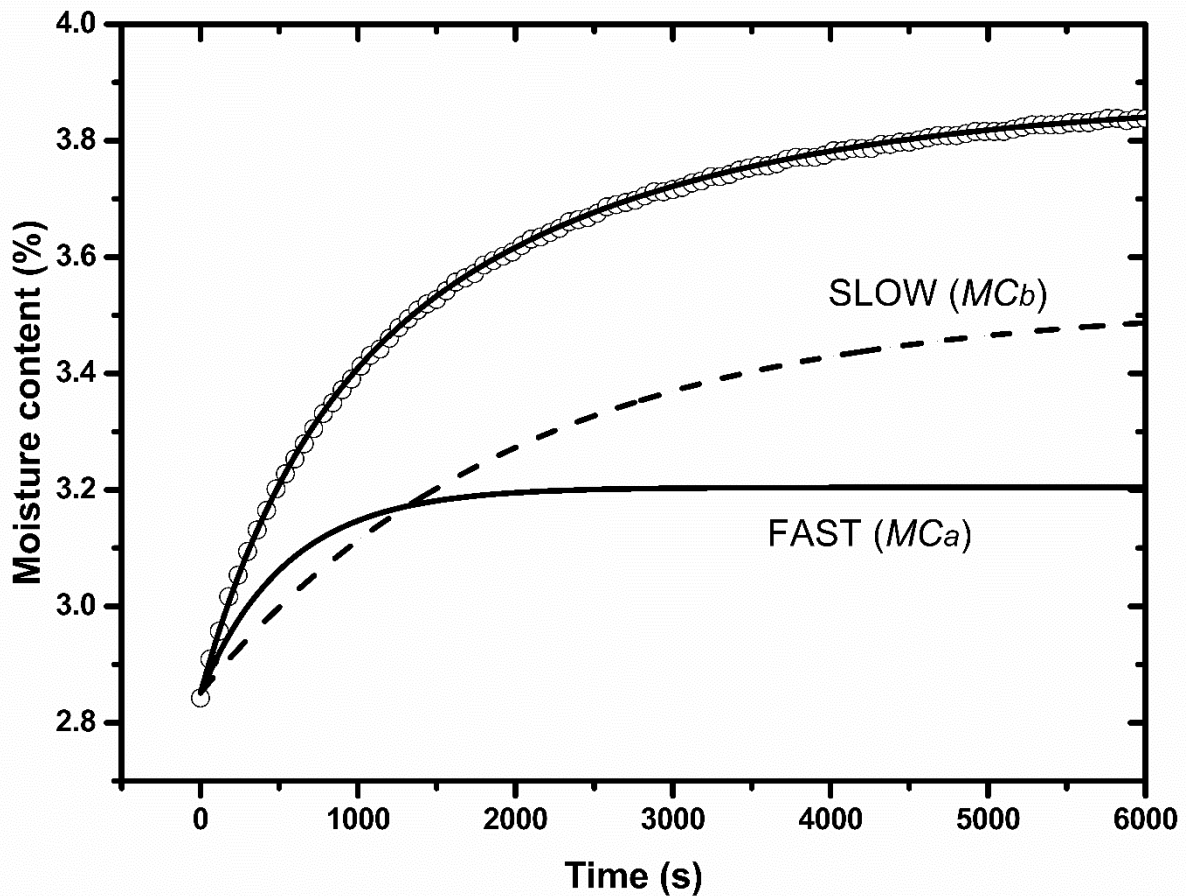


Figure 5.6: A typical PEK analysis of the sorption and desorption curves of Welsh wool

The results for sheep wool fibres in this study (Figure 5.7) also show that open pseudo-isotherms are obtained and that below an RH of 70%, the hysteresis in the sorption isotherms is not associated with the slow process, as is observed with flax and hemp (Popescu and Hill, 2013; Xie et al., 2010). With the alpaca wool, both the fast and slow processes show differences between sorption and desorption throughout the hygroscopic range, as well as open pseudo isotherms; although the fast process makes a greater (positive) contribution and that of the slow process is negative to the overall hysteresis. Meanwhile, many wood species, as well as jute, sisal, cotton and cellulose exhibit closed pseudo isotherm loops (Popescu and Hill, 2013; Xie et al., 2011, 2010). This difference in behaviour is characteristic of the material studied and is reproducible. The water associated with the fast and slow processes, has been previously attributed to different sorption sites within the material (Kohler et al., 2003), or to different states (e.g., amorphous and crystalline regions) of sorbed water in the material (Okubayashi et al., 2004). In both cases this requires an explanation as to why the water suddenly transfers from fast to slow sites or locations (or vice versa) when sorption changes

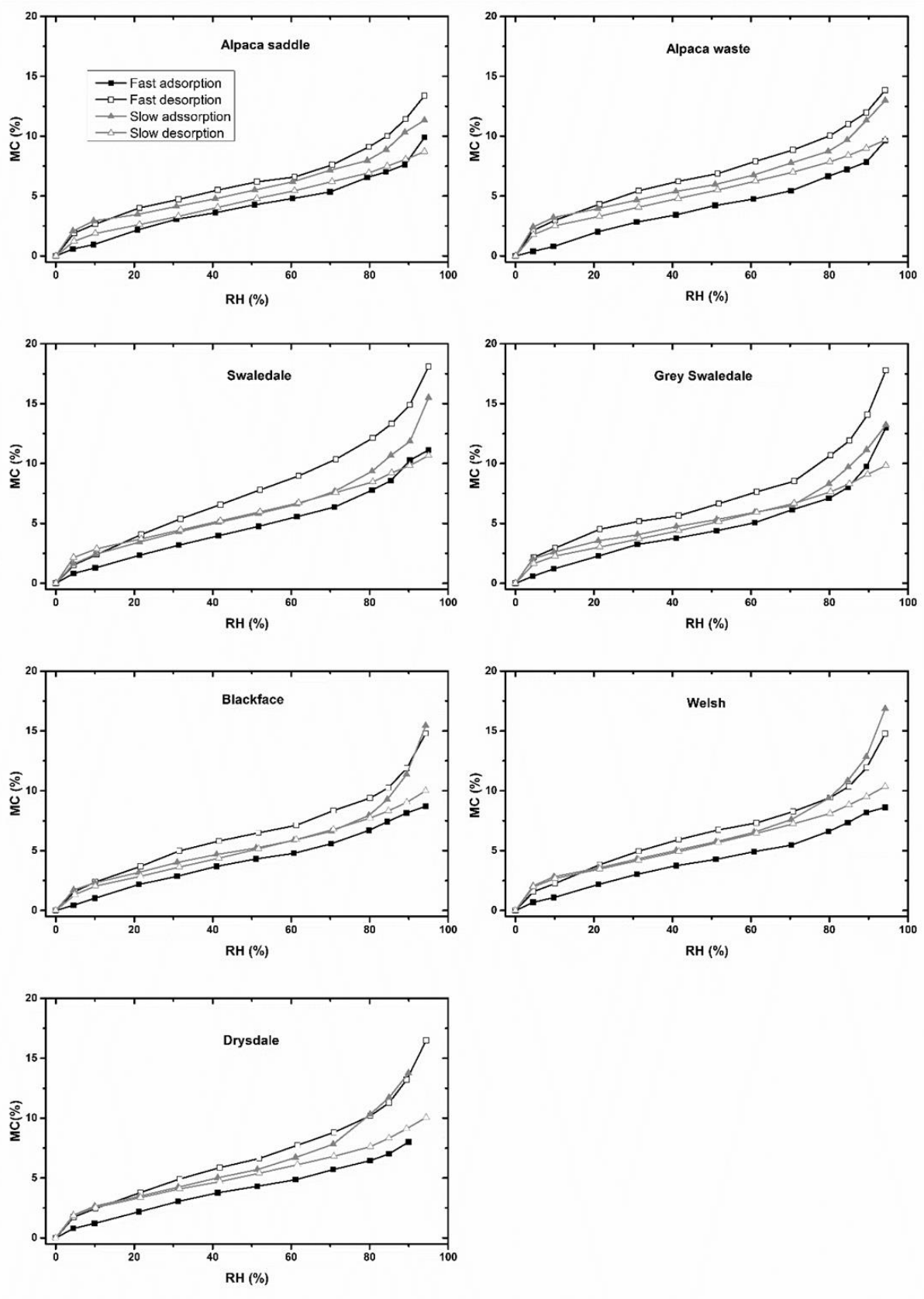


Figure 5.7: Constructed pseudo-isotherms by cumulative addition the MC_a or MC_b values for each incremental RH step and subtracting them for the corresponding RH decrements, showing how the sorbed water is distributed between the fast and slow sorption processes.

to desorption conditions, where open pseudo-isotherm loops are observed. A more viable explanation is to assign the two processes to relaxation kinetics (Hill et al., 2011), or to a combination of diffusion and relaxation kinetics (Popescu and Hill, 2013). In the latter case, the fast process was attributed to a linear driving force mass transfer diffusion model, which has also been used to describe sorption kinetics in rigid materials, such as charcoal (Harding et al., 1998). The majority of the difference in MC between sorption and desorption is associated with the fast process with the sheep wool and it is only at RH values in excess of 70%, where the slow process makes any contribution. The MC associated with sorption exceeds that associated with desorption above 70% RH with the slow process, meaning that it is this behaviour that is responsible for closing the isotherm loop of the experimental isotherm. The slow process makes a greater contribution to the overall hysteresis with the Alpaca wool, but as with the sheep wool, it is a negative contribution (sorption MC is greater than desorption MC). In other reported cases where open pseudo-isotherms are observed, the MC of the fast process always makes a greater overall contribution to the hysteresis and the slow process makes a negative contribution to the hysteresis in the upper end of the hygroscopic range (Popescu et al., 2015; Xie et al., 2010). This is the same as the observation of 'extra water' in the slow process pseudo-isotherm first noted for flax (Kohler et al., 2003).

The PEK sorption parameters MC_a (fast process) and MC_b (slow process) were used to calculate the modulus of the wool fibres using the equations referred to in section 5.5.3:

$$\varepsilon = \sigma_0/E [1 - e^{-t/\varphi}]$$

Equation 5.8

$$\text{and } \Pi = -\left(\frac{\rho}{M}\right)RT \times \ln(p_i/p_f)$$

Equation 5.9

The results shown in Figure 5.8a (fast) and Figure 5.8b (slow). The plots show a decrease in modulus from approximately 17-30GPa (fast) and 12-20GPa (slow) at 5% RH to in the region of 0.2 to 2.0GPa at 95% RH. These values at low RH are rather higher than those quoted for the modulus of wool in the literature, which are of the order of 4-5GPa in the Hookean region for the dry fibre (Müssig, 2010b). The reduction in modulus with increasing fibre content is a well-known property of wool fibre, which is also observed in the data here (Wortmann and Jong, 1985). An initial modulus of approximately 2.7GPa was recorded for Romney ewe wool (Dunn and Weatherall, 1992) at 20°C and 65% RH, in reasonable agreement with the values presented in Fig 8 at 65% RH, although the values for the modulus at low RH are much greater than those reported from mechanical tests. There is also a significant reduction in the modulus with increasing fibre moisture content. The torsional modulus of wool exhibits a much greater reduction from the dry to the wet fibre condition (1.2GPa to 0.1GPa) compared with the

extensional modulus (4-5GPa to 2-3GPa) (Müssig, 2010b). It is reasonable to assume that the sorbed water molecules occupy the amorphous regions of the wool fibre, which results in a much larger reduction in the torsional modulus (Farran et al., 2009). Given that the derived moduli values in this study are obtained from an internal swelling pressure, it is reasonable that the values obtained would more closely resemble torsional rather than extensional moduli. The values obtained appear to be reasonable at the upper end of the hygroscopic range, but over-estimate the moduli at lower RH values. A similar analysis conducted on the sorption properties of a nanocellulose reinforced guar gum composite also found that the calculated modulus values associated with the slow process were much larger than the experimental values at the lower end of the hygroscopic range (Keating et al., 2013). Interestingly, that study also found that the fast process modulus values were considerably higher than the slow process values, in contrast with the results presented here, where they are similar.

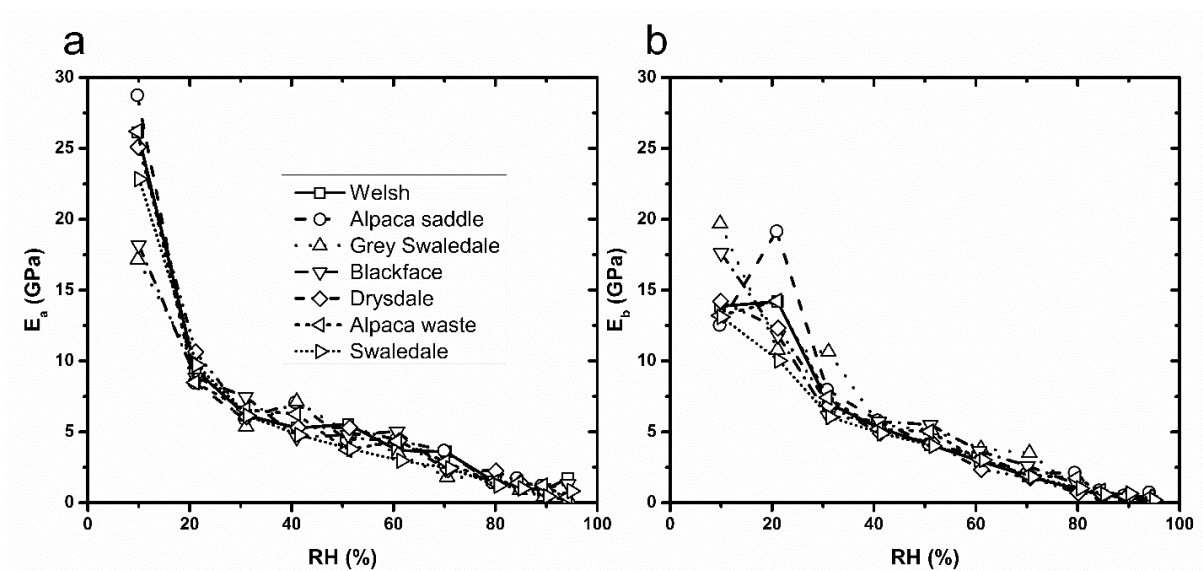


Figure 5.8: Calculated modulus of the wool fibres for the (a) fast processes (b) slow process

5.7 Conclusions

- Satisfactory fits for moisture sorption isotherms and sorption hysteresis using the Vrentas and Vrentas model were possible only by modifying some of the input parameters (especially the glass transition temperature of water – T_{g1}) in a way that is not permitted by the model and also using what are probably unrealistic values for T_{g1} . One possible reason for the model not working suitably is the assumption in the underlying Flory-Huggins approach that clustering of sorbate molecules is not occurring.
- The Zimm-Lundberg model showed the onset of water clustering in the fibres at moisture contents in excess of 15-18% EMC, which is somewhat lower to where water

clustering is observed in wool according to literature-reported specific heat determinations.

- Parallel exponential kinetics model was found to provide extremely good fits to the experimental data. The pseudo-isotherms for sheep wool, obtained by cumulatively adding the moisture content at infinite time for the fast or the slow process, showed behaviour that has previously been observed with flax and hemp. The sorption hysteresis was associated with the differences in moisture content (MC) associated with the fast process only below an RH of 70%, after which the slow process contributed negatively to hysteresis in that the MC associated for sorption was of a value larger than that for desorption (also been observed for flax and hemp).
- By assuming that the sorption kinetics was relaxation limited, the calculated fibres moduli were much larger than experimental values at the lower end of the hygroscopic range, but were in reasonable agreement at the upper end of the hygroscopic range. The variation of the calculated modulus with increasing moisture content showed behaviour consistent with plasticization of the amorphous regions of the wool fibres.

Chapter 6: Modification of wool fibre surface

6.1 Introduction

In an effort to enhance the ability of wool fibre to sorb v/VOCs and to shed more light on the interactions between the fibre surface and surrounding gases, wool fibres were subjected to different modifications. Fibre surfaces were altered either mechanically or chemically, and some possible additives were also investigated in this regard. This chapter outlines some of the relevant alterations reported in the literature and the modifications applied to be subsequently assessed for v/VOC sorption.

6.2 Changes in structure with mechanical stress

Stress-strain causes changes in the molecular structure of the fibre, as shown in Figure 6.1a (Hearle, 2000; Kreplak et al., 2004). Deformation caused by strain reaching 2%, called the hookean region, is attributed to bond angles and bond spacing change. The strain in the hookean region, named after Hooke's law, is not sufficient to cause a change in structure, and the deformation it causes is reversed once the strain is released. At about 5% strain, α -helical coils which are stabilised by non-covalent hydrogen bonds start to unravel. A strain up to 30% changes α -helical structures to the extended β -lattices as illustrated in Figure 6.1b. These changes can be seen via infrared spectroscopy, specifically in the amide I region ($1630-1695\text{cm}^{-1}$) as depicted in Figure 6.2. The effect of such changes on VOC uptake is not discussed in the literature.

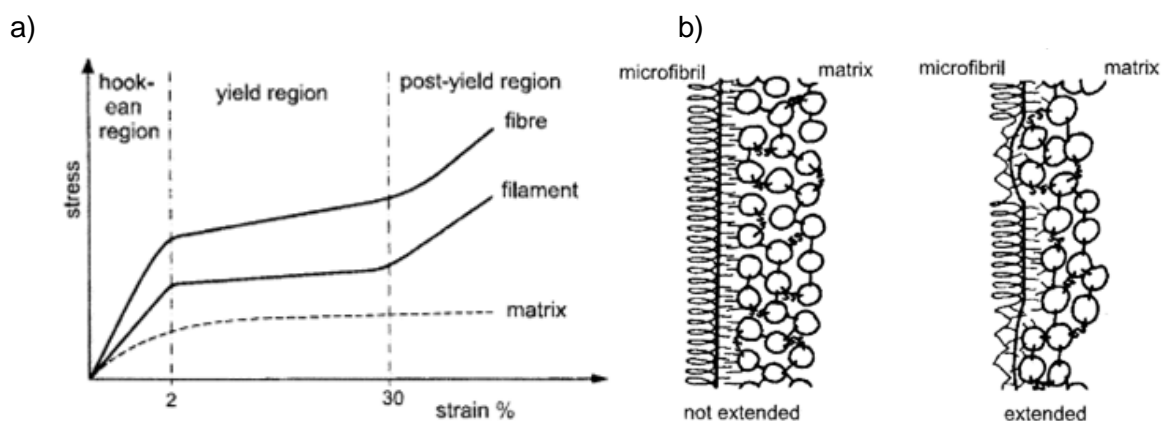


Figure 6.1: a) Changes in strain percentage caused by increasing stress, not drawn to scale (Hearle, 2000). b) An illustration of the change in the microfibril and matrix structures when put under strain (Hearle, 2000).

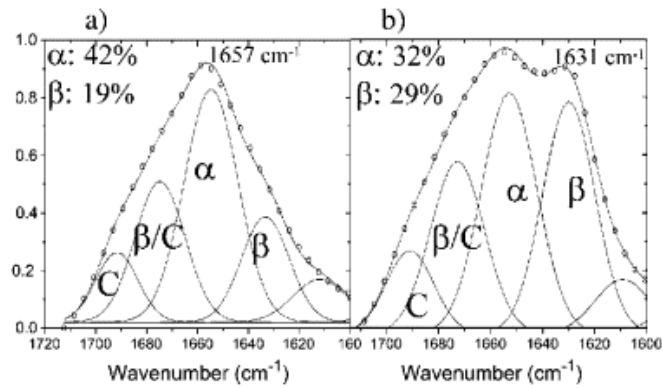


Figure 6.2: A fitted infrared amide I band spectra taken in the cortex of a horsehair fibre at 0% strain (a) and stretched to 100% extension in steam (b). α represent the content of α -helices, β of β -lattices, and C of disordered structure (Kreplak et al., 2004).

6.3 Changes in structure with chemical alterations

Surface proteins in general, such as those found on cellular and viral cell walls, are known to undergo enzymatic derivatisation - mainly acylation (addition of a $O=C-R$ group) (Schultz et al., 1988). The side chain involved is usually a large one and increases the hydrophobicity of the surface. Figure 6.3 shows three types of linkages (Roger, 1989; Towler et al., 1988): “thioester or ester bond to cysteine, serine, or threonine residues”; “myristoylation of proteins on amino-terminal glycine residues via an amide linkage”; and “carboxyterminal addition of a phosphatidyl inositol-containing glycan moiety” which occurs on amino acids such as serine. Other linkages are possible, such as amide-linkage of palmitic and stearic acids. The analytical identification of the different acylation sites and species is described by Bizzozero (Bizzozero, 1995b) and can also be identified by other methods such as 3D-scanning electron microscopy (Bahi et al., 2007).

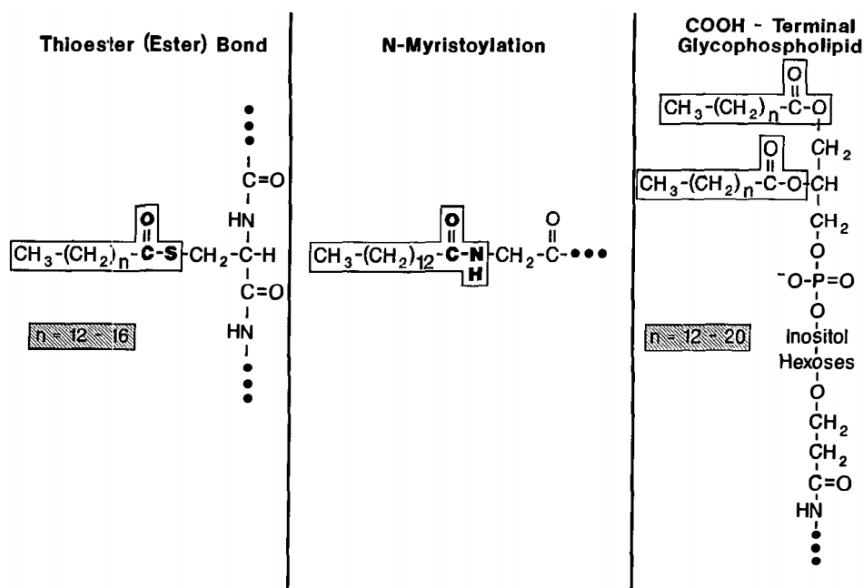


Figure 6.3: Some fatty acid linkage to eukaryotic proteins (Towler et al., 1988).

Imparting shrink resistance to wool fibres has been of great interest to the textile industry. The most common chemical methods to 'shrinkproof' wool are acid chlorination (Makinson, 1979) or by using permonosulphuric acid – prepared by reacting gaseous sulphur trioxide with liquid hydrogen peroxide (Marshall, 1964) – followed by a polymer application (Bamford et al., 1998).

Hydrogen peroxide can be used to disrupt the -S-S- bonds crosslinking of the fibres and results in the formation of cysteic acid (Jovančić et al., 2001). This results in changing the surface from being hydrophobic to a negatively charged one, which “leads to the release of 18-methyleicosanoic acid from the fibre surface and underlying cell membrane complex attached to the surface scales”. It enhances the fibres shrinkage resistance, more so than enzymatic treatments (Cardamone et al., 2004).

Concerning hair care, dyeing products normally contain ammonia, or another alkalizing agent like alkanolamines (monoethanolamine or aminomethylpropanol), and an oxidising agent (hydrogen peroxide) (Schmenger and Schmitt, 2012). The dye molecules are mixed with the oxidising agent just prior to application. When applied, the alkalizing agent and the oxidising agent cause the hair to swell. This helps the dye molecules, which are based on benzene rings, to penetrate into the cortex. As this happens, the oxidising agent causes the dye molecules to react forming large molecules that are unable to escape the cuticle. When these molecules that contain a series of double bonds are present with electron rich groups (amino or hydroxyl groups), they exhibit colour.

Hydroxides or a mixture of protein denaturant (urea, guanidine, or their derivatives) and a base are used to unfold the keratin structure, causing the hair to relax and straighten under heat. Some peptides have been identified to have an affinity to hair, and are used in conditioners and colorants (Benson et al., 2012).

In the carpet industry, treating wool with “a variety of combinations of sulfonated resin, sulfonated phenolic compounds, compounds of sulfonated phenolics and aldehydes, fluorochemicals, modified wax emulsions, acrylics and organic acids of low molecular weight” allows it to be stain and water resistant (Knowlton and Elgarhy, 1991).

Similar approaches to the ones described above may prove effective to introduce chemical functionalities on and underneath the cuticle.

6.3.1 Modification with anhydrides

Modification of natural polymers with anhydrides is reported frequently in the literature (Hill, 2008; Ormondroyd, 2007; Santayanon and Wootthikanokkhan, 2003). For wool, high weight gains are reported when it is reacted with anhydrides (Freddi et al., 1999). The weight gain is an indication that molecular functionalities have been added onto the surface. There are

various means to prove that the surface's functionalities have been altered, such as by FTIR, and differences in some properties such as hydrophobicity are noted (Arai et al., 2001).

Of relevant interest is binding anhydrides which cover a good range of polarities, mimicking the variety of VOCs, on fibre surfaces. They can potentially be used a 'bridge' to physically attract and sorb these VOCs on the basis of polar similarities. An example that follows the same line of thinking is the modification of wool by succinic anhydride, followed by the addition of chitosan onto the surface (Ranjbar-Mohammadi et al., 2010a); the advantage of modifying with succinic anhydride prior to the addition of chitosan is an enhanced bonding of the latter onto the fibre's surface.

6.3.2 Enzymatic modifications

Enzymatic treatments are seen as environmentally friendly substitutes for surfactants and chemical processes that enhance clothing quality with regards to domestic washing (Nolte et al., 1996). Proteases sorbed onto the fibre cause hydrolysis – breaking down of the fibre into smaller molecules like peptides, amino acids and fatty acids – which is more pronounced when applied after scouring. Lipases likewise degrade fatty molecules. Both cause an increase in fibre softness, presumably by reducing fibre-bending stiffness.

Proteases are one of the major enzymes investigated for applications on wool (Beynon and Bond, 1989; Duran and Duran, 2000; Heine and Höcker, 1995). They decrease the fibres' tensile strength due to the degradation they cause. However, they have been used to 'shrinkproof' wool by descaling some of the cuticle, removing the bound hydrophobic lipids with it, but given time it also reaches and attacks the cortex. Studies show that this increases their uptake and sorption of dyes, as seen in Figure 6.4 (Parvinzadeh, 2007b; Riva et al., 2002; Tsatsaroni et al., 1998). Several factors increase the extent of enzymatic activity, the most relevant being how much the fibre has been subjected to dyeing or oxidation by potassium permanganate for example. However, it is also possible to limit their activity; modified proteases, such as with polymer polyethylene glycol (Jus et al., 2007; Silva et al., 2005; Smith et al., 2010) or Eudragit S100 (a reversible soluble–insoluble polymer) (Shen et al., 2007), can restrict their action and target them to the cuticle only (Schroeder et al., 2004), with visual changes as seen in Figure 6.5 and lower weight loss compared to unmodified protease treatment. As expected, the sorption of dyes by fibres treated with modified protease is usually less than that of ones treated with the more penetrating unmodified protease, as depicted in Figure 6.6 via florescence.

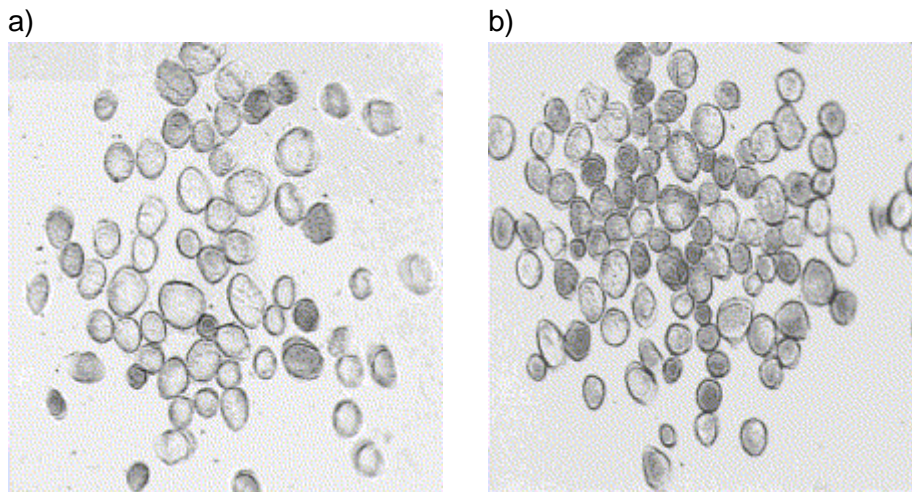


Figure 6.4: Cross-sections of (a) untreated and (b) protease treated (19.5 mU g^{-1}) fibres dyed with Lanazol Blue 8G dyeing for 1 hour (Schumacher et al., 2001).

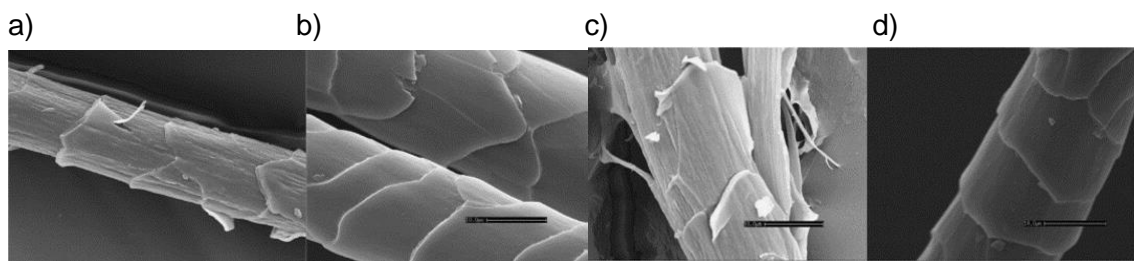


Figure 6.5: SEM images of treatments for 3 hours with (a) *B. lentus*, (b) modified *B. lentus*, (c) *B. subtilis*, and (d) modified *B. subtilis* (Jus et al., 2007).

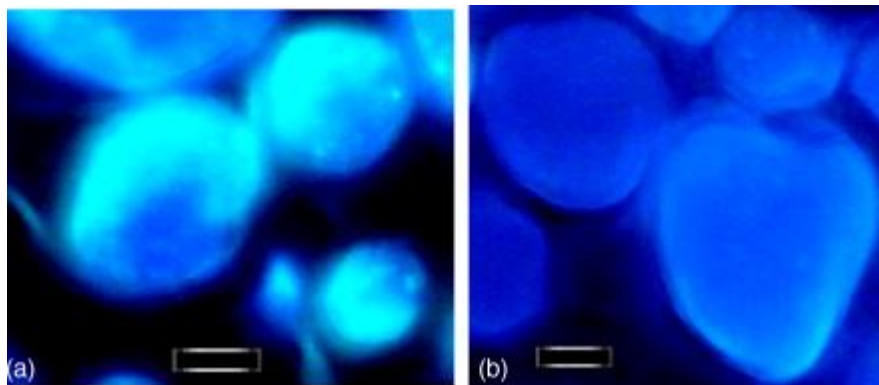


Figure 6.6: Fluorescence microphotographs of fibre cross-sections of wool treated with (a) protease and (b) modified protease (Silva et al., 2005).

Transglutaminase is an enzyme that is isolated from guinea pig liver or *Streptovorticillium mobaraense*; both are commercially available (Ando et al., 1989). Like protease, transglutaminase decreases fibre shrinkage but also has an opposite effect in that it increases its strength (Figure 6.7a and b), and can therefore be used to compensate the degradation caused by protease or oxidative or reductive chemical treatment (Cortez et al., 2004). Results also suggest that a more pronounced effect is observed when transglutaminase is applied after protease, indicating that the degradation caused by the latter gives transglutaminase

access to additional chemical functionalities. It works by catalysing the formation of a bond between an amine group of any protein's amino acid, such as that found on lysine for example, and the acyl group of the wool fibre's amino acid glutamine. The study demonstrated the formation of such bonds by using fluorescein cadaverine, after which more or less uniformly distributed fluorescence is seen (Figure 6.7c). The authors rightly conclude that "active functional agents that have the requisite primary amine group may be incorporated in this way to provide a beneficial effect, e.g. anti-microbial agents, sunscreens, water repellents and perfumes." The technology has been patented for human skin, nails and hair applications (Bailey et al., 1996).

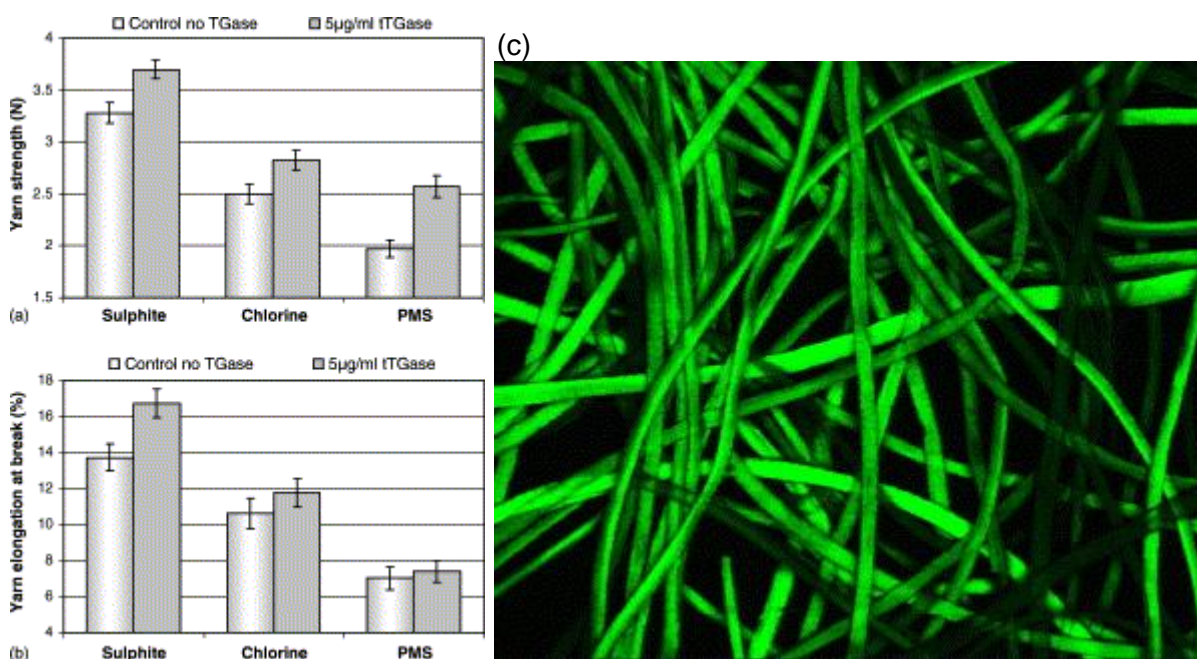


Figure 6.7: Wool yarn (a) breaking force and (b) elongation at break with and without incubation with 5 µg/ml of guinea pig liver transglutaminase in Tris-HCl pH 8.5mM DTT and 5mM Ca²⁺ at 37°C for 2 h; (c) Confocal microscope photographs of wool fibre samples treated with 5µg/ml guinea pig liver transglutaminase and 0.5mM fluorescein cadaverine, 5mM DTT, and 5mM Ca²⁺ in 50mM Tris-HCl buffer pH 7.4 at 37°C for 1h (Cortez et al., 2004).

Phenolic compounds such as dodecyl gallate has been successfully bound on wool surface structure via enzymatic routes (Hossain et al., 2009). Dodecyl gallate on its own is a known food additive and pharmaceutical agent used for its antioxidant and preserving properties (Aruoma et al., 1993; Kubo et al., 2002), and therefore when grafted imparts antioxidant, antibacterial and water repellent properties to wool. Grafting of phenolic compounds giving similar advantages have been achieved on natural polymers using enzymes: horseradish peroxidase for chitosan (Vachoud et al., 2001), tyrosinase for wool (Jus et al., 2008) and chitosan (Chen et al., 2000), and laccase for a variety of applications (Couto and Toca Herrera, 2006). Since these systems are heterogeneous, enzyme activity is dependent on their diffusion to and into the fibre, in addition to other factors such as concentrations, temperature,

pH, the solution/medium used, and the size of enzyme (Heine and Höcker, 1995). Hence the removal of the lipid layer (i.e. scouring prior modification) should help increase the loading of grafted molecules (Silva et al., 2005).

Different pre-treatments have been investigated to increase the activity of enzymes on wool fibres. For transglutaminase and tyrosinase, the best accessibility was observed post treatment with permonosulphuric acid, followed by chlorination and plasma treatments (Lantto et al., 2012).

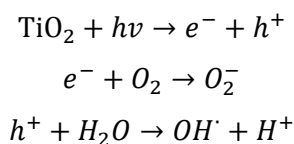
Enzymes themselves can be immobilised on wool fabric. One example is lysozyme that can be covalently bonded to the surface of fibres activated with glutaraldehyde, giving the fabric antibacterial properties (Wang et al., 2009). Lipase can likewise be stabilised on the surface (Feng et al., 2013). They can also be used to immobilise nanoparticles on the surface (Montazer and Seifollahzadeh, 2011).

6.4 Possible additives to enhance sorption

6.4.1 Nanotechnology

Fabrics that remain clean without the need of any action are a fascinating notion. The concept is observed in nature, such as in the case of butterfly wings or lotus leaves, where hydrophobic surfaces remain dirt-free by simply allowing water droplets to collect the debris and slide-off (Marmur, 2004; Zheng et al., 2007). Materials may exhibit such properties through geometric or chemical modification (Extrand, 2002). The self-cleaning properties have the potential to be applied for passively improving indoor air quality, but also may impart potential disadvantages.

Surfaces can also be modified to be hydrophilic and self-cleaning mainly through incorporating photocatalytic particles (Tung and Daoud, 2011). Particles are distributed and bound on fibres' surfaces, and the surfaces of the nanoparticles themselves act as oxidation/reduction sites of organic compounds in the presence of certain light wavelengths surface according to the following reactions (Figure 6.8):



Where $h\nu$ is light energy (UV), e^- is an electron, and h^+ is a photohole.

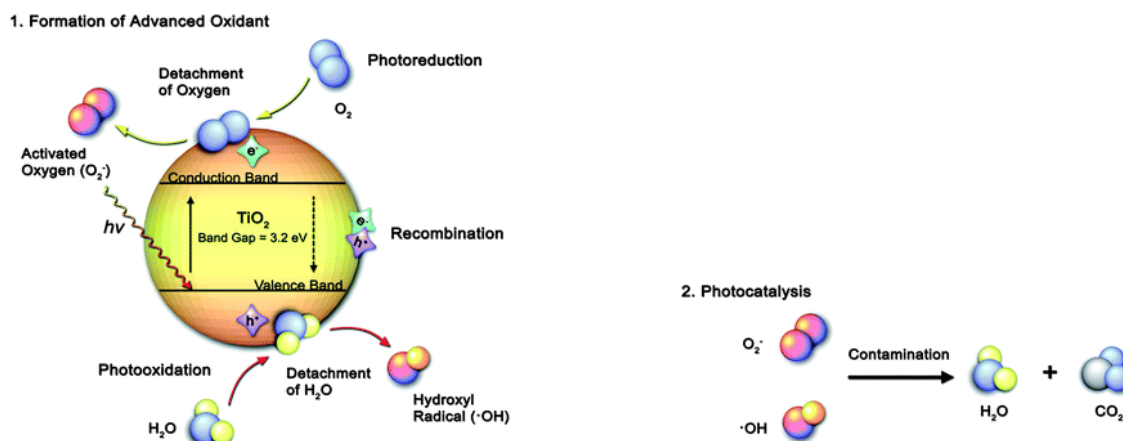


Figure 6.8: Mechanism of photo-degradation caused by TiO₂ (Tung and Daoud, 2011).

Antimicrobial and antifungal properties have also been attributed to coated fabrics. Titanium dioxide is the most popular of the nanoparticles (Fujishima and Zhang, 2006), and can have an anatase, rutile, and brookite crystalline structure, of which anatase seem to be the most active (Oh et al., 1997).

Although organic fibres are not such a robust support as thermally resistant solids, nanoparticles can be incorporated onto fibres by different methods: hydrothermal treatment (Daoud and Xin, 2005), sol-gel processing (Bozzi et al., 2005; Daoud and Xin, 2005; Qi et al., 2006), impregnation (Dong et al., 2006), liquid phase deposition (Liuxue et al., 2007), chemical spacers (Meilert et al., 2005), sputtering (Carneiro et al., 2007), or using enzymes (Montazer and Seifollahzadeh, 2011).

Cotton fibres were given a self-cleaning ability using the sol-gel process at 97°C and ambient pressure, where 20nm anatase TiO₂ grains were densely dispersed on a coating (Daoud and Xin, 2004). An enhanced method requiring only a temperature of 60°C followed by irradiation with UV light for 8h removed cibacron Blue F-R (blue dye), wine and coffee stains (Qi et al., 2006). However, this seem to come at the cost of a 56% reduction in fibre tearing strength, which is attributed to the application of TiO₂ and not to photo-degradation to the cellulose; in fact, it slightly protects the cotton from degradation caused by UV light. Aqueous dispersion with curing at 170°C for 1min results in cotton fibres capable of decomposing gaseous ammonia. A dispersion of 5g/l resulted in the degradation of the ammonia in the gas reactor within 35mins, whereas the dispersion of 15g/l yielded the optimum degradation within 15mins. Again, a compromise in the breaking strength retention is observed, although it is relatively mild (≈6% for a 15g/l dispersion). Interestingly, coated cotton was much more effective on its own when compared to a mixture of cotton and polyester, indicating that polyester acts as an inactive spectator. This correlates with the assumption that TiO₂ nanoparticles and/or ammonia bind with the hydroxyl group of the fibre, or are disposed within the loose microstructure of cotton, but not on the less polar and smoother surface of polyester.

The more hygroscopic the substrate is, the better the photo degradation effect would be, as demonstrated in the case treating the cotton to be more hydrophobic and in the case of ethanol photo-degradation (Sanongraj et al., 2007).

Wool (90%)-polyamide(10%) fabric has also been successfully coated with TiO₂ (Bozzi et al., 2005). The coating process involves pre-treatment with RF-plasma, MW-plasma, or vacuum UV, which functionalise the surface with short-lived COO⁻ and O-O⁻ groups. Following immediate application of TiO₂ colloidal solution and heating at 100°C or less for 15mins binds TiO₂ electrostatically. The treated fabric showed an ability to at least partially degrade wine and coffee stains.

6.4.2 Activated carbon

Activated carbon may come from a variety of sources such as peat, coal, nut shell, lignite, saw dust, and synthetic polymers (Chiang et al., 2001). Mixed as an additive with fibrous material, they can increase the amount of sorbed VOCs. They are also known to catalyse the oxidation of some VOCs they trap, including some ketones such as methyl-ethyl-ketone, acetone, and cyclohexanone (Akubuiro, 1993). However, there are downsides: the sorption is mainly physical, and therefore the amount sorbed decreases with increasing temperatures (Chiang et al., 2001). Relative humidity can also hinder sorption for some VOCs such as benzene, which exhibits a rapid sorption decrease at RH>65%. Water molecules are reported to possibly block the pores, prohibiting water insoluble VOCs from getting in contact with most of the surface area of the activated carbon (Cal et al., 1996). Another possibility is that water molecules simply compete with VOCs in sorption. Both explanations make sense, especially when looking at low concentration studies, where sorption increases with smaller pore diameters (Lorimier et al., 2005). Other than that, sorbed VOCs may undergo polymerisation and close off the pores, leading to reduced efficiency (Zhao et al., 1998). This polymerisation is catalysed by ashes present on the surface, which in turn result from the high temperatures required to activate or reactivate the carbon.

The carbon resulting from paper mill sewage sludge carbonisation and activation by steam is shown to be able to remove both methylene blue and reactive red 24 dyes from aqueous solutions (Li et al., 2011). Their maximum sorption is significant (34.36-263.16mg/g), of which 90% is sorbed over a wide range of pH (4 to 12). The activated carbon can be regenerated, but this requires high temperatures (300°C) and decreases its full sorption potential. If regeneration is required for their application in household products and materials, their use will be limited and short-lived. However, the focus of this work is the sorption of gases instead of dyes; this effect might be more significant with the less-bulky VOCs, in which case the

activated carbon might exhibit a buffering effect. One attractive feature of this additive is its low cost (USD 365/tonne).

Activated carbon has been demonstrated to work as a support of catalysts such as Pt, which promote the complete oxidation of VOCs. This would remove the need for regeneration. Pt/activated carbon achieved complete oxidation of VOCs at lower temperatures than other catalysts, but remains high for general use: 140-180°C, compared to ≈200°C for Pt/Al₂O₃.

A very interesting and relatively new form of carbon is carbon fibre, which can also be activated and performs as a gas sorber (Navarri et al., 2001). Its advantages include an sorption capacity of up to 54% due to its superb surface area, reaching up to 2,000m²/g. Active sites on the surface are most accessible when there is least contact between the fibres; the sorption capacity was shown to increase from 30 to 39% when woven fibre is compared to a needle-felted equivalent. This makes it ideal for incorporating into non-woven products. Still it is not without its limitations; the more volatile the gas is, the lower the sorption is.

For low concentrations ($p/p_0=0.004$), higher sorption is achieved with higher pore size distribution (i.e. use of lower activation temperature), and the nature of the VOC has an effect on the extent of interaction (Fuentes et al., 2003). Non-polar VOCs (n-butane, n-hexane) or those with low dipole moments (toluene, trichloroethylene) sorb well (0.29 to 0.32 cm³/g), whereas polar VOCs (methanol, ethanol, methyl-ethyl-ketone) do not (0.03 to 0.17 cm³/g). Generally, a diameter less than 2nm is suitable (Bandosz, 2006). A mathematical equation that describes the sorption potential at low concentrations is:

$$V = W_0 e^{\left[- \left(\frac{RT \ln(p_0/p)}{\beta E_0} \right)^2 \right]}$$

Equation 6.1

Where:

- V is the volume sorbed per weight unit of sample at a relative pressure p/p_0
- W_0 is the micropore volume
- β is a characteristic of the sorbate
- E_0 is a characteristic of the sorbent

As the concentration is increased, pore volume becomes the dominant factor. At considerable concentrations, industrial application of activated carbon fibre cloths has proved very efficient. As an example, a system of two cylindrical filters was used to sorb dichloromethane. While one cylinder sorbs, the second is made to desorb electro-thermally, and the dichloromethane

was recovered in a cryogenic trap. The system successfully reduced concentrations from 3-30g/m³ to less than 0.4mg/m³ (Subrenat and Le Cloirec, 2006).

6.4.3 Conditioners

Conditioners are applied on human hair to increase the smoothness and reduce the electrostatic charge, resulting in healthier looking hair. Conditioners work by sticking on the hair primarily through Van der Waals attractions, forming a very thin coating (Figure 6.9). The coating can be made more uniform by chemically treating the hair (reported as cycles of colouring and permanent wave treatment, washing, and drying), which damages its surface structure (LaTorre and Bhushan, 2006).

Conditioner contains cationic surfactants, fatty alcohols and silicones. A choice of proper key ingredients, especially fatty alcohols and perhaps functionalised silicones, may coat wool fibres with a thin layer that is efficient in sorbing VOCs. However, it is logical to conclude that any type of micro/nano-scale coating will decrease wool fibres' direct contact with any gas and decrease its natural sorption potential.

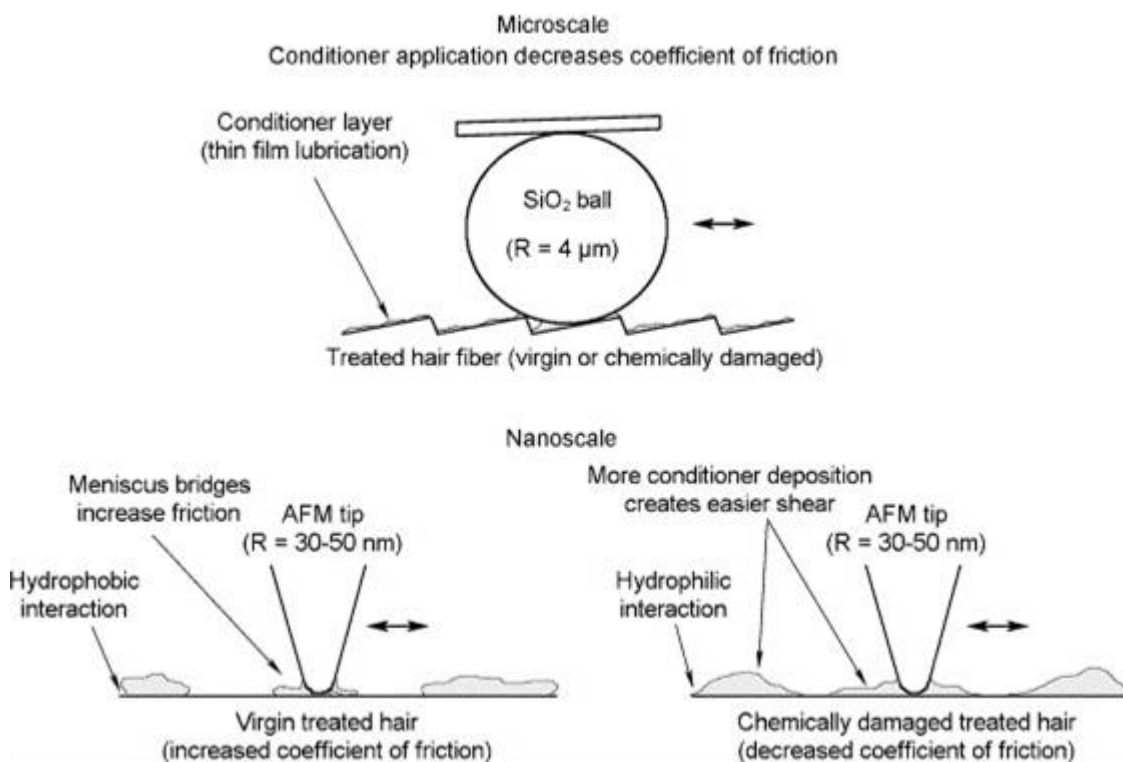


Figure 6.9: Interaction of micro- and nano-scale atomic force microscope tips with hair treated with a conditioner (LaTorre and Bhushan, 2006)

6.4.4 Chitosan

Chitosan is a polysaccharide with free amine and hydroxyl groups, which can perhaps provide chemical anchors for further functionalising. It is derived from shrimp and other crustacean shells.

Chitosan can be incorporated on the surface of wool fibre. This can be done by treatment with polyurethane/chitosan bio-composite emulsion (Shi et al., 2014) or via enzymes (Jovančić et al., 2001). Such treatments have other effects such as reduction in shrinkage and a softer feel.

6.4.5 Zeolites

Zeolites are microporous, aluminosilicate minerals, and are commercially available as sorbents. One difference they have to activated carbon is that they can be hydrophobic, such as silicalite-1 and zeolite Y; therefore, these zeolites can get over the problem of being saturated with water rather than VOCs. One particular zeolites, MCM-41, is reported to desorb VOCs at relatively low temperatures (50 to 60°C), whereas others desorb at temperatures in the range of 100-120°C (Zhao et al., 1998).

6.4.6 Urea as a scavenger of formaldehyde

For particle boards that utilise a urea-formaldehyde resin, addition of urea is known to reduce the emission of free formaldehyde into the atmosphere (Johnsson et al., 2014). In the simplest form, formaldehyde reacts with urea reversibly to form monomethylolurea (de Jong and de Jonge, 1952). Using urea as an additive or transforming a nitrogen functional group found on the surface of wool fibre into a urea-like function may enable the capture of formaldehyde and possibly other volatile aldehydes and ketones.

6.5 Effect of plasma, UV, and microwave radiation on fibre surface

RF-plasma can introduce functional groups on fabric surface (C-O, C=O, -O-C=O, -C-OH, -COOH) when applied under vacuum (Bozzi et al., 2005; Grace and Gerenser, 2003). They result from the reaction between the fabric and active O-species (singlet $^1\text{O}_2$, atomic O, anion-radical O^- , and cation-radical O^+). This treatment therefore makes the fibres more hydrophilic. 10 to 40nm of fabric depth are altered when treated for ≈ 30 mins.

One paper investigated the sputtering of wool fibres with low-temperature plasma and showed that such treatment increases the dyeing rate as seen in Figure 6.10 (Kan et al., 1998). Scanning electron microscope (SEM) images show grooves (Figure 6.11) that are hypothesised to facilitate the accessibility of the dyes. The same principle should apply to gases, or to possible chemical functionalization of the surface. Because low temperature is used, the changes are only on the surface (up to 100nm) alluding to that thermal, physical and mechanical properties would not be significantly affected post treatment; glossiness for example is reported to remain unaltered. However, due to the increase in polar groups on the surface, the fibres are much more wettable (get completely wet in under a second compared to over 900s) and have a higher electric discharging power; the time needed to discharge half of the charges present in a specimen decreased by about 8-12%.

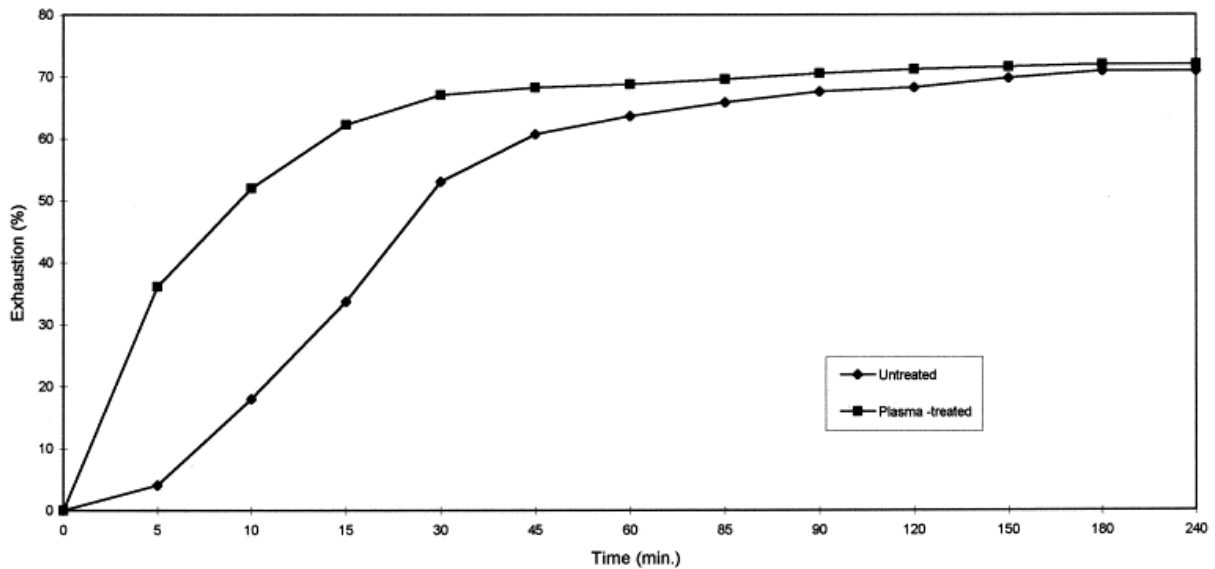


Figure 6.10: Exhaustion rate of the dye Neolan Red GRE (CI Acid Red 183) with an untreated specimen and a low temperature plasma-treated specimen (Kan et al., 1998).

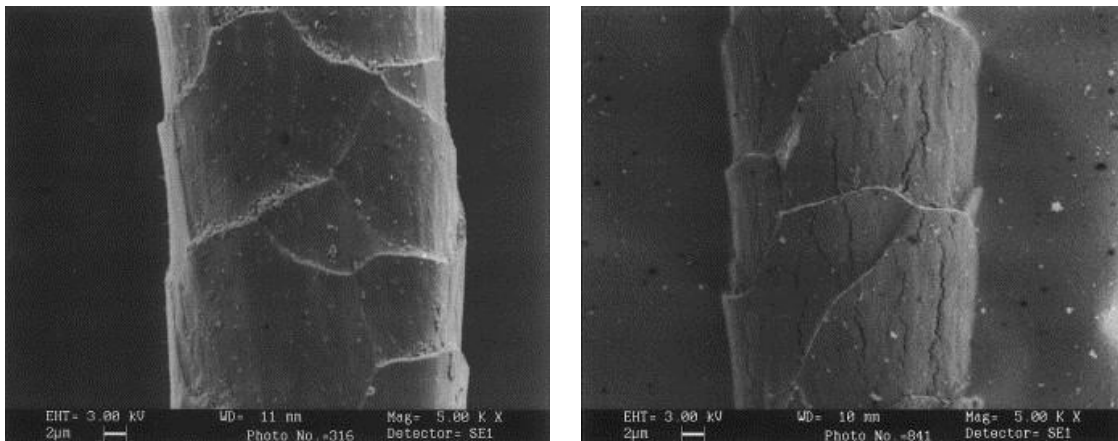


Figure 6.11: SEM picture of an untreated fibre (left) and treated fibre (right) (Kan et al., 1998).

Vacuum-UV uses less energy than plasma, and results in active atomic and excited O^- species, and non-ionic species - enough residual oxygen allows this when operating at 0.8torr in an oxygen atmosphere. This apparently results in a more controlled and uniform surface modification comparable to RF-plasma's effect. Only 10nm of fabric depth is affected by radiation (50 atomic layers with an average thickness of 0.2nm/layer) (Bozzi et al., 2005). Better sorption of dyes is achieved post exposure to UV irradiation (Periolatto et al., 2014)

Microwave irradiation appear to have a similar oxidation effect, as seen in the case of polypropylene (Mirabedini et al., 2004).

6.6 Selection of modifications

All the above mentioned modifications of sheep's wool and hair fibres have been well studied for the purposes of textile and hair care enhancements. None of these studies consider the change of fibres' uptake of VOCs. The methods taken forward and carried out were selected

using a process of elimination, prioritised according to the ease, practicality, and cost effectiveness of them being adopted to industrial processing.

Mechanical modifications of wool fibres in both its afore mentioned forms may provide an inexpensive and easily scaled-up means to enhance v/VOC sorption by products used in the indoor environment. In reality, wool fibres undergo a certain level of mechanical strain during their processing; yarn making involves stretching of the fibres, and scouring and other industries subject fibres to randomly oriented forces.

Chemical modification allows the introduction of a plethora of chemical functionalities which may in turn act as anchoring sites for VOCs. Although enzymatic routes seem to provide a very versatile surface modification, there are other factors to contemplate. Considering the general costs of enzymes and the mediums they need for activation, the financial implications of applying such treatments are substantial. One major problem with binding phenolics and non-polar substrates to fibre surface is that they are not water soluble, and the solvents required decrease the enzymes' activity. Utilising liquid or supercritical CO₂ as a reaction medium is an option that would avoid some of the running costs; again, though, applying this technology on an industrial scale calls for a very large capital cost. Adding to that, the use of enzymes seem to change the other properties of the fibre, such as strength and feel. On the other hand, utilising a methodology of inserting new functionalities similar to that of hair dyeing would not guarantee that these functionalities would interact with the surrounding atmosphere, as they would be trapped underneath the other surface. Out of the other possible chemical applicable modifications, the most straightforward and frequently investigated is the use of anhydrides. They provide great flexibility with the range of functionalities they can add where the same method can be used (Freddi et al., 1999), and they are proven to be good bridging functionalities on wool fibres (Ranjbar-Mohammadi et al., 2010a)

For the use as additives, the use of many materials is reported for v/VOC sorption, but some practical difficulties exist. For Zeolites and urea, fixation onto the wool fibre is a challenge. Use of functionalised conditioners will simply reduce the surface area of the wool fibre, and therefore would be more applicable to fibres having no sorption potential to begin with. Photocatalytic nano-particles may be ruled out as light is not guaranteed to reach the fibres in domestic use, such as when used as insulation. Also, the fibre surface is not always expected to be hydrophilic, depending on its surroundings, which reduces photocatalytic activity (see chapter 4). Incorporating activated carbon fibre or chitosan seems to be a relatively cheap method of dramatically increasing the products' overall surface area and ability to sorb v/VOCs, especially non-polar ones – the question is how to incorporate it? Powdered carbon would be a challenge in this aspect, but carbon fibre is accessible and would easily blend in

with other fibres. Similarly, chitosan would provide large platform molecules for polar v/VOCs to be attracted to.

Irradiating the fibres may seem to be a simple and useful technique, but applying it to large scale processing of wool fibre does not seem straightforward, and is known to have an effect on other important and desirable fibre properties such as strength.

6.7 Mechanical modifications

An investigation was made to the changes in surface properties after inducing a mechanical strain. If an improvement is noted, a relatively easy and cheap method of modification can be applied on an industrial scale.

6.7.1 Tensile stress

6.7.1.1 Method

30cm long DK Falkland wool yarns were conditioned for over a week and tested for their tensile strength at the same conditions of 22°C and 65% RH. An Instron tensile tester was used along with suitable clamps and a 100N load cell. The sample of yarn was attached and stretched at a rate of 3mm/min until the breaking point, with the exerted load being recorded at the rate of 10readings/sec. Extension values were adjusted to start from when the load starts from 0.1N, and is ended after 2 values (200msec) after the breaking point. This was repeated for 5 samples in order to assess the average loads required to extend the yarns by a set percentage – 100% being the maximum extension value just before the yarn breaking/severing, 85% being 85% of that maximum value and so on.

Following that, 5 new samples of the same yarn were subjected to a load that is expected to extend them by 25% of their original length. This was done by attaching a weight to the end of the yarn with the other end being fixed such that the extended length of yarn was 30cm. After each yarn was left to extend by the attached weight for 10sec, it was collected and directly scanned using Thermo Scientific attenuated total reflectance (ATR) technique; each sample was scanned after a background spectrum has been acquired. The spectrum were obtained using a resolution of 2cm⁻¹ and 160 scans of the same point in the middle of the yarn. In order to ascertain the relative contents of surface fibre structure (Kreplak et al., 2004), the curves were baseline-corrected followed by smoothing using Savitzky-Golay method (9pts) (Gorry, 1990). Then they were deconvoluted using the Levenberg Marquardt method (Levenberg, 1944) to find 2 to 6 positive Gaussian peaks based on second derivative (peak minimum height is 3% of the absorbance scale). The surface structural content of the sample was calculated based on the relative areas of the deconvoluted peaks (Kreplak et al., 2004).

After each spectrum was obtained for each sample, the same yarn was extended by 50% and analysed by ATR, after which the same process was done for 75% and 85% extension of the same samples.

6.7.1.2 Analysis and results

The tensile tests performed using Instron gave an indication onto what sort of load would lead to a specific extension. The results are summarised in Figure 6.12, where 100% extension corresponds to the maximum extension reached just before breaking/severing the yarn. Weights exerting the same load were used to extend samples for analysis as described above.

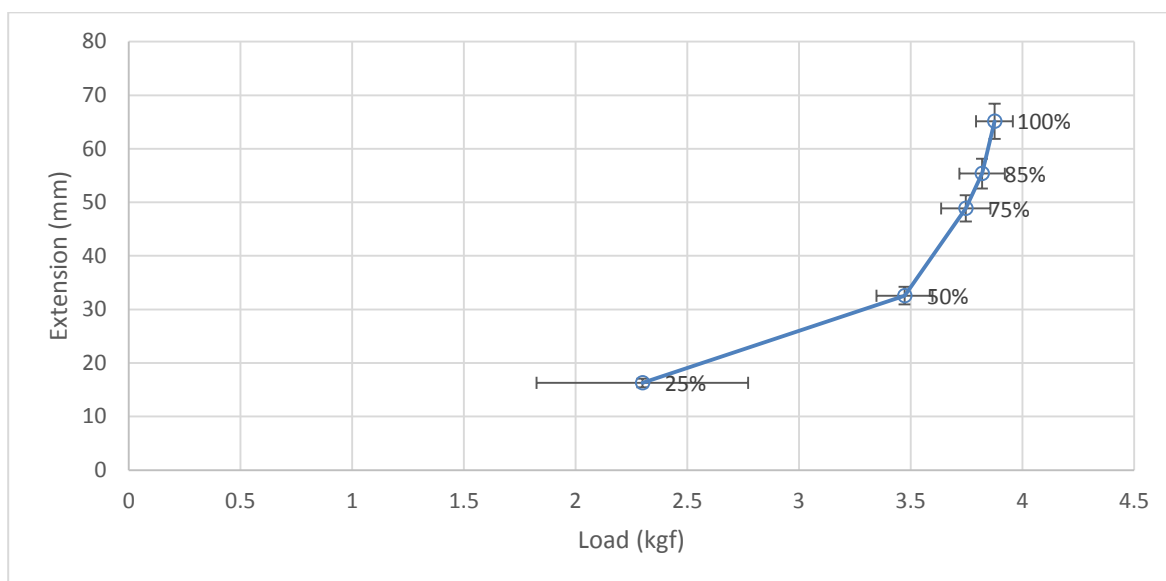


Figure 6.12: Average values of extension (where the written percentages are based on 100% representing the maximum extension prior to breaking) and their corresponding loads obtained from tensile testing analysis of 30cm long DK Falkland wool yarns. Bars represent standard deviation.

IR analysis of the 5 samples at 0, 25, 50, 75, and 85% extension (Figure 6.13) showed no notable trend in the results, as seen in Figure 6.14. This lack of structural change can be explained by the possibility that wool yarns have are subjected to tensile stress during manufacturing; it is most likely that irreversible structural changes had already taken place before the experiment could be started. Since it would be impractical on laboratory or industrial scale to perform a similar experiment on individual un-stretched wool fibres, this means of modification was no longer pursued.

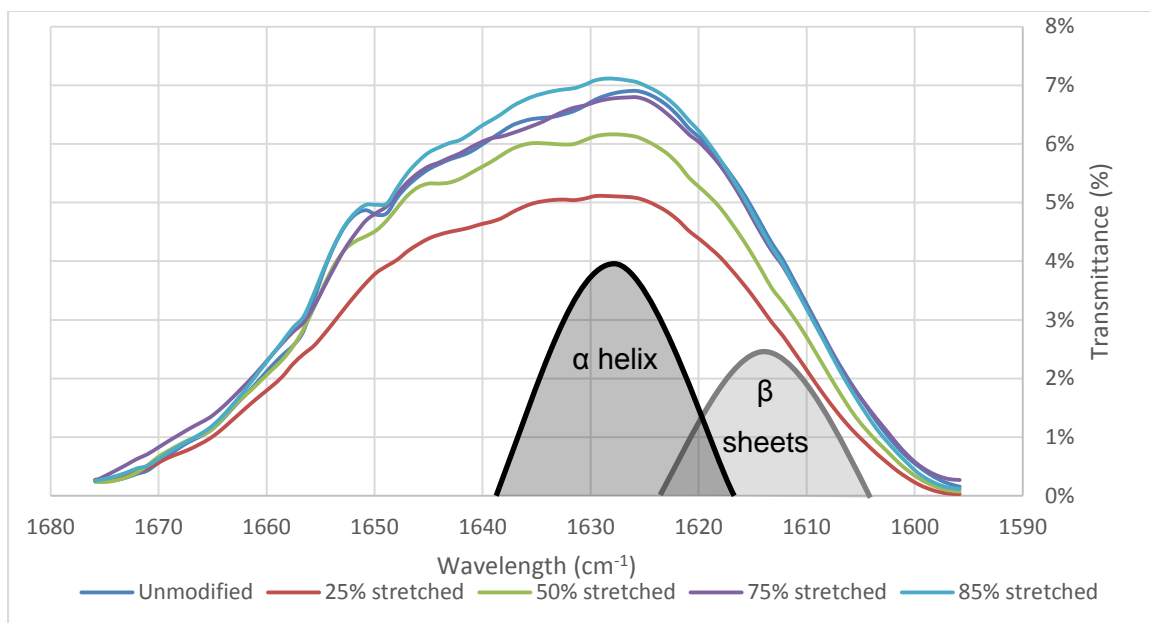


Figure 6.13: Examples of smoothed FTIR spectra of amide I regions of the same yarn sample stretched to different levels, showing no significant difference in peak shapes. Approximate positions of expected deconvoluted peaks attributed to α helix and β sheets are indicated.

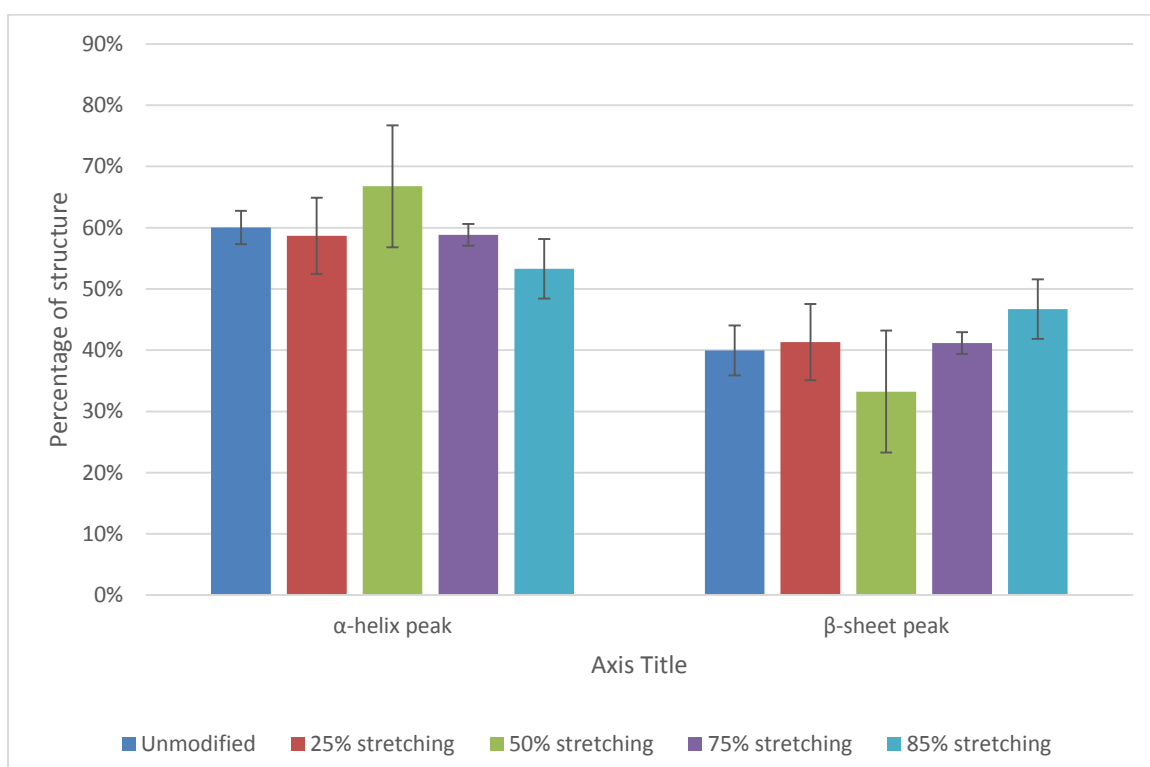


Figure 6.14: Calculated surface structural composition of DK Falkland wool before and after submission to tensile stretching.

6.7.2 Ball milling

6.7.2.1 Method

13.8g of Alpaca wool was placed in a small cylindrical drum containing different-sized ceramic balls. The drum was left to rotate and samples were collected after 2, 4, and 6hrs. The same

was repeated with 13.8g of Light Herdwick wool, which was used for assessment of sorption and other tests (see section 7.3),

A Phenom scanning electron microscope (SEM) was used to capture images in order to assess structural changes on the fibre surface.

6.7.2.2 Analysis and results

As seen in Figure 6.15, after 2 hours, some damage on the cuticle is observed, which intensifies as the wool is milled for longer. After 6 hours of milling, there is also a significant amount of debris ranging in size from about a few μm to about $25\mu\text{m}$.

This all contributes to an increase in surface area (see section 7.6.2) and potentially opens access to new chemical functionalities that would interact with surrounding gases.

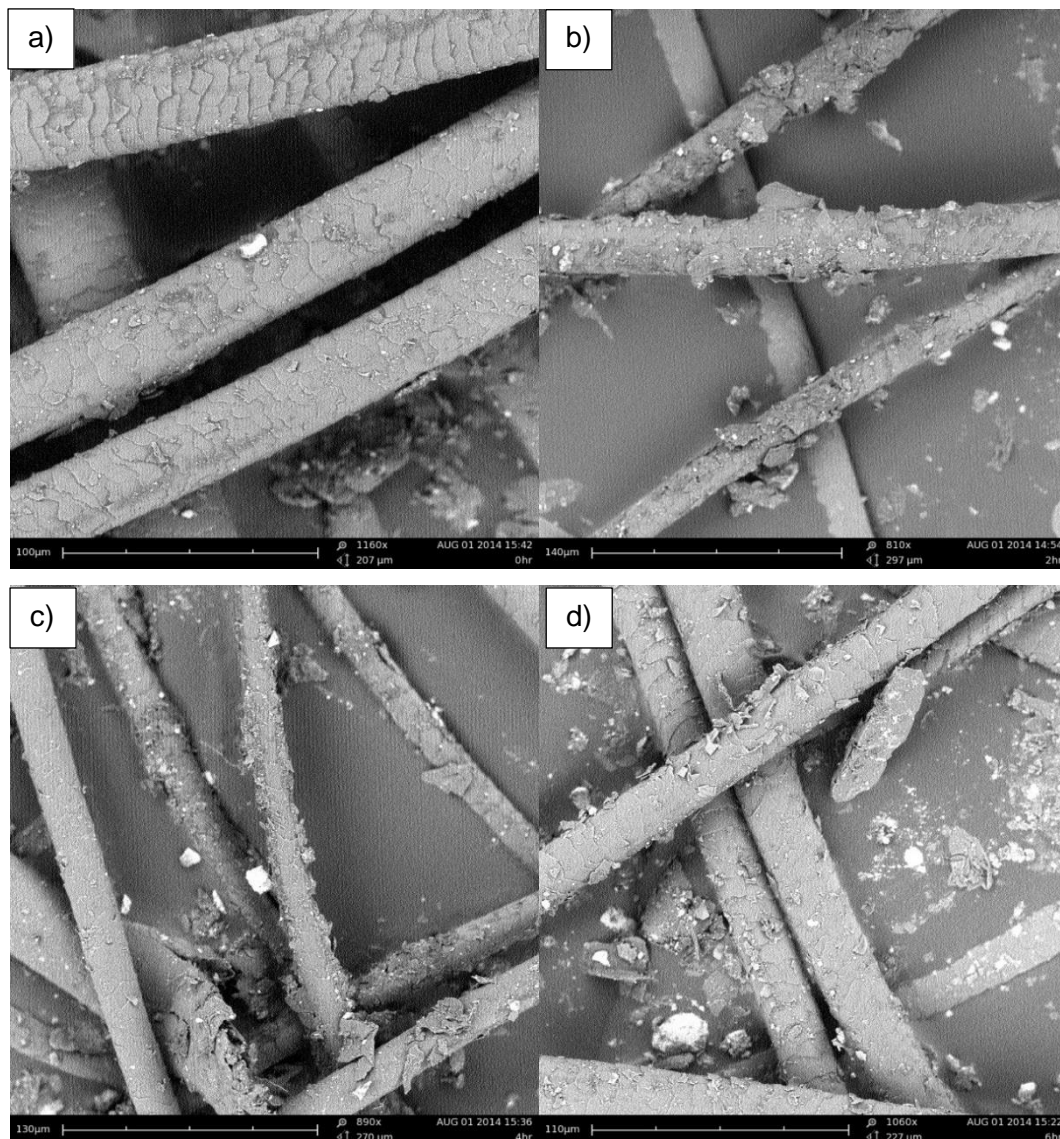


Figure 6.15: SEM images of Alpaca wool fibres: a) unmodified; b) after 2hrs of ball milling; c) after 4hrs of ball milling; d) after 6hrs of ball milling.

6.8 Chemical modifications

For the purposes of this study, three different anhydrides were considered to introduce three different surface chemical functionalities onto the wool surface: succinic anhydride to introduce a very polar surface functionality, phthalic anhydride to introduce a non-polar aromatic surface functionality, and (2-dodecen-1-yl)succinic anhydride (DDSA) to introduce a very non-polar surface functionality.

The suggested mechanism along with the resulting new functionalities for each anhydride used is outlined in Figure 6.16.

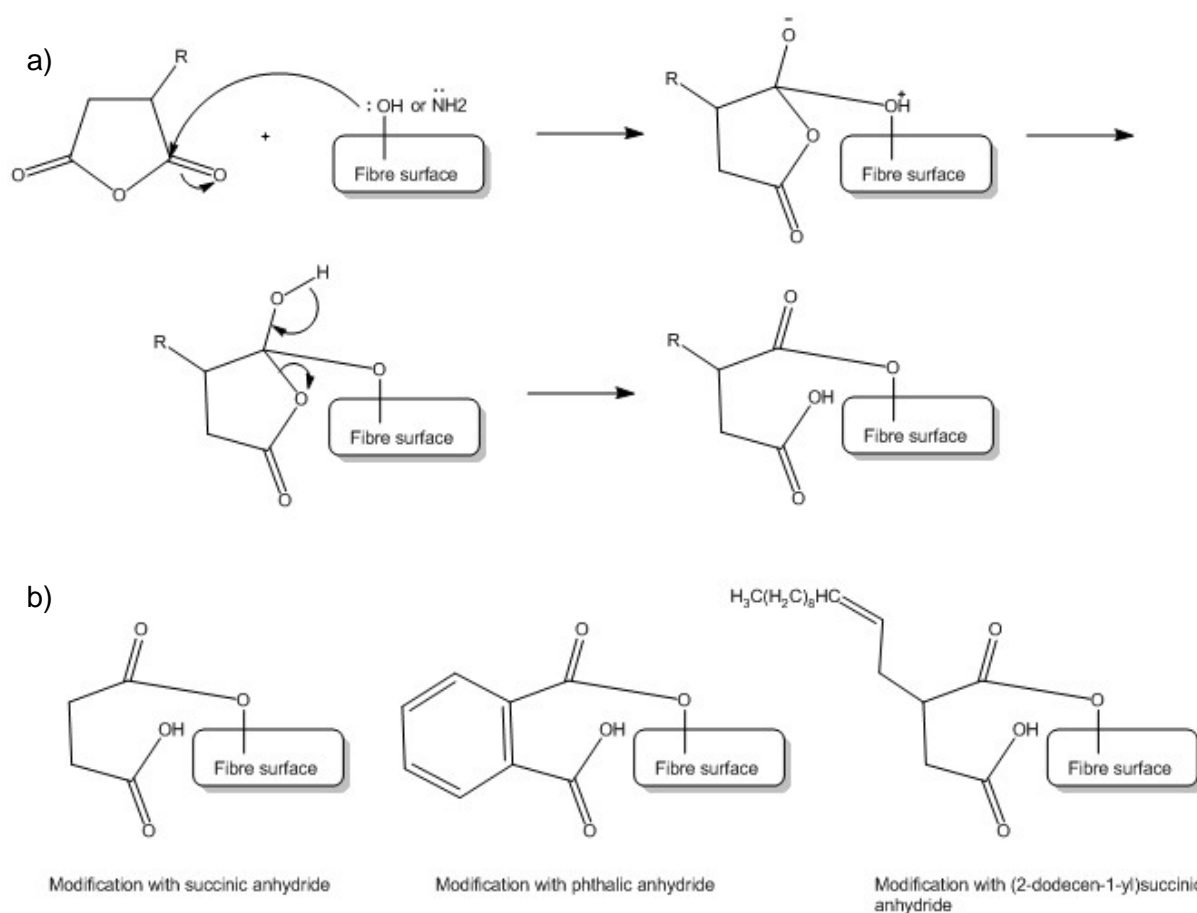


Figure 6.16: a) Suggested mechanism for the formation of an ester between a hydroxyl or amino group on the surface and an anhydride (Dubey et al., 1997; Ranjbar-Mohammadi et al., 2010b). b) New surface functionalities resulting from the modification of wool fibres with three different anhydrides.

6.8.1 Anhydrides

6.8.1.1 Method

Wool samples of different types, all dried in a 50°C oven for at least 1 week were reacted with 3 different anhydrides: phthalic anhydride, DDSA, and succinic anhydride. Control runs were also performed following the same process except no anhydride was used.

Dimethylformamide (DMF) was used as a solvent in a 1:30 weight of wool by volume ratio, with a large excess of anhydride (1:3 weight of wool by weight of anhydride) dissolved. The solution was heated and stirred to 80°C before the wool was added and left stirring at that temperature for 2hrs; this method was based on Freddi et al.'s (1999).

The wool sample was then collected, washed with plenty of acetone, followed by Soxhlet extraction with acetone for 5hrs. The sample was then left to partly dry in a fume cupboard and then fully dry in a 50°C oven overnight. This was done to ensure that no unbound anhydrides or DMF was left on the fibre surface.

The modified fibres were weighed at dry conditions and also directly scanned using Thermo Scientific ATR technique; each sample was scanned after a background spectrum has been acquired.

6.8.1.2 Analysis and results

Table 6.1 shows the weight gains between control runs and anhydride runs, indicating an addition of chemical structures onto the fibre surface and possibly inside the capillaries.

Table 6.1: Weight change post modification of wool samples dried in a 50°C oven.

Wool	Control	Phthalic anhydride	DDSA	Succinic anhydride
Swaledale	-4.28%	13.12%	21.64%	19.30%
Light Herdwick	-4.05%	13.67%	17.77%	15.09%

FTIR spectra (Figure 6.17) show some differences in surface chemical functionalities between the control and wools modified with anhydrides. The same method was followed as detailed in section 4.4.1.1. Results were interpreted according to the literature (Aluigi et al., 2007; Krimm, 1960; Li et al., 2009; Wojciechowska et al., 1999; Xiao and Hu, 2016; Xu et al., 2006).

The differences in the spectra of chemically modified wools are as noted:

- CH₂ stretching at 2930cm⁻¹ and 2850cm⁻¹. Compared to unmodified wool, it is seen to be slightly less intense for control wool, showing that the chemical process likely removes some of the bound surface lipids (18-MEA). Modification with succinic acid intensifies the absorbance owing to the new short CH₂ chain per introduced groups, and modification with DDSA intensifies it even more owing to the new long CH₂ chain per introduced group. Modification with phthalic anhydride causes an absorbance in this region similar to the control's, as no CH₂s are present in the introduced groups.
- The common feature that stands out in contrast to the control is the presence of C=O group indicated by the absorbance at 1720cm⁻¹; the presence of the carbonyl group is

an indication that the anhydride has bound itself to the surface. This absorbance is most intense for wool modified with succinic anhydride, probably because the introduction of another C=O group per chain.

- In coherence with the absorption at 1720cm^{-1} , C-O-C ether bond stretching causes the peaks at 1260 and 1160cm^{-1} in the cases of phthalic anhydride and the other two anhydrides respectively. Again, in the case of the control, this absorption is missing likely due to the loss of some naturally found surface groups containing ether bonds.
- Some out of plane stretching of aromatic group is also noted for the case of phthalic anhydride at 785 , 731 and 712cm^{-1} .

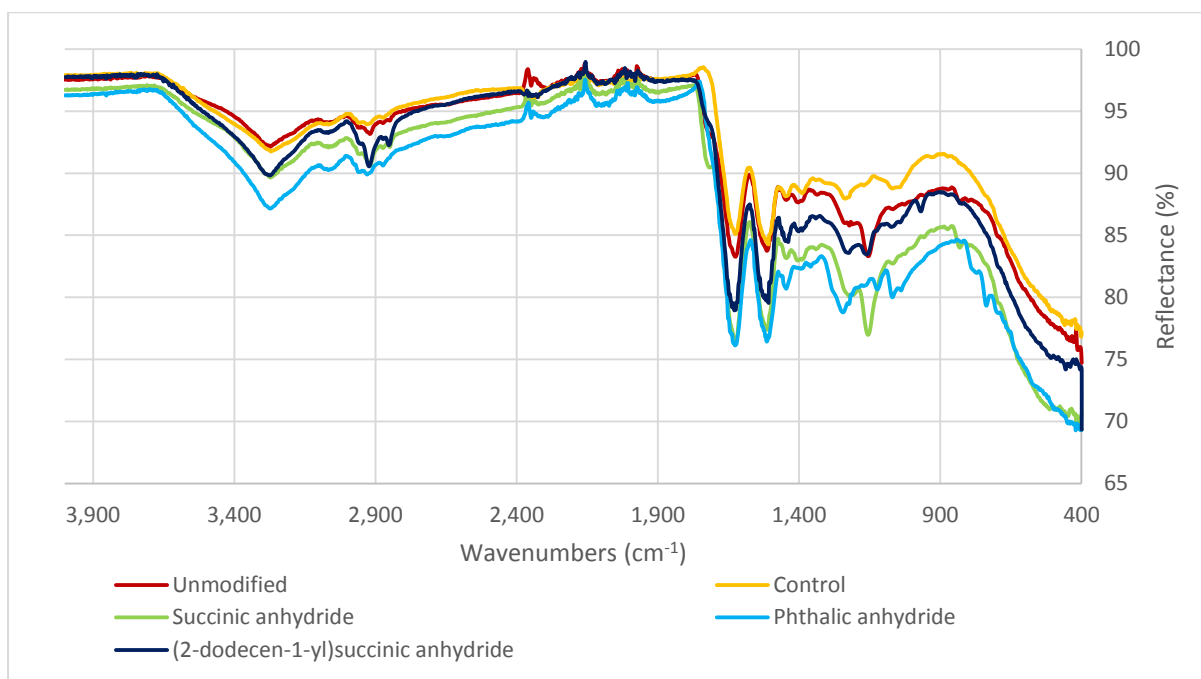


Figure 6.17: FTIR spectra of Swaledale wool post chemical modification.

6.9 Additives

6.9.1 Carbon fibre

Carbon fibre Carbisio C6/60 was provided courtesy of ELG Carbon Fibre Ltd. The fibres are of a recycled origin and non-activated. Their intended use is to be simply mixed in wool fibres, allowing their versatile blending in wool-incorporating products.

6.9.2 Chitosan

Chitosan powder with molecular weight of 100,000-300,000 was coated onto wool fibres. 5% of the wool sample weight of chitosan was dissolved at room temperature in 99% water and 1% acetic acid to make a 20g/l solution. The solution was thereafter sprayed on the wool fibres simply using a spray bottle for small wool samples or using a nozzle-fitted rotating drum for large wool samples. The wool was then left to dry for at least 2 days in a 50°C oven.

Chapter 7: Assessment of modified wool fibres' sorption and other properties

7.1 Introduction

The purpose of this chapter is to assess the modified wool fibres for any changes in their sorption trends compared to their unmodified counterparts, which were assessed in chapter 4. Results are outlined per each modification to highlight the different effects each produced on sorption capacities and profiles. Other properties are also investigated to examine to what extent the modifications change the nature of the wool fibres.

7.2 Methods followed

The methods used for sorption assessments are exactly the same as those followed for the assessment of different wool types. The method to assess a sample's total capacity of sorption of formaldehyde is described in section 4.2.1, where the modifications were done on scoured Swaledale wool. The method to assess Light Herdwick samples' sorption of low levels of formaldehyde is described in section 4.3.1.1, and that for toluene, limonene and dodecane in section 4.3.1.2. Also included in low formaldehyde levels sorption assessment is a sample of 1.000g of wool insulation, which is composed of a mixture of at least 3 different types of wools plus a small percentage of low melt polyester, and a similar sample that had chitosan sprayed onto its surfaces following the method described in section 6.9.2.

7.3 Sorption profile of mechanically modified wool

7.3.1 Sorption profile of toluene, limonene and dodecane

The sorption profile of v/VOCs at low concentration and flow rates by mechanical modified wool with ball milling was assessed. Ball milling increases sorption of all the three non-polar VOCs (Figure 7.1) due to either an increase in surface area or accessibility to non-polar functionalities. If it is the latter, then a decrease in formaldehyde sorption should be noted. If that is not the case, then the increase in the sorption of these three VOCs is simply due a general increase in surface area. The increase for toluene sorption follows an unclear trend ($F(3,8) = 1.876$, $p = 0.212$ for all samples), but in the case of limonene the trend is proportional to the amount of time the wool fibres were subjected to milling ($F(3,8) = 14.537$, $p = 0.001$ for all samples). In the case of dodecane the trend is an increasing one although sorption seems to reach 100% after 4hrs of milling ($F(3,8) = 12.493$, $p = 0.002$ for all samples).

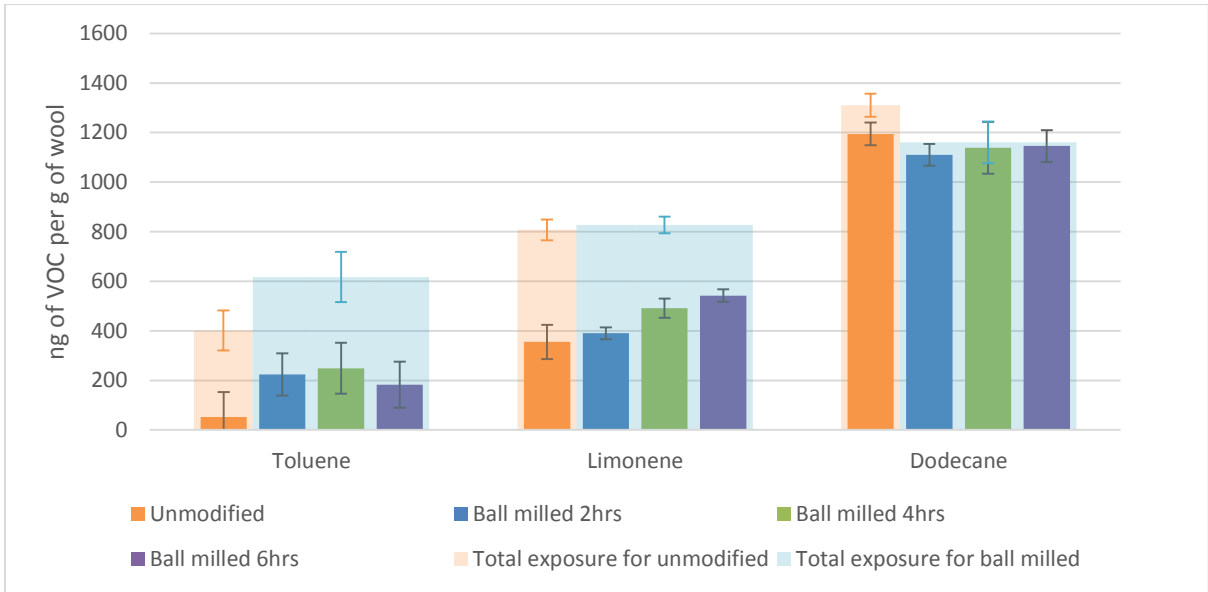


Figure 7.1: Sorption of a low concentration flow of toluene, limonene and dodecane by 1.000g of Light Herdwick wool before and after mechanical modification by ball milling.

7.3.2 Sorption profile of formaldehyde

Ball milling of wool shows a clear enhancement in the sorption of formaldehyde (Figure 7.2), which increases by $24 \pm 4\%$ ($F(1,4) = 78.348$, $p = 0.001$). As noted above in section 7.3.1 concerning the effect ball milling has on the sorption of non-polar VOCs, the enhanced sorption offered by ball milling is not restricted to polar VOCs. Therefore, this enhancement is simply due to the increase in the surface area exposed to the surrounding gases. This conclusion is confirmed by testing, as detailed in section 7.6.2.

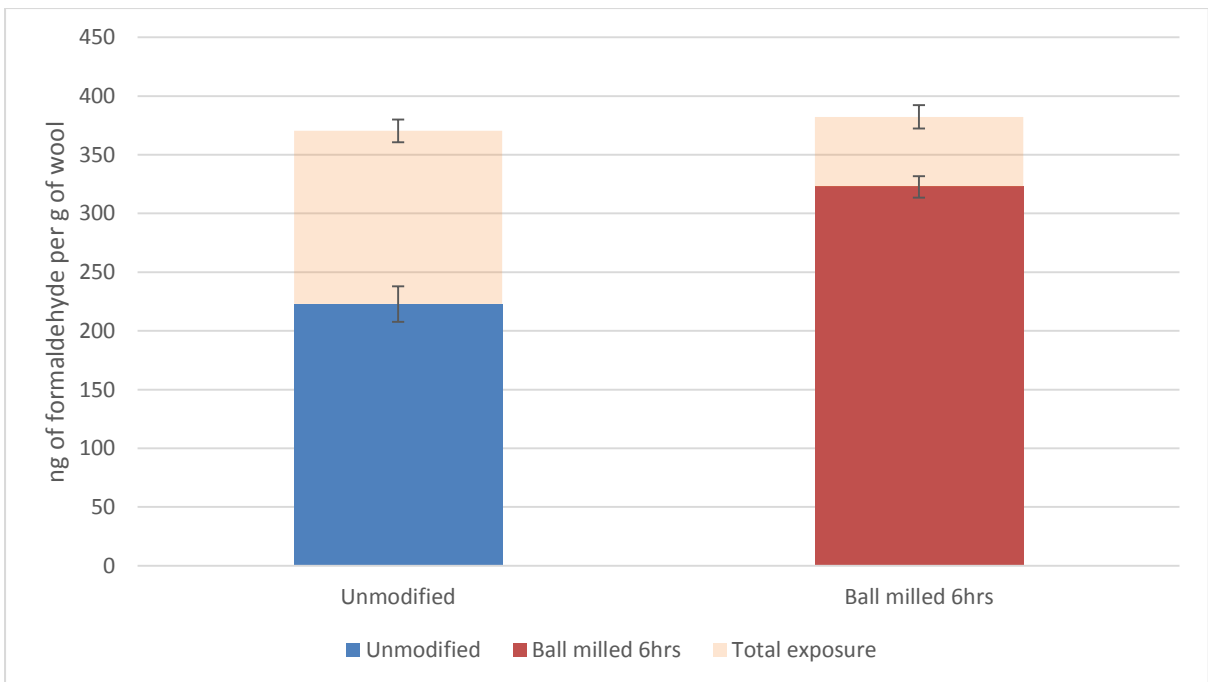


Figure 7.2: Sorption of a low concentration flow of formaldehyde by 1.000g of Light Herdwick wool before and after ball milling for 6 hours.

7.4 Sorption profile of chemically modified wool

7.4.1 Sorption profile of toluene, limonene and dodecane

The sorption of the 3 VOCs showed significant changes after chemical modifications were performed. The control (wool that has gone through the same process of those modified with an anhydride, with the exception of the anhydride being introduced into the reaction mixture, see section 6.8.1.1) and wools modified with phthalic and succinic anhydrides showed a general decrease in sorption compared to the unmodified wool, whereas wool modified with DDSA showed a general increase (Figure 7.3).

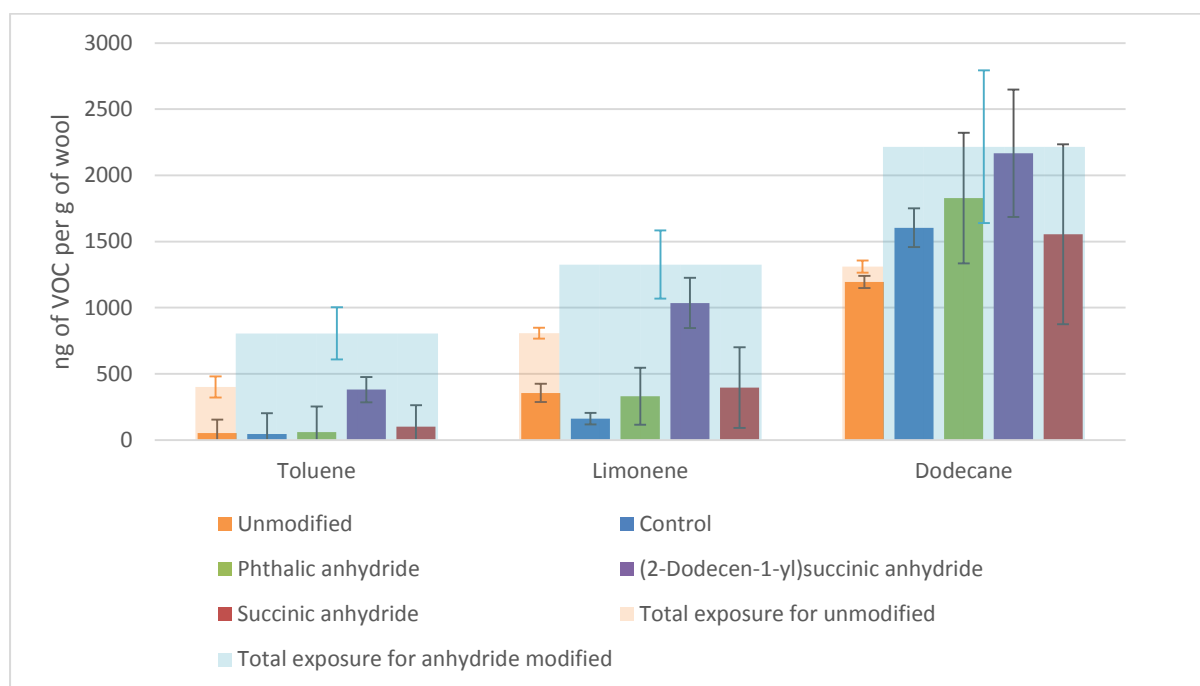


Figure 7.3: Sorption of a low concentration flow of toluene, limonene and dodecane by 1.000g of Light Herdwick wool before and after chemical modifications, in addition to a control sample.

In the case of toluene, the percentage sorbed is very poor prior to modification and shows no enhancement by chemical modifications except in the case of DDSA, which is still statistically insignificant ($F(1,4) = 4.579$, $p = 0.099$). This result is surprising, especially in the case of phthalic anhydride modified wool; the aromatic function that is expected to be bound to the surface should theoretically increase the physical sorption of toluene on the principle of like-attracts-like. There are three possible explanations for this:

- Upon further investigation, the literature does support the formation of an ester bond with the presence of a hydroxyl group (Dubey et al., 1997), which is present on the surface of the wool. However, the solvent used as the reaction medium seems to have an effect, and utilising DMF at room temperature for 4hrs is reported to yield phthalic acid as a product rather than the ester. Hence, it is possible that no aromatic functional

group resulted on the fibre surface from the reaction with phthalic anhydride using DMF as a solvent. Nevertheless, the weight gain and FTIR and spectra resulting for the wool after the modification seem to suggest otherwise (see section 6.8.1.2).

- Another explanation is the effect of steric hindrance caused by the long chain structure of 18-MEA; the aromatic functional group would be bound to the fibre surface by short $-O-C=O$ group, and therefore would have its length overshadowed by the surrounding long-chained 18-MEA group.
- The third and most likely explanation is the presence of the carboxylic function on the aromatic function. This will impart a polar functionality right on the aromatic group (Figure 6.16b) and causes the disruption of the dynamic movement of the lipid layer (see section 4.3.2.2), as well as repel to the non-polar VOCs.

In contrast with phthalic anhydride, modification with DDSA leads to the replacement of polar surface groups with long-chained non polar groups, therefore decreasing surface polarity. Sorption of non-polar VOCs is therefore enhanced since the new functionalities are not hindered by the already existing 18-MEA groups. In addition, the carboxylic acid functionality on this new non-polar group is located near the fibre surface, nearer other polar groups and spatially away from the non-polar end of the chemical function (Figure 6.16). In fact, in terms of its structure, the carboxylic acid functionality in theory should aid the dynamic movement of the whole new group on the surface in response to the surrounding environment (see section 4.3.2.2).

In the case of limonene, the percentage of the VOC sorbed decreases for the control ($F(1,4) = 36.262$, $p = 0.004$). This is most likely due to the disruption of the surface structure of the wool and the possible loss of some of the bound 18-MEA. Modification with succinic or phthalic anhydride leads to an insignificant increase of sorption compared to the control ($F(2,6) = 3.991$, $p = 0.079$), but remains lower than that of the unmodified wool (when taking into consideration the amounts the fibres were exposed to). This is expected as the modification with anhydrides having a degree of polar functionalities replaces the surface hydroxyl and amino groups with less polar groups, aiding sorption in comparison with the control sample but not sufficiently to counteract the loss of 18-MEA. Similar to the case of toluene, modification with DDSA leads to an increase in sorption of limonene when compared to unmodified wool ($F(1,4) = 35.482$, $p = 0.004$).

The sorption of dodecane shows exactly the same trend as that of limonene, with the difference being that the percentages sorbed are at such a higher level that the difference in the percentage sorbed between unmodified wool and wool modified with DDSA is not as noticeable but still significant ($F(1,4) = 10.398$, $p = 0.032$). This better sorption of dodecane

compared to limonene is simply due to the fact that dodecane is less polar than limonene, and the overall surface would be non-polar.

7.4.2 Sorption capacity of formaldehyde

Chemical modification with anhydrides, any of the three used, leads to a decrease in the sorptive capacity of formaldehyde (Figure 7.4). The introduction of polar chemically bound functionalities through succinic anhydride is expected to increase the polarity of the surface, which naturally has a bound 18-MEA lipid layer (see section 2.2.5). However, the more polar the modified surface is, the less its formaldehyde sorption capacity, which is contrary to expectation seeing that formaldehyde is polar. Therefore, it must be concluded that the more polar the modified surface is, the more it is disrupting the suggested dynamic fibre surface motion mechanism of formaldehyde sorption (see section 4.3.2.2).

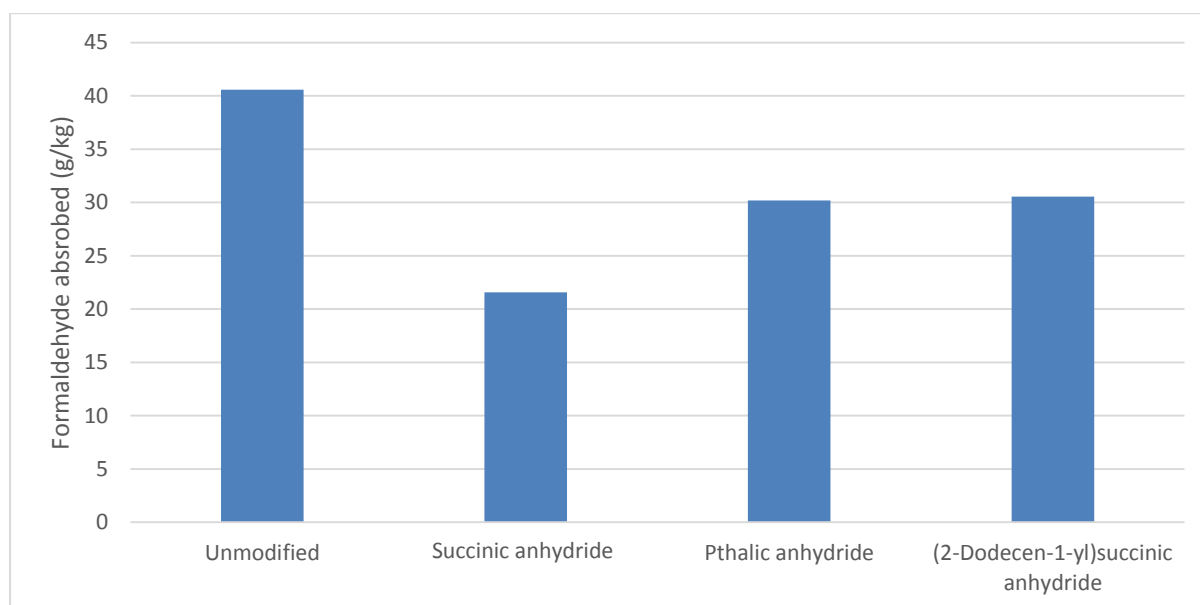


Figure 7.4: Maximum capacities of the sorption of formaldehyde gas by Swaledale wool pre- and post-chemical modification, determined by exposure to several cycles of excess levels of formaldehyde.

Observing the increase in mass of wool at each cycle of exposure to formaldehyde (Figure 7.5) illustrates the difference. The most prominent change is in the case of modification with succinic anhydride, giving the most polar of surface resulting from a chemical modification. At the first cycle, very little formaldehyde is seen to be sorbed. This can be explained by the increased difficulty the non-polar 18-MEA lipid layer experience as it is moving away from the surface into the fibre itself. The presence of polar functionalities around non-polar 18-MEA would cause a repelling effect against its movement; these new polar functionalities are larger than the OH and NH₃ groups they replaced, but still are shorter and closer to the surface than of 18-MEA is. As a small amount of formaldehyde is sorbed during the first cycle, it is possible that these sorbed gases would cause a bridging effect, where polar functionalities extend by attraction and enables them to reach more of the surrounding environment. In such a case,

the movement 18-MEA functionalities becomes easier as they amalgamate towards each other, away from the polar functionalities. This facilitates the sorption at the second cycle and the ones that follow. Hence, contrary to the intended effect, the presence of the natural non-polar 18-MEA functionalities and their dynamic movement in response to their surrounding environment explains why adding polar functionalities onto the fibre surface hinders the total sorption capacity of surrounding polar gases.

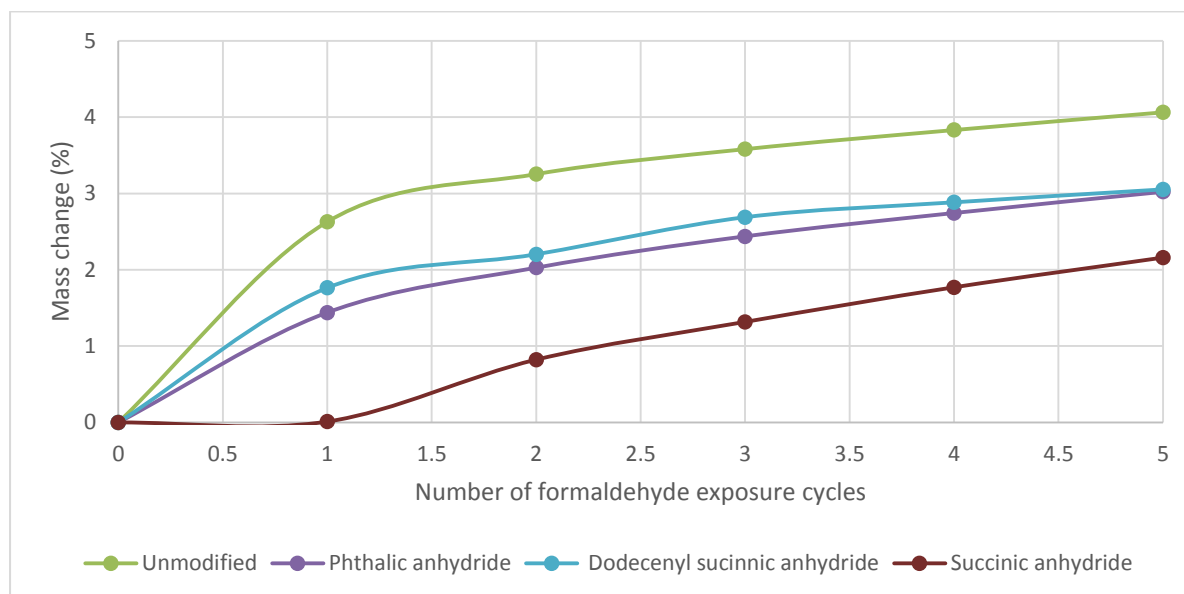


Figure 7.5: Increase in mass of unmodified and chemically modified Swaledale wool per each formaldehyde exposure cycle.

Modifying wool with phthalic or DDSA, which result in new non-polar surface functionalities, decrease formaldehyde sorption. As anticipated, they reduce the presence of the natural polar surface functionalities of the wool fibre (OH and NH₃) by simply replacing them. As the surface functionalities caused by phthalic anhydride are slightly more polar than those of DDSA (due to the presence of an aromatic ring which causes its carbon atoms to have a positive permanent dipole, in addition to the possibly more-exposed carboxylic group), they result in a lesser sorption capacity compared to the latter. This can be explained in manner like that of the effect surface functionalities caused by succinic acid have.

7.4.3 Sorption profile of formaldehyde

As seen in Figure 7.6, chemical modification of wool fibres has a negligible effect on their sorption of low formaldehyde concentrations ($F(2,6) = 3.206$, $p = 0.113$). This shows that chemical modification with DDSA, although it enhances the sorption of non-polar VOCs (see section 7.4.1), does not cause a compromise with regards to the sorption of polar v/VOCs. These observations are not in line with the results seen for total formaldehyde sorption capacity via the DVS method (see section 7.4.2), but they are still coherent as this method is

not based on an alternating the surrounding environment – there is no continuous dynamic movement of the surface functionalities.

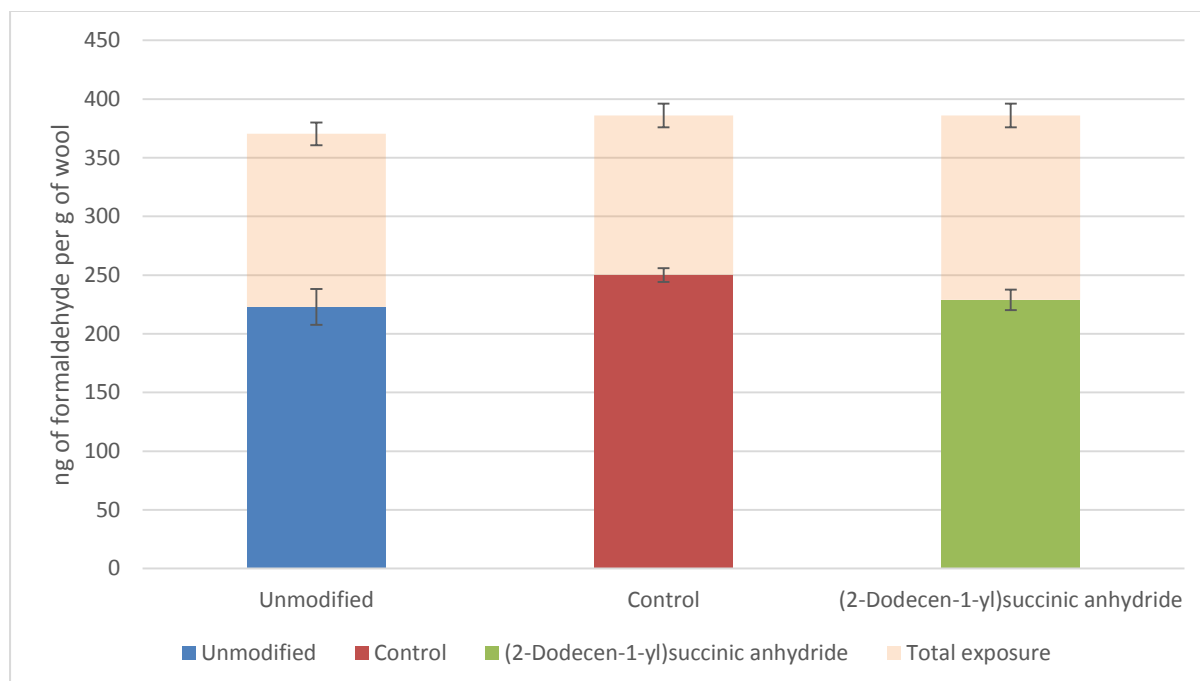


Figure 7.6: Sorption of a low concentration flow of formaldehyde by 1.000g of unmodified and chemically modified Light Herdwick wool.

Chemical modification with DDSA enhances the sorption of the three non-polar VOCs at low concentrations, and it does not have an effect on the sorption of polar formaldehyde at such concentrations. Although the total capacity of formaldehyde sorption does decrease with modification with DDSA, since such high levels along with alternating surrounding gases is not encountered in real indoor atmospheres, this modification is promising as it enhances the sorption of non-polar v/VOCs without compromising on the sorption of polar v/VOCs.

7.5 Sorption profile of additives to wool

7.5.1 Sorption profile of toluene, limonene and dodecane

The effect of chitosan as an additive on the sorption of wool fibre and the sorption by carbon fibre is summarised in Figure 7.7. Adding 5% by weight of chitosan on fibre surface has no tangible effect on the sorption of any of the 3 VOCs ($F(1,4) = 0.441$, $p = 0.534$ for toluene, $F(1,4) = 0.595$, $p = 0.484$ for limonene and $F(1,4) = 6.280$, $p = 0.066$ for dodecane). That is seen as a positive result as chitosan is not aimed at increasing the sorption of these 3 VOCs, rather it is hoped to increase the sorption of formaldehyde. When chitosan is added to wool fibre already chemically treated with DDSA, an increase in the sorption of the 3 VOCs is still noted compared to unmodified wool ($F(1,4) = 2.126$, $p = 0.219$ for toluene, $F(1,4) = 14.703$, $p = 0.019$ for limonene and $F(1,4) = 20.363$, $p = 0.011$ for dodecane); although post chemical

modification the sorption is lessened when chitosan is added ($F(1,4) = 82.861$, $p = 0.001$ for toluene, $F(1,4) = 26.511$, $p = 0.007$ for limonene and $F(1,4) = 20.251$, $p = 0.011$ for dodecane), this demonstrates that using chitosan as an additive is compatible with chemical modifications. Therefore, adding 5% chitosan by weight onto the fibre surface only masks the chemical functionalities on the fibre surface to a small degree, as far as VOC sorption is concerned. Carbon fibre, on the other hand, excels at sorption as only 0.1g sorbed the entire amounts of all three VOCs it was exposed to.

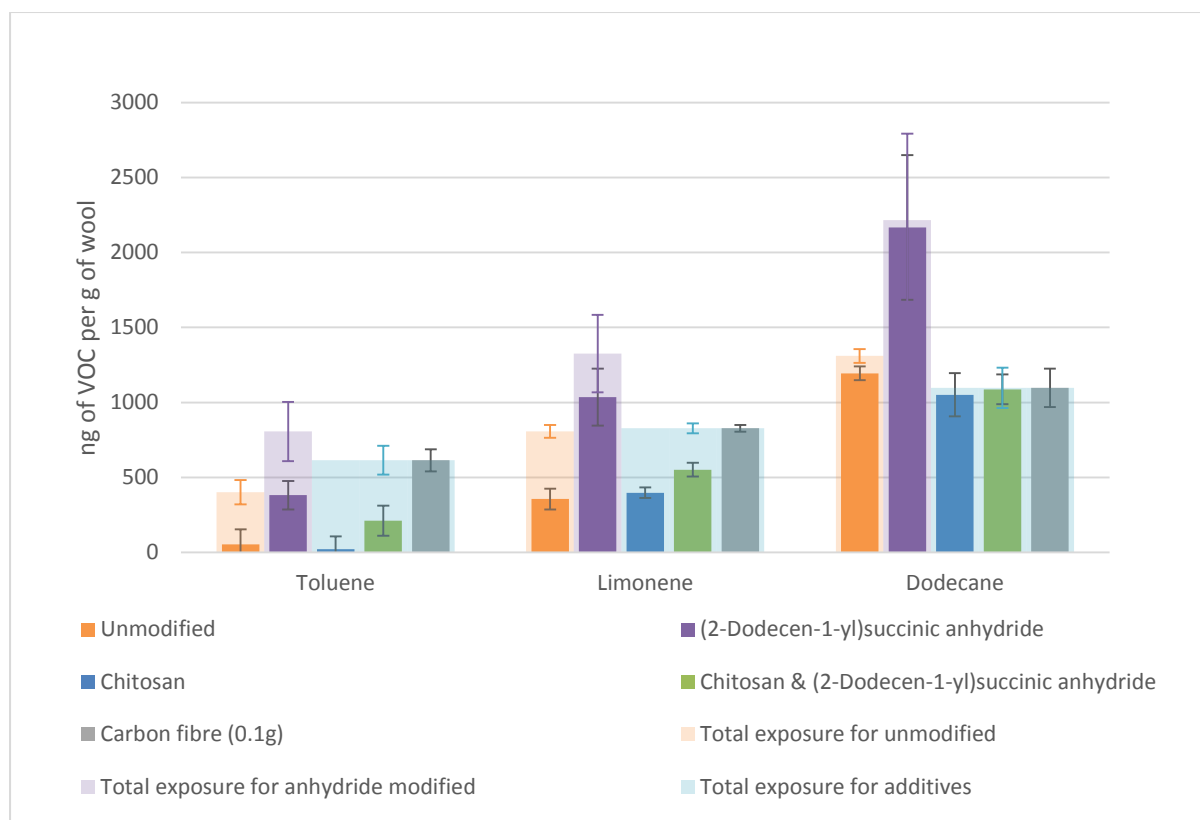


Figure 7.7: Sorption of a low concentration flow of toluene, limonene and dodecane by 1.000g of unmodified and chemically modified Light Herdwick wool before and after the addition of chitosan, in addition to 0.1g of carbon fibre.

7.5.2 Sorption capacity of formaldehyde

As seen in Figure 7.8, carbon fibre as an additive shows almost no sorption capacity for formaldehyde as expected. Activated carbon is known to preferentially sorb non-polar VOCs and those with a low dipole moment (see section 6.4.2).

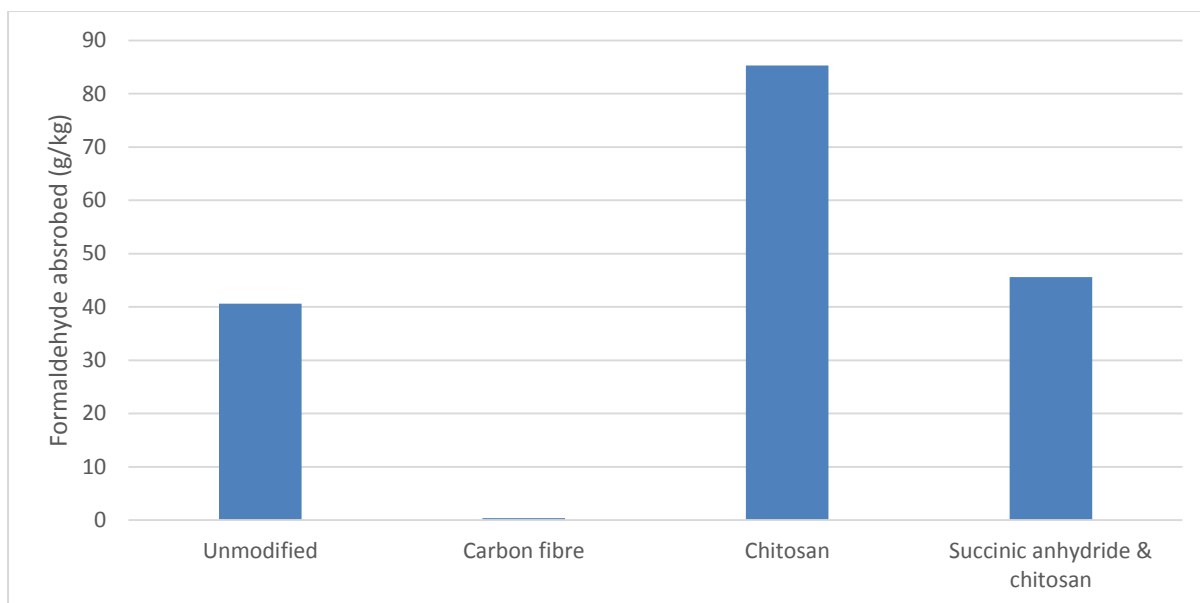


Figure 7.8: Maximum capacities of the sorption of formaldehyde gas by Swaledale wool pre- and post-application of chitosan, where carbon fibre being tested as an additive on its own, determined by exposure to several cycles of excess levels of formaldehyde.

Wool fibre with chitosan on its surface leads to a large increase in its sorption capacity of formaldehyde. Opposite to the nature of carbon, chitosan is a very polar molecule and is fully expected to have a strong intermolecular interaction with nearby polar molecules such as formaldehyde. As it is used as an additive and has not chemically modified the wool fibre itself, this observed increase does not contradict the effect noted when polar functions are chemically added onto fibre surface. Adding to that, chitosan is a very large polymer and is larger in size than naturally bound 18-MEA, meaning that it would not be over-crowded by the 18-MEA functionalities like in the case of polar functionalities resulting from chemical modification with polar anhydrides. It also does not seem to disrupt the dynamic movement of the surface lipid layer in response to the polarity of the surrounding environment.

Another experiment was run for a sample of wool modified with succinic anhydride and then coated with chitosan showed an overall slight increase in sorption capacity of formaldehyde. This shows that the chitosan has an overall effect of increasing formaldehyde sorption capacity even when applied to previously modified wools. Figure 7.9 shows that it negates the effect of the surface functionalities resulting from modification with succinic acid, starting from the first cycle. Thus, the addition of chitosan is compatible with other modifications as far as formaldehyde sorption is concerned.

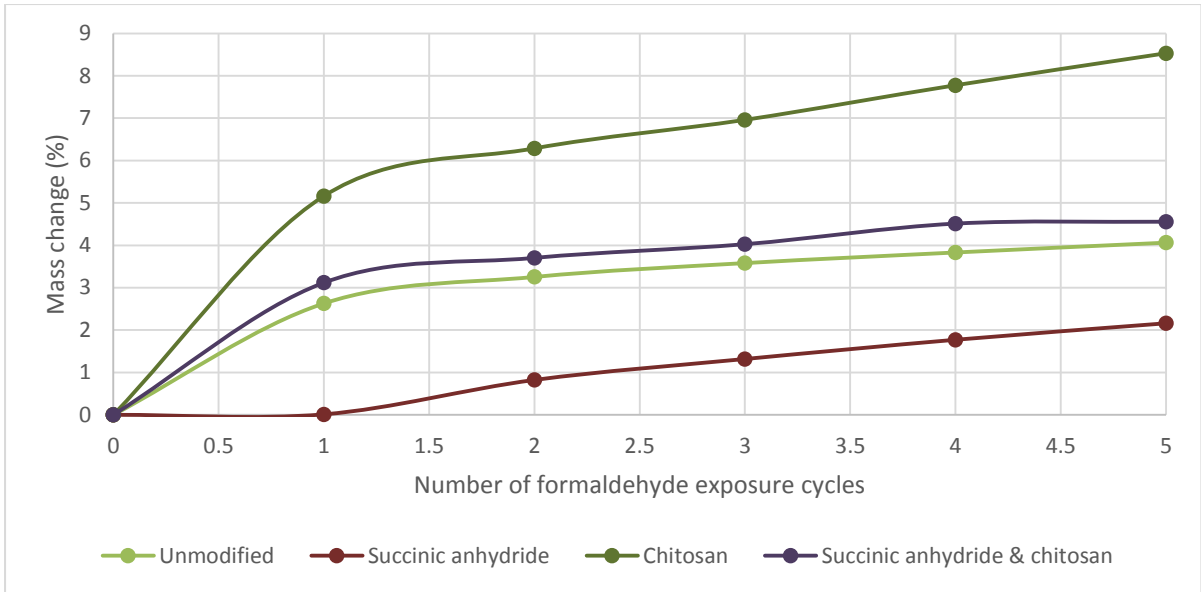


Figure 7.9: Increase in mass of unmodified and Swaledale wool sprayed with chitosan, including post chemical modification with succinic anhydride, per each formaldehyde exposure cycle.

7.5.3 Sorption profile of formaldehyde

As seen in Figure 7.10, the addition of chitosan onto wool fibres shows a slight and insignificant detraction in formaldehyde's sorption profile ($F(1,4) = 6.479$, $p = 0.064$). This is a somewhat surprising result, as the polar vVOC is expected to be attracted to the added large polar molecules. A similar effect is seen when chitosan is added onto fibres that have been previously chemically modified with DDSA ($F(1,4) = 9.326$, $p = 0.055$). This is expected as the chemical modification considered has been seen to have no significant effect on the sorption of low level formaldehyde (Figure 7.6).

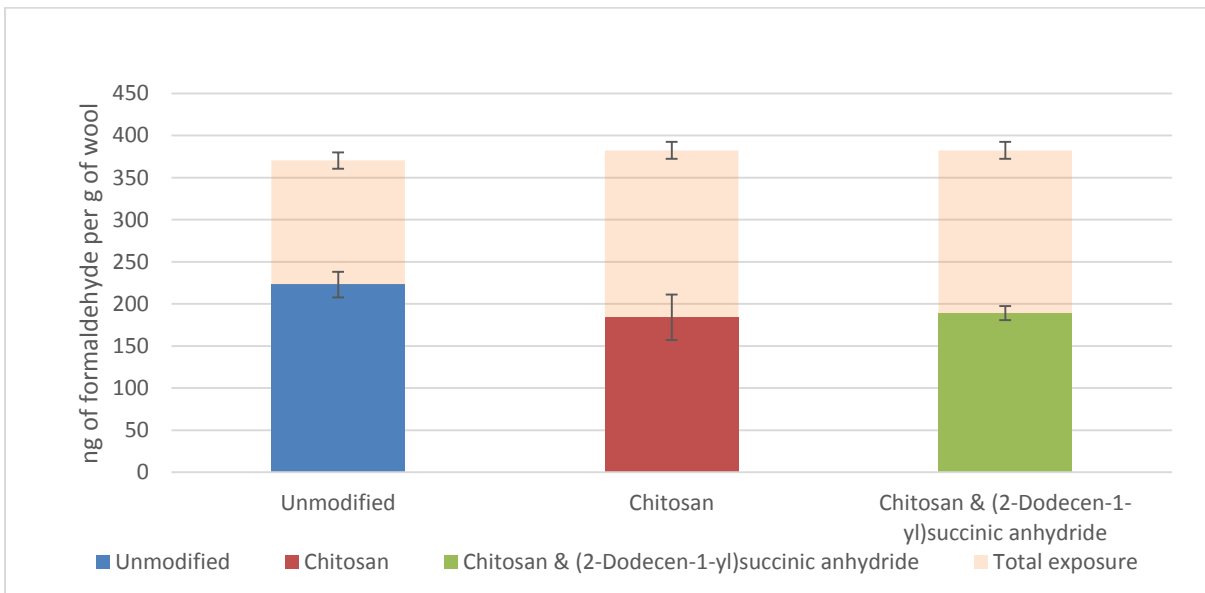


Figure 7.10: Sorption of a low concentration flow of formaldehyde by 1.000g of Light Herdwick wool before and after spraying with chitosan and treatment involving chemical modification in addition to spraying with chitosan.

To check if the addition of chitosan may have a significant effect on the sorption of low formaldehyde concentrations, wool based insulation, composed of a mixture of different wool types, was also tested. The same effect is noted (Figure 7.11), confirming that the addition of chitosan has no significant effect on the sorption of low levels of formaldehyde, but does increase the total capacity of formaldehyde sorption (see section 7.5.2).

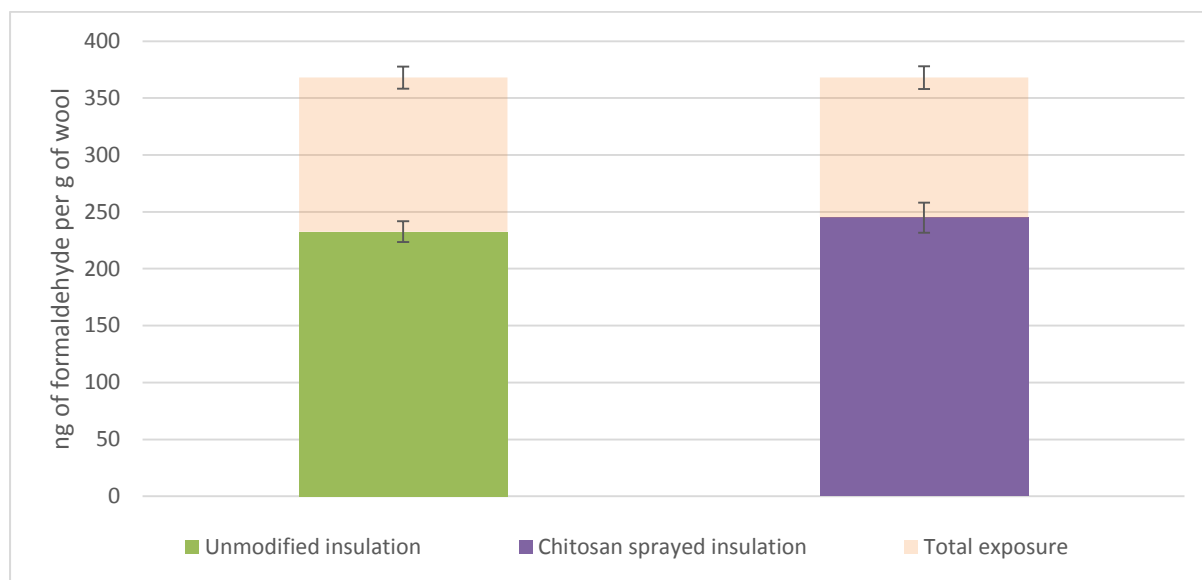


Figure 7.11: Sorption of a low concentration flow of formaldehyde by 1.000g of wool-based insulation before and after spraying with chitosan.

Carbon fibre is seen to excel at sorbing non-polar VOCs, but to be inadequate for the sorption of polar v/VOCs. Chitosan on the other hand is seen to enhance the total capacity of formaldehyde sorption; although it offers no sorption enhancement of any of the v/VOCs at low concentrations, it does not hinder them either, and it is compatible with sorption enhancements offered by chemical modifications.

7.6 Characterisation of different wool types

7.6.1 Fourier transform infrared spectroscopy (FTIR)

7.6.1.1 Method

The same method was followed as detailed in section 4.4.1.1.

7.6.1.2 Results and discussion

Results were interpreted according to the literature (Aluigi et al., 2007; Krimm, 1960; Li et al., 2009; Wojciechowska et al., 1999; Xiao and Hu, 2016; Xu et al., 2006).

For chemical modifications, the differences in the spectra along with their explanations is outlined in section 6.8.1.2.

For mechanical modifications with ball milling (Figure 7.12), there are two notable differences:

- CH_2 stretching at 2930cm^{-1} and 2850cm^{-1} intensifies probably due to the exposure the beneath-the-surface backbone chemical structure
- The disappearance of the 1160cm^{-1} C-O-C bridge of ester functions, which is possibly due to residues on the surface of the wool.

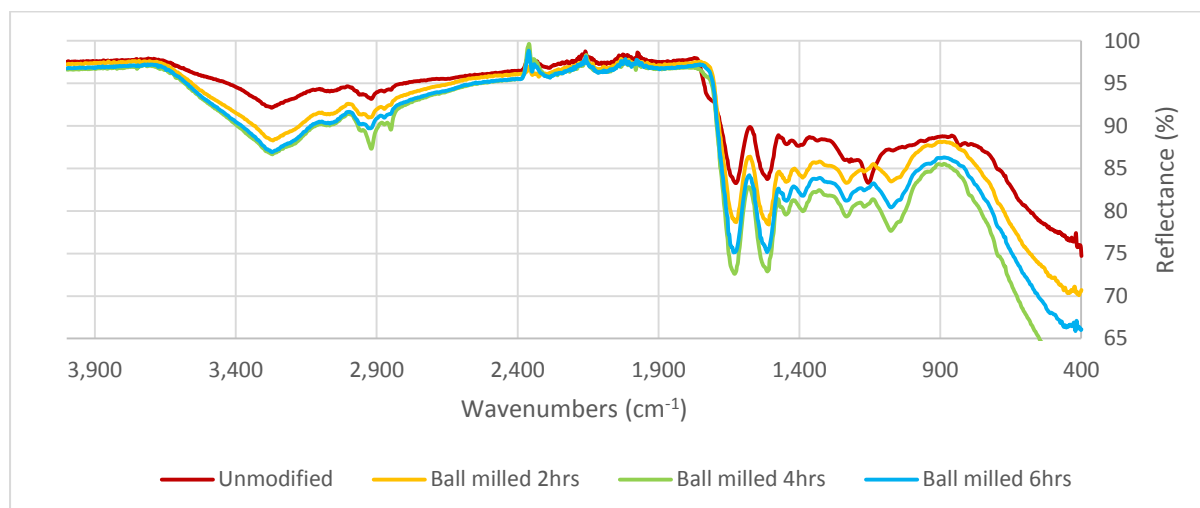


Figure 7.12: FTIR spectra of Light Herdwick wool before and after hours of ball milling.

Coating the fibre with chitosan is seen to mask some chemical groups such as the $\text{C}=\text{O}$ group at 1720cm^{-1} and the C-O-C bridge at 1160cm^{-1} (Figure 7.13); however, these functionalities are not masked when the fibre is previously chemically modified with DDSA, owing to the new chemical groups possessing both these functionalities (Figure 6.16b). This observation corresponds to the observed compatibility of the addition of 5% chitosan with the chemical modification as regards to v/VOC sorption, as both this analytical technique and sorption are based on fibre surface structure.

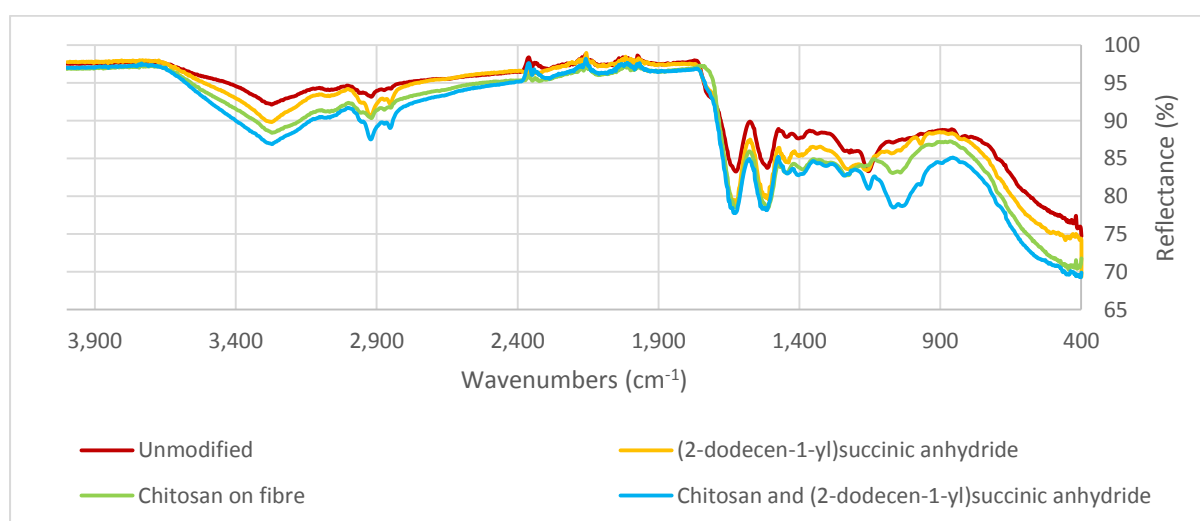


Figure 7.13: FTIR spectra of Light Herdwick wool before and after modification with DDSA, in addition to after spraying chitosan onto the afore-mentioned wools.

7.6.2 Surface area and pore size distribution

7.6.2.1 Method

The same method was followed as detailed in section 4.4.2.1, with the exception that the wool modified with both chitosan and DDSA had its pore size distribution and cumulative pore volume averages calculated based on only 2 repeats.

7.6.2.2 Results and discussion

Chemical modification of wool fibre has no significant effect on surface area ($F(4,10) = 0.402$, $p = 0.803$), as seen in Figure 7.14.

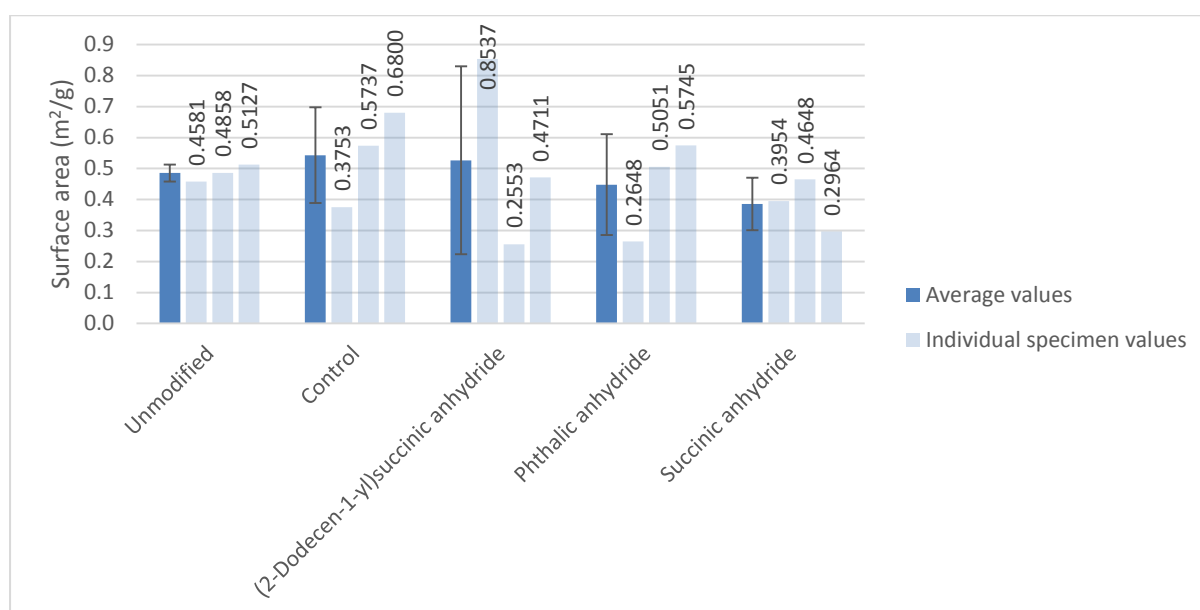


Figure 7.14: Surface area of Light Herdwick wool fibres before and after chemical modifications with different anhydrides.

Mechanical modification via ball milling on the other hand has a significant effect ($F(1,4) = 42.910$, $p = 0.003$) as seen in Figure 7.15. This confirms the conclusion that ball milling enhances sorption of v/VOCs regardless of their polarity, and therefore is aided by increased surface area rather than a change in fibre surface polarity (see section 7.3.2).

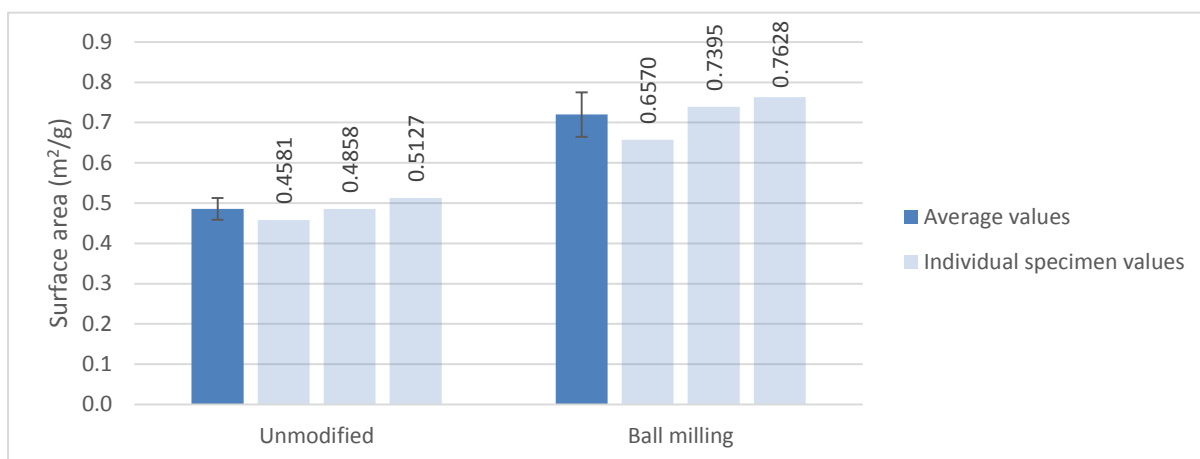


Figure 7.15: Surface area of Light Herdwick fibres before and after ball milling for 6 hours.

With regards to the addition of chitosan (Figure 7.16), no significant difference to surface area is seen between unmodified wool before and after the addition ($F(1,4) = 6.929$, $p = 0.058$). The difference becomes significant though if the addition is applied to wool previously chemically modified with DDSA rather than unmodified wool ($F(1,4) = 12.447$, $p = 0.024$). If this decrease in surface area was simply due to the washing off of debris or contaminants during the chemical process, a similar decrease would have been noted in other cases of chemical modifications (Figure 7.14). The combination of a chemical modification and addition of chitosan does the unexpected and results in a decrease in surface area. Bearing in mind that the difference and significance are small in this case, the variation could simply be coincidental, as sheep wool fibres vary – even on the visible scale – in the same batch.

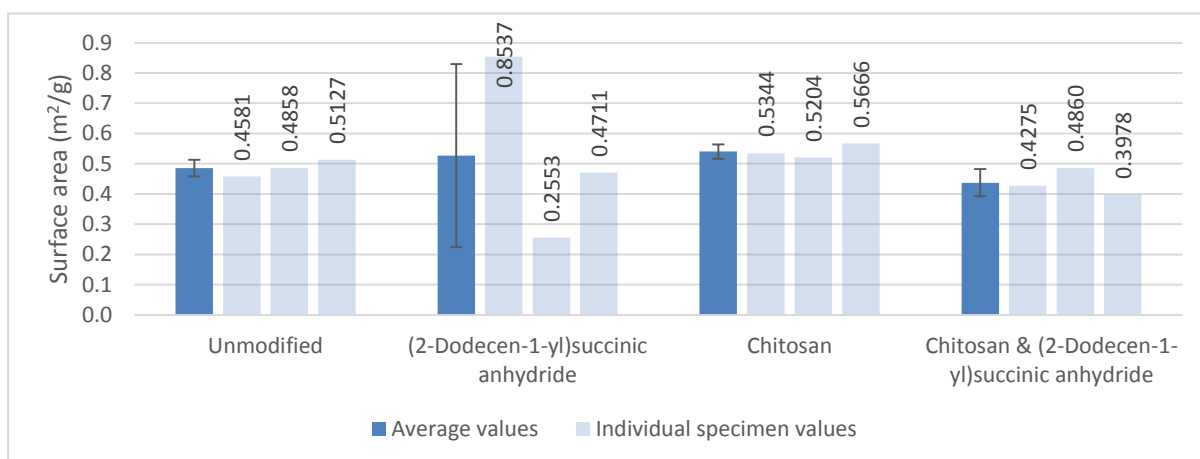


Figure 7.16: Surface area of Light Herdwick wool fibres before and after modification with DDSA, in addition to after spraying chitosan onto the afore-mentioned wools.

Pore size distribution and cumulative pore volumes remain mostly unaltered with chemical modifications (Figure 7.17). One observation is the increase in the control's distribution and cumulative volume for pores of a size larger than $\approx 20\text{nm}$, i.e. larger mesopores, likely due to

the removal of impurities left by the scouring process or possibly due to the patchy removal of some of the 18-MEA; this is also highlighted by the mass loss of control samples post their modification (see section 6.8.1). The indication is that the new chemical functionalities offered by the reaction with anhydrides mostly reside in such pores, as the distribution for such sized pores of fibres modified with the anhydrides decreases to a similar level of the unmodified wool's.

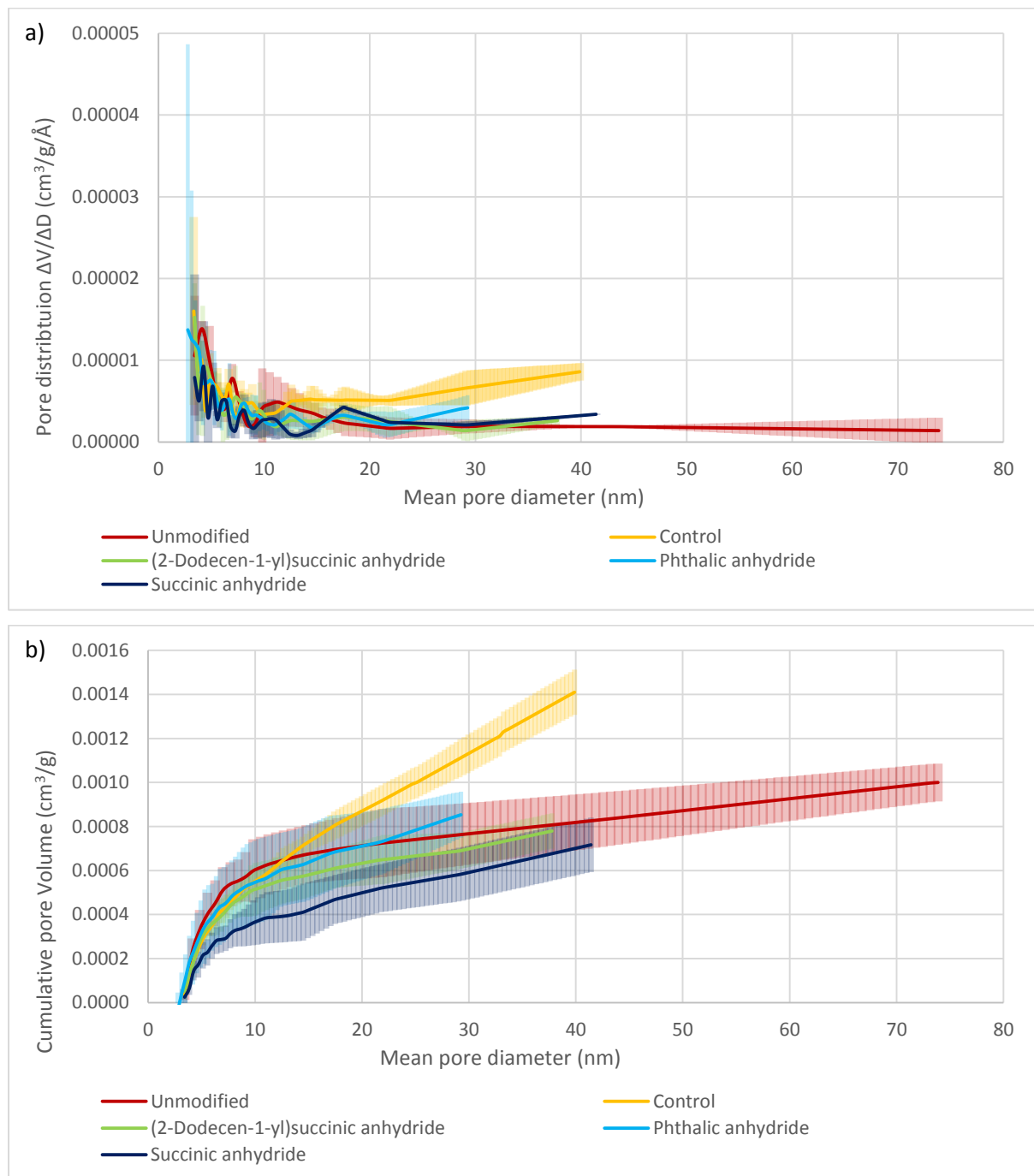


Figure 7.17: a) Pore size distribution and b) cumulative pore volume of Light Herdwick wool fibres before and after chemical modifications with different anhydrides. The shaded areas represent the standard deviation for all pore distribution and cumulative pore volume values.

Ball milling on the other hand shows a sharp increase in distribution and cumulative volume for pores of a size larger than $\approx 25\text{nm}$ (Figure 7.18). These increases are probably due to the debris – most probably cuticles detached from the surface of the fibre – that results from the milling (see section 6.7.2.2).

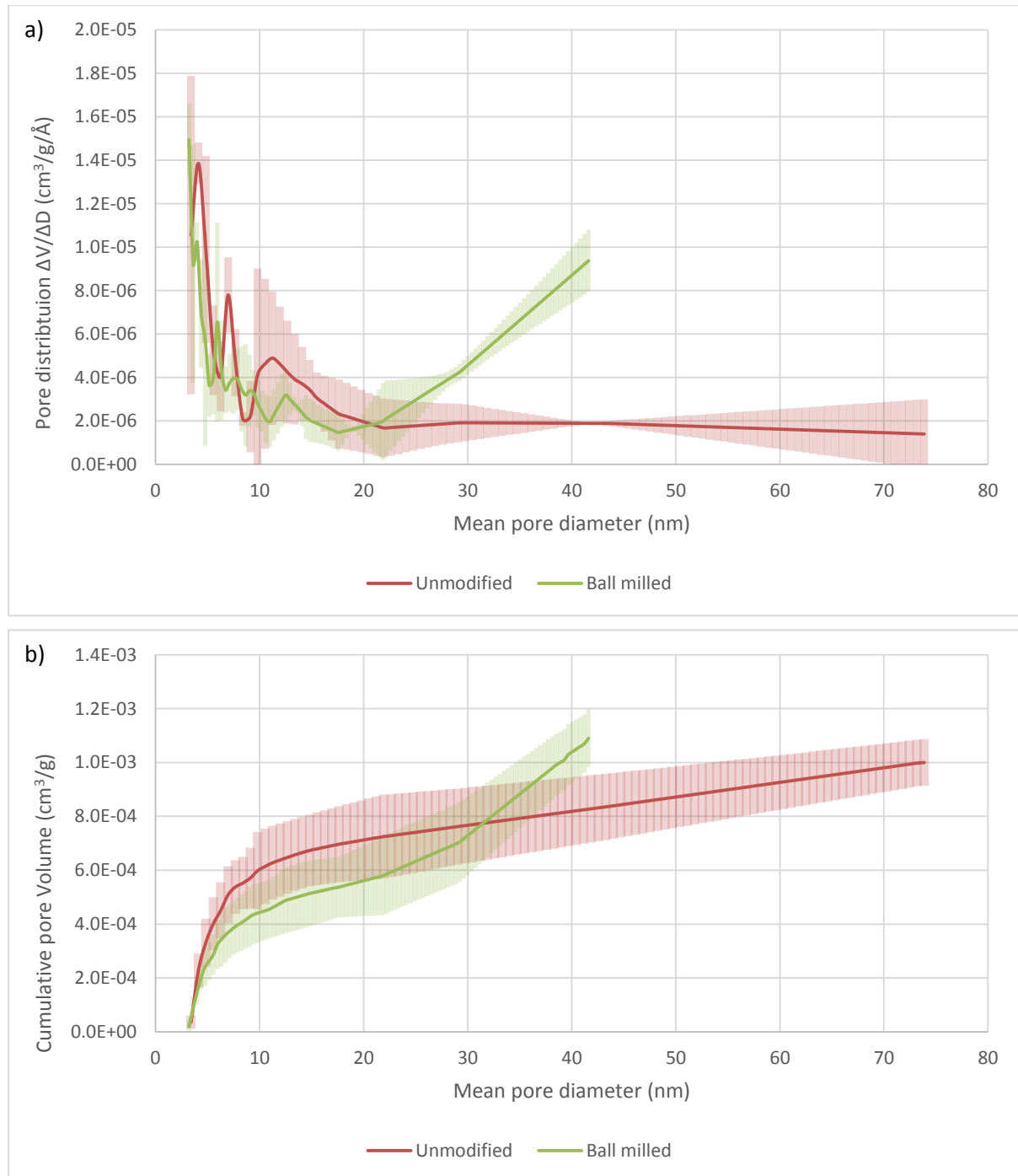


Figure 7.18: a) Pore size distribution and b) cumulative pore volume of Light Herdwick wool fibres before and after ball milling for 6 hours. The shaded areas represent the standard deviation for all pore distribution and cumulative pore volume values.

Addition of chitosan seems to have no effect on the pore distribution or cumulative volumes, except in the case of wool modified with DDSA and also sprayed with chitosan (Figure 7.19).

This observation is similar to that seen in the change in surface area and would be explained with the same line of reasoning.

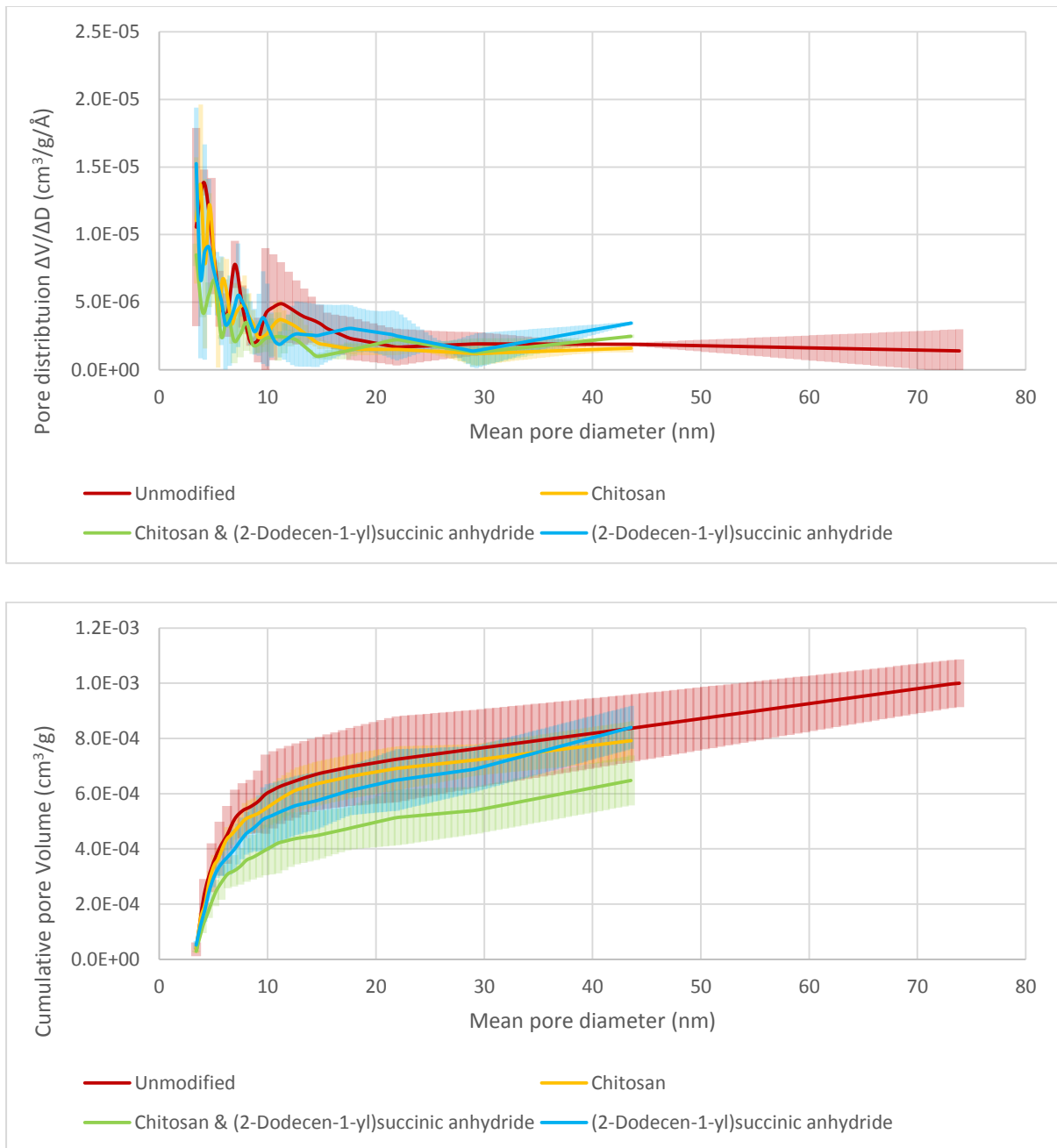


Figure 7.19: a) Pore size distribution and b) cumulative pore volume of Light Herdwick wool fibres before and after modification with DDSA, in addition to after spraying chitosan onto the afore mentioned wools. The shaded areas represent the standard deviation for all pore distribution and cumulative pore volume values.

7.6.3 Specific heat capacity and moisture uptake

7.6.3.1 Method

For specific heat capacity, the same method was followed as detailed in section 4.4.3.1. For moisture uptake, DVS was utilised in a method similar to the one described in section 3.5, having the following alterations:

- Instead of a formaldehyde solution, water was used.
- The sample was subjected to only one cycle consisting of reaching equilibrium states (dm/dt less than 0.002%) at 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 85, 90 and 95% RH. Weight change for desorption in the reverse order was also measured.

7.6.3.2 Results and discussion

Specific heat capacity is altered with chemical modification in the temperature range of about 50 to 110°C (Figure 7.20a). The control, having similar values as unmodified wool, shows that this drop is not due to the processing but to the presence of the added functional groups. This reduced capacity to contain heat post chemical modification implies that the fibres' molecules are not able to vibrate as much as prior to modification. This could be due to one or two reasons:

- The take-up of physical space by the added chemical functionalities, which would provide a hindrance for molecular vibration. The fact that surface area and pore distribution is not affected significantly with chemical modification (see section 7.6.2.2) does not contradict this possibility as the molecular size of the added functionalities is small enough (see section 4.4.2.2) to thinly line the pores along with the rest of the fibre surface; this is expected to result in a very small change to surface area, if any.
- Water sorption differences of unmodified and chemically modified fibres. This is logical when the temperature range where this drop in specific heat capacity occurs is taken into consideration. Considering the moisture uptake of the fibres before and after modification (Figure 7.20b), there are no large differences in sorption or desorption curves of unmodified and modified wools, except in the case of the control sample. It is expected to see such results as the control samples would have some of the non-polar 18-MEA removed from the surface, but fibres modified with DDSA would have non-polar surfaces, thereby resisting water sorption. Nevertheless, these water sorption trends do not explain fully the change in specific heat capacity.

Mechanical modifications and the addition of chitosan on the other hand had no real effect on the fibres' specific heat capacity (Figure 7.21). Fibres that are chemically modified and thereafter sprayed with chitosan still exhibit this drop in specific heat capacity in the same temperature range of about 50 to 110°C.

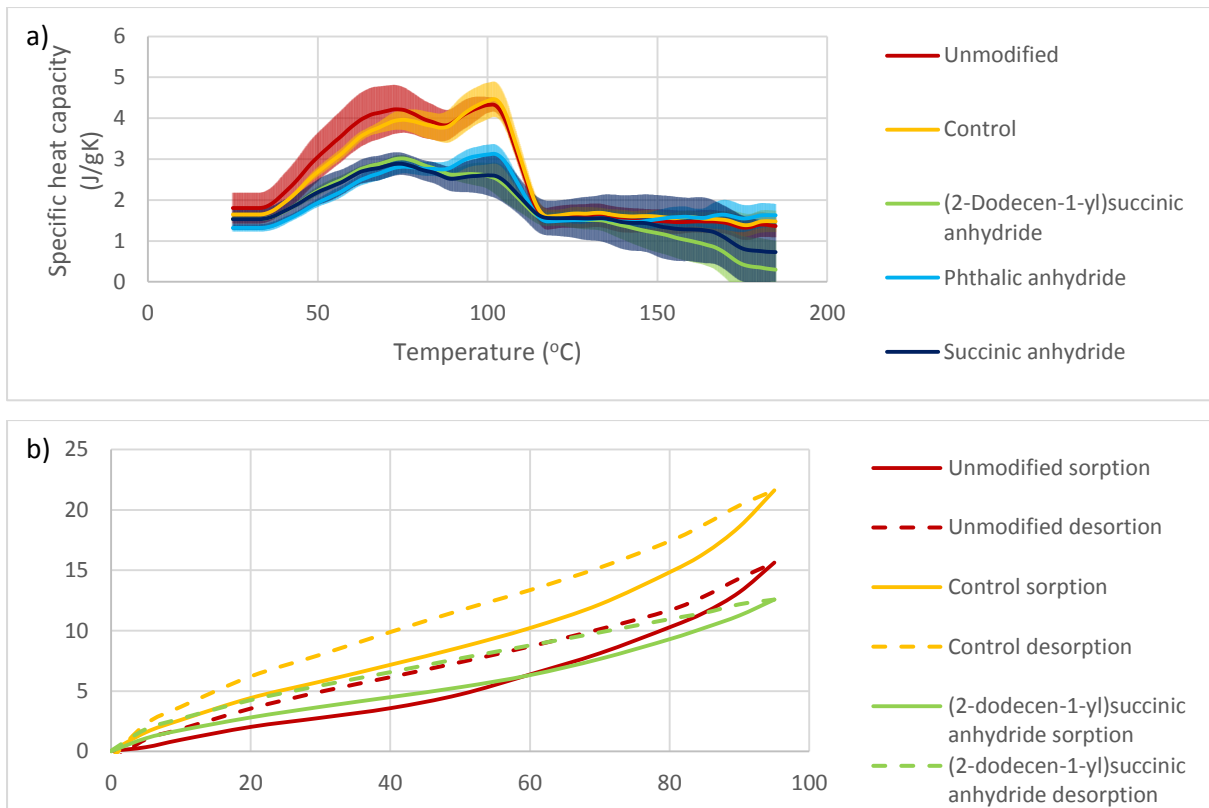


Figure 7.20: a) Specific heat capacity measurements and b) moisture uptake measurements of Light Herdwick wool fibres before and after chemical modifications with different anhydrides. The shaded areas represent the standard deviation for all specific heat capacity values.

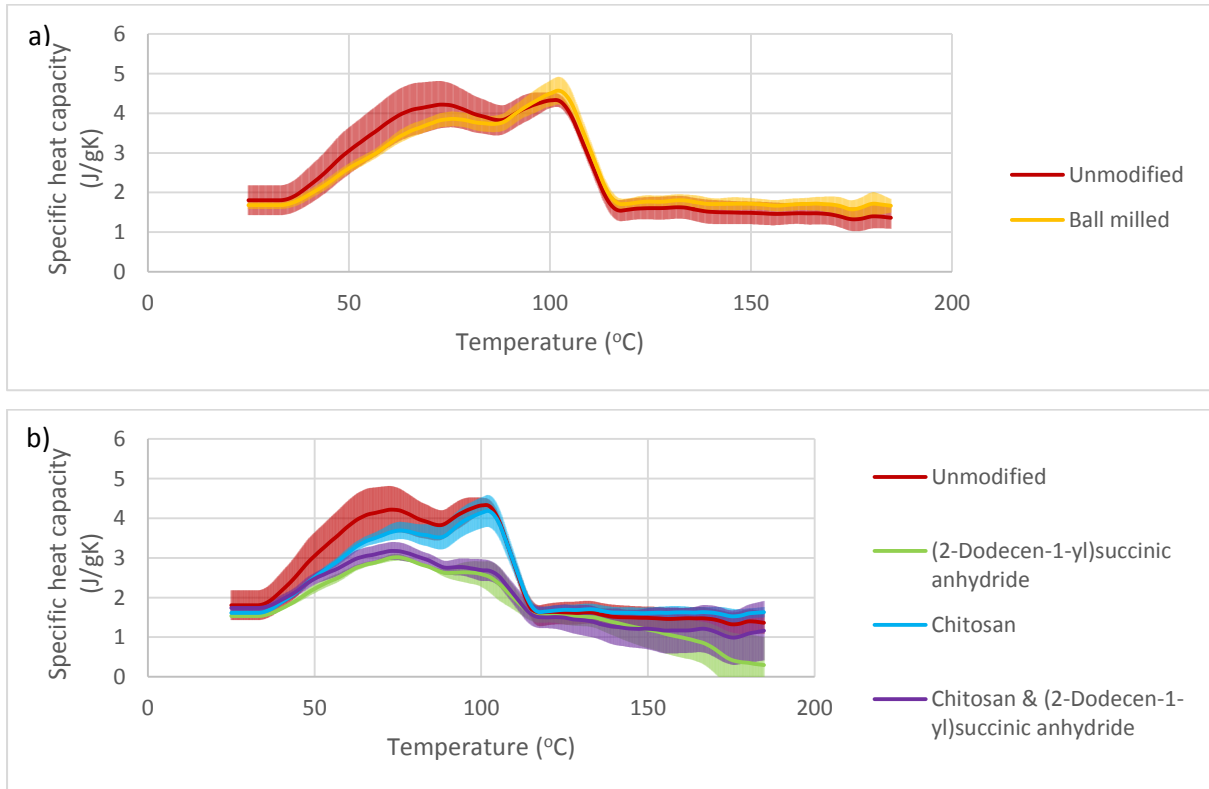


Figure 7.21: Specific heat capacity measurements of Light Herdwick wool fibres a) before and after ball milling for 6 hours and b) before and after modification with DDSA, in addition to after spraying chitosan onto the afore mentioned wools. The shaded areas represent the standard deviation for all specific heat capacity values.

7.6.4 Thermal conductivity

7.6.4.1 Method

The tests were done on loose wool samples using FOX600 and compared to the tests done on unmodified wool insulation using FOX314, as indicated in section 4.4.4.1. For the use of chitosan as an additive, wool insulation was sprayed with 2.5% chitosan by weight on the top surface and 2.5% by weight on the bottom surface, making the combined amount of chitosan the same percentage by weight as previously applied (see section 6.9.2)

Table 7.1 lists the dimensions and densities of the samples tested.

Table 7.1: Dimensions and densities of the samples tested for thermal conductivity.

Sample	Length (mm)	Width (mm)	Thickness (mm)	Density (kg/m ³)
Loose Swaledale	400	400	25.4	59.1
Phthalic anhydride treated	400	400	26.8	56.0
Dodecenyl succinic anhydride treated	400	400	27.2	55.0
Unmodified wool insulation	310±6	310±6	56±12	22.6±0.7
Chitosan sprayed wool insulation	400	400	50	36.2

7.6.4.2 Results and discussion

The results (Figure 7.22) show a very slight decrease in thermal performance (i.e. increase in thermal conductivity of $\leq 0.0012\text{w/mK}$) for chemically modified wool, but it should be noted that only one loose wool specimen per modification (and for unmodified loose wool) was tested, having differences in thicknesses and densities.

With regards to the addition of chitosan, again there are no apparent change in thermal conductivity of wool insulation before and after the addition. However, the density of the chitosan sprayed wool insulation was significantly higher than that of the unmodified wool insulation – this should contribute to an increase in thermal performance (i.e. reduction of thermal conductivity). Likewise, though, differences in experimental conditions exist.

Of course, experimental set-ups with more repeats per sample, where dimensions and densities are more uniform, would give a more accurate and definitive clarification on the effect that modifications and additives have on the thermal performance of wool fibres. Due to lack of time and resources, the tests performed are indicative and give a general outlook on this matter and mainly gives the impression that no severe changes in thermal performance occur.

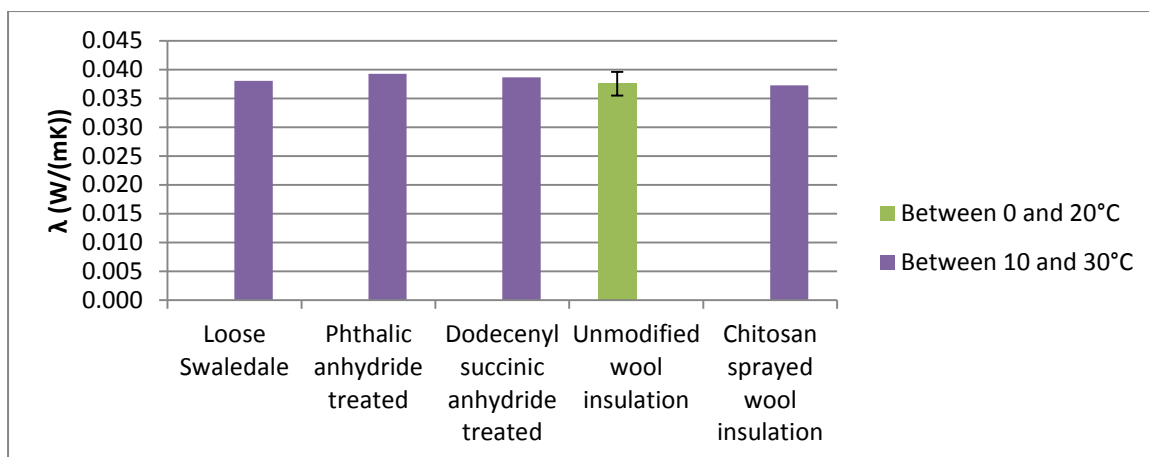


Figure 7.22: Thermal conductivity results for loose Swaledale wool and wool insulation products.

7.7 Conclusions

- Chemical modifications:
 - Adding polar functionalities onto the fibre surface (using succinic anhydride) hinders the total sorption capacity of polar formaldehyde gas. This can be explained by the presence of the natural non-polar 18-MEA functionalities and their dynamic movement in response to their surrounding environment. Chemically adding non-polar functionalities onto the fibre surface also hinders the total sorption capacity of polar formaldehyde gas, but to a lesser extent than polar functionalities. As non-polar functionalities replace the already-existing small polar surface OH and NH₃ groups, they do not disrupt the dynamic movement of the 18-MEA as much as new large polar functionalities would.
 - Toluene is sorbed in small quantities regardless of which anhydride is used except for DDSA. This is probably due to the presence of a polar carboxylic group on the newly added chemical functionalities that repels the non-polar VOC and possibly to a steric overshadowing of these new functionalities by the surface bound 18-MEA. Both these factors are minimised in the case of DDSA.
 - Limonene sorption is enhanced only with DDSA, which non-polarity is sufficient to counteract the loss of 18-MEA caused by the chemical process.
 - Dodecane, being the most non-polar of the VOCs, is sorbed in exactly the same trend as that of limonene, with the difference being that the percentages sorbed are at a higher level that the difference is not as large but is still significant.
 - Chemical modification with DDSA, although enhances the sorption of non-polar VOCs, does not cause a compromise with regards to the sorption of formaldehyde at low levels, although it does decrease to total capacity of formaldehyde sorption.
- Mechanical modifications:

- Ball milling enhances the sorption profile of all four v/VOCs at low concentration levels. This enhancement is not due to a change in surface polarity but to an increase in surface area.
- Additives:
 - Carbon fibre as an additive:
 - Shows almost no sorption capacity for formaldehyde.
 - Shows a very high potential in sorbing low levels of the non-polar VOCs.
 - Addition of 5% chitosan onto wool fibre surface:
 - Leads to a large increase in its sorption capacity of formaldehyde, owing to its polar functionalities and large molecular size that prevents it from disrupting the natural dynamic movement of fibre surface functionalities. However, it does not lead to a change in the sorption of low levels of formaldehyde or the 3 non-polar VOCs.
 - Is compatible with chemical modifications, as a combination of both (when DDSA is used) results in an increase in total formaldehyde sorption capacity, no decrease in the sorption of low formaldehyde levels, and only a slight decrease – which is still an increase when compared to unmodified wool – in the sorption of the non-polar VOCs.
- FTIR analysis confirms the modifications' effect on the fibre surface and that the combination of chemical modifications and the addition of chitosan onto the fibres' surface is compatible; added chemical functionalities are not masked from the surface by the chitosan coating.
- Changes in surface area and pore distribution and volume is notable when the fibre is mechanically modified by ball milling, confirming that this modification enhances the sorption of all ranges of polarities of v/VOCs.
- New chemical functionalities offered by the reaction with anhydrides mostly reside in larger mesopores, as the distribution for such sized pores of fibres modified with the anhydrides increases for control samples but remains on a similar level to that of unmodified wool's when an anhydride is used to modify the fibres.
- Chemical modifications cause a decrease in the specific heat capacity at temperatures between 50 to 110°C, not due to the difference in the fibres' water content, but probably due to the take-up of physical space by the added chemical functionalities.

Thermal conductivity test give an indication that no sever changes occur due to wool fibre modification or the addition of chitosan on the surface of a wool insulation product. Better experimental parameters could be established to give a more detailed clarification on the subject.

Chapter 8: Summary, further work and conclusions

8.1 Indoor air quality and sheep wool structure

Indoor air pollution and the dangers of a huge and variable array of v/VOCs in the atmospheres we are almost always present in hosts a real and growing concern. Although not every detailed effect caused by each v/VOC or their synergistic effects is documented, enough is known to start scientific, commercial and some legal movements. The use of sheep's wool has already been studied and shows promise in the field of sorbing v/VOCs (see section 1.3)

Sheep's wool fibre structure is complex, having multiple morphological and chemical components, and is subject to natural and industrial variation. There are distinct differences between fibres' inner and outer surfaces, as the cuticle is amorphous and less polar than the α -helical cortex (see section 2.2.4). Also, the outer surface is dynamic and responsive to the surrounding environment, changing the exposed surface's polarity to be more like that of the surroundings.

8.2 Summary of work

A gas tight set-up was designed and made to allow the entrapment of v/VOCs. Sources of formaldehyde, toluene, limonene and dodecane were created to result in known low concentration flows within the set-up. These four v/VOCs were selected for testing as they represent a wide range of polarity and basic chemical diversity. The v/VOC flow was made to pass through a sample holder, where sheep wool and mineral wool fibres were allowed to sorb v/VOCs. The unsorbed v/VOCs were analysed using thermal or solvent desorption connected to a GC-FID or HPLC, and the amounts of v/VOCs that were sorbed were subsequently calculated. This set-up allowed the determination of v/VOC sorption profiles by fibres exposed to gaseous concentrations close to what would be encountered in real life scenarios.

To determine the total sorption capacity of fibres, a DVS set-up was used; this was only done for formaldehyde. It allowed small fibre samples to be exposed to several cycles of very high formaldehyde concentrations whilst recording the fibres' weight change.

8.2.1 Sorption profiles

Consistently throughout all sorption experiments with any of the v/VOCs used, mineral wool sorbed less than any of the sheep's wools, and unscoured wools sorbed more than their scoured counterparts. This shows that the keratinous surface of wool fibres offers more interactive platforms for surrounding molecules than non-organic fibres do. Also, although scouring of wool is a requirement for industrial processing, the material removed obviously

enhances sorption profiles. It is probable that this material consists mainly of lanolin, but also contains a host of biological and inorganic contaminants.

Variations in the sorption profiles of different scoured wool types were clearly evident. Although not significant in the case of low levels of formaldehyde, the total sorption capacity clearly differed. More so, the higher the sorption capacity for polar formaldehyde for a fibre type was, the lower its sorption of low concentration non-polar VOCs proved to be, and vice versa. This shows that surface polarity has an effect on the sorption profile of a specific v/VOC. It was concluded that, for Light Herdwick wool, sorption of non-polar VOCs was preferred over the polar vVOC. This preference was highlighted by the fact that it sorbs most of the dodecane (most non-polar VOC used) it is exposed to even at low concentrations; the percentage of sorbed limonene (non-polar VOC) on the other hand increases at higher concentrations, but that of formaldehyde (polar v/VOC) decreased at higher concentrations. This preference is also in agreement with Van der Wal et al. (1998), who showed that “adsorption increases as the boiling point of the compound increases and the vapour pressure decreases.” However, these relationships may vary to a slight or considerable degree, or perhaps even reverse for other wool types having different surface polarities.

Maxwell and Huson’s explanation of the dynamic outer lipid layer fits well with the fact that several cycles of formaldehyde and no-formaldehyde exposure are required to achieve full sorption capacity. The movement of the surface lipids in response to the nature of the surrounding gases logically have to do with the sorption process. If their movement does not assist with furthering sorption and the locking-in of formaldehyde, then there would be no need for fibre to undergo several cycles of exposure; in that case, upon the first exposure formaldehyde would have passively diffused through the fibre surface, increasing the mass of the fibre in one cycle only. The dynamic nature of the lipid layer also fits in with the fact that when constant low concentration flows of formaldehyde were used, no differences are notable between unscoured wool types. It is reasonable to expect the degree of movement of the lipids to be dependent on surrounding environment; if more lipids are present, they move inwards more and if less are present, they move inwards less. This means that the percentage sorbed at this level would be the same regardless of the formaldehyde concentration, in accord with experimental results. Adding to that, modifications that cause an alteration of the lipid layer and/or its neighbouring fibre surfaces is clearly seen to disrupt this process – chemical modifications that result in the addition of polar functionalities lead to a reduction in the total sorption capacity of formaldehyde.

FTIR spectra reinforces the conclusion that fibre surface polarity effects sorption, with the C=O peaks at 1720cm^{-1} giving an indication of relatively how much 18-MEA is bound as a lipid layer via thioester linkages.

The higher distribution and cumulative volume of pores greater than 30nm for Blackface is likely a result of patches within the surface lipid layer. This coincides with enhanced formaldehyde sorption capacity.

Satisfactory fits for moisture sorption isotherms and sorption hysteresis were possible, and can be used as a basis for kinetics studies of different v/VOC sorption. Using the Vrentas and Vrentas model, fits were possible only by modifying some of the input parameters - especially the glass transition temperature of water. The Zimm-Lundberg model showed the onset of water clustering in the fibres at moisture contents in excess of 15-18% equilibrium moisture content. Parallel exponential kinetics model was found to provide extremely good fits to the experimental data, and clarified the effect the fast and slow sorption processes have on hysteresis; hysteresis is accompanied with the differences in moisture content associated with the fast process only below an RH of 70%, after which the slow process contributes negatively. The calculated fibres moduli were much larger than experimental values at the lower end of the hygroscopic range, but were in reasonable agreement at the upper end of the hygroscopic range.

8.2.2 Modifications and additives

Although tests regarding mechanical modification with tensile stretching were inconclusive, ball milling the fibres certainly enhances low-concentration formaldehyde, toluene, limonene and dodecane sorption. Such an enhanced sorption over the whole range of v/VOCs polarities tested shows that the cause of it is the simple increase of surface area. Although FTIR analysis shows an increase in CH_2 and loss of C-O-C groups on the surface, there does not seem to be a preferential exposure of chemical functionalities of a certain polarity. Keratinous debris, evident from SEM imaging, pore size distribution and cumulative pore volumes, contribute to the aforementioned observations.

Chemical modifications, regardless of the polarity of the introduced function, led to a decrease in the total sorption capacity of formaldehyde. This is likely to the disruptive effect of new polar functions on the dynamic surface movement, and the repelling effect of new non-polar functions on formaldehyde gas. Of the two, the disruptive effect of polar functionalities seems to have a larger effect, as they result in a lower sorption capacity. When examining low concentration levels, where no cycles of polar/non-polar environments are being employed, chemical modifications (control and with DDSA) seem to have no diminishing effect on

formaldehyde sorption, but alter toluene's, limonene's and dodecane's sorption. Modification with DDSA enhances the sorption of all three of these non-polar VOCs, but the other anhydrides diminish the sorption of limonene and dodecane. The latter effect can be explained by the steric hindrance the new functionalities are subjected to by the naturally occurring 18-MEA molecules, and/or by the effect of the carboxylic group the new functionalities possess. In short, modification with DDSA enhances wool fibres' sorption of low levels of non-polar v/VOCs and does not reduce that of polar v/VOCs, although it does reduce the total sorption capacity of polar v/VOCs. Pore size distribution and cumulative pore volumes imply that newly introduced chemical functionalities occur in larger mesopores. The modification leads to a decrease in specific heat capacity, possibly due to the reduction in vibrational space on the molecular level, and not due to a change in moisture uptake behaviour. It also may lead to a very slight decrease in thermal performance as an insulator; a more detailed and comprehensive experimental procedure would clarify the matter.

Carbon as an additive is compatible in its fibrous form with wool fibres and is extremely efficient at sorbing low levels of non-polar v/VOCs. On the other side of the spectrum, chitosan can be used to enhance the total sorption capacity of polar v/VOCs without hindering the sorption of v/VOCs at low concentrations. That is because it does not mask the wool fibre's surface functionalities; although C=O and C-O-C groups are not detected by FTIR post coating, sorption at the molecular level does not seem to be affected. It is also compatible with chemical modification of wool fibres for the same reason, with the newly introduced chemical functionalities being still visible on the FTIR spectrum post coating. However, the enhancement in sorption capacity of polar v/VOCs is not as large as that of chitosan-sprayed unmodified wool.

8.3 Real life implications

8.3.1 Estimated sorption on the larger scale

Wool fibres can be utilised in indoor products to sorb low-level concentration of polar and non-polar v/VOCs. Taking a European standard room for example, a volume of 30m³ would be available and a wall surface area of 31.4m², not including the door and window (BSI, 2013). If 100mm thick sheep wool-based cavity insulation is used, in conjunction with fully breathable walls to allow v/VOC's free mobility, about 45kg of wool would be available for v/VOC sorption – assuming a typical 18kg/m³ product density and 80% wool content (Black Mountain Insulation, 2012; Thermafleecce, 2013).

Table 8.1 summarises gaseous amounts that would be found in a European standard room based on literature reported mean and highest levels of the four investigated v/VOCs. It also

notes the amounts that would be encountered in the same room if experimental conditions were scaled up, in addition to the amounts that would be expected to be sorbed if the wall cavities were filled with 100mm thick Light Herdwick wool insulation. Although the experimental conditions do not depict the same interactions encountered in an actual European standard room, the amounts expected to be present are not hugely higher than the amounts reported in the literature. Therefore, the calculated amounts that would be sorbed should not be far from reality.

Table 8.1: Approximate v/VOC amounts expected in a European standard room and experimental sorption values by wool scaled up to a European standard room.

	Formaldehyde	Toluene	Limonene	Dodecane
Mean amounts expected in a European Standard room according to literature (mg)	1.55 [*]	1.35 [†]	0.21 [¶]	0.11 [¶]
Highest amounts expected in a European standard room according to literature (mg)	2.96 [‡]	4.64 [§]	4.2 [¶]	2.16 [¶]
Amounts expected in a European standard room according to experimental conditions (mg)[‡]	9.94±0.21	20.16±2.70	11.50±0.30	9.93±0.53
Amounts 100mm thick Light Herdwick wool wall cavity insulation would sorb in a European room according to experimental conditions (mg)	5.58±0.35	2.85±2.12	2.76±0.17	5.93±0.09

* Based on an average concentration of all values summarised in Figure 2.4a, which is 51.67µg/m³.

† Based on an average concentration of all values summarised in Figure 2.5a, which is 44.95µg/m³.

‡ Based on an average concentration of all values summarised in Figure 2.4b, which is 98.65µg/m³.

§ Based on an average concentration of all values summarised in Figure 2.5b, which is 154.82µg/m³.

¶ Based on limonene median concentration of 7.1µg/m³ and highest concentration of 140µg/m³, and dodecane median concentration of 3.5µg/m³ and highest concentration of 72µg/m³ (Girman et al., 1999b)

‡‡ Based on the experimental conditions of using a flow of 15.1ml/min for 30mins, resulting in 0.000453m³, and the lowest flow concentrations used.

8.3.2 Current experimental constraints with regards to real-life scenarios

Of course, a more suitable experiment can be conducted by scaling up to a suitably sized room to calculate the exact deviation of a real-life scenario from the numbers given by this thesis. Designing and building the required setup for such an assessment is not easy, as there are several factors to consider. Mainly, how much wool would be present in a standard room?

Where would it be located? If we consider furnishings, the amounts can vary considerably depending on the occupants. For example, one aspect to consider is irritation and allergies to wool, which is encountered by a minority of people (Maiphethlo, 2007). For such occupants, no wool furnishings would be present. On the other hand, depending on the culture and socio-economic circumstances, other occupants would opt to utilize much wool furnishings.

However, a large passive use of wool can be achieved through insulation products, as previously mentioned (see section 8.3.1), placing the wool out of sight in between wall cavities (Figure 8.1). In such a case, there will be no direct interaction between the occupants and the fibres. Unfortunately, there also will be limited interaction between the indoor v/VOCs and the fibres. Some limited air flow will still take place towards the cavities the insulation is in, through electric sockets for example. Yet better interaction with the surrounding gases can be achieved by using a vapour permeable membrane (Metz et al., 2005; Waggoner et al., 2002). It must be checked, though, that all the v/VOCs that are to be studied are able to pass through the membrane, including the larger compounds relative to the small structure of water.

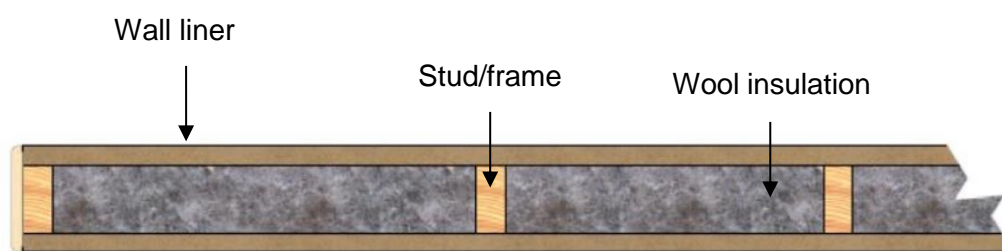


Figure 8.1: A birds eye view of a cross section of wall panel with wool insulation in the cavities (Peter Walker, 2017).

Such an experiment can provide a more accurate assessment of sorption potential by introducing factors encountered in real life scenarios, such as moisture at varying degrees, temperature changes, etc. The influence of desorption may also be assessed by radically changing the v/VOCs concentrations, possibly in a cyclic manner to assess the changes that has on sorption trends and capacities. This in turn would shed light on the longevity of the sorption effect – would the enhancement of indoor air quality be an infinitely buffering effect as the rate desorption eventually reach that of sorption's, or would the rate of desorption be too slow and cause a saturation of the fibres?

Other future work is discussed in the section 8.4.

8.3.3 Practicalities of using different wool types and proposed modifications

The fact that sorption of different VOCs alters with different wool types can be taken advantage of. If polar v/VOCs are known to be present in high concentration in a certain indoor

environment, wool containing products can be tailored to contain the wool type that is better at sorbing that range of the spectrum – Blackface for instance. On the other hand, if non-polar VOCs are more abundant, wool types that are more suitable, such as Swaledale or Light Herdwick, would better contribute to a healthier indoor environment.

With regards to which studied modification would be the most suitable, it seems that increasing fibre surface area enhances the sorption of the whole range of VOCs whilst requiring little economic and environmental resources. Many wool-related industrial processes already induce one type or another of mechanical stress on the fibres; yarn spinning induces tensile stress, and carding contributes to random mechanical stresses as well. The only downside to inducing mechanical stress is the resulting of shorter fibres and dust particles. Shorter fibres may hinder the product's performance in some way or create a waste stream along with wool dust particles, which may be airborne and possibly cause an industrial hazard if not properly addressed (Mansour et al., 2014). There are no other major cost or life cycle implications caused by this modification, especially when considering that wool fibre is a biodegradable material and hence, as an insulation product, does not have serious end-of-life concerns (Murphy and Norton, 2008).

Chemical modifications on the other hand would be accompanied with more pronounced cost and life cycle impacts. Even after perfecting the process, including which chemicals and solvents are to be used, as environmentally friendly as it may be it will call for the establishment of a supply chain and the incorporation of a new process in an industrial setting. The cost and environmental implication would vary depending on these two factors. Also, the end-of-life and biodegradability of wool might be called into question, and tests would be needed to check if the biodegradation products can be safely released into the environment safely.

The additives studied in this thesis are beneficial at sorbing v/VOCs of different polarities. Chitosan is seen to increase the storage capacity of polar v/VOCs, and similarly the carbon fibre very efficiently sorbs non-polar VOCs. Therefore, their use would be especially useful for indoor areas with relatively high v/VOC concentrations, such as refurbished buildings. With regards to total formaldehyde sorption capacity, it is noteworthy that reaching this value requires alternating cycles of gaseous formaldehyde plus moisture and non-polar nitrogen. Translating this to a real case scenario may be achieved by changing the polarity of the indoor atmosphere. Air is composed primarily of nitrogen, so frequent alteration between ventilation and the introduction of a high moisture atmosphere, mimicking a polar atmosphere, should help sorb more formaldehyde gas from high concentration environments or from a long term emission source.

8.3.4 Other means to passively reduce indoor v/VOC concentrations

There are multiple construction materials that can be assessed and modified to sorb or degrade indoor v/VOCs. For example, other insulation products are available, including cellulose (“Nesocell Bio,” 2018) and plant based products (“NatuHemp - Natural Hemp Insulation,” 2018, “Thermafleece NatraHemp Insulation,” 2018) as well as mixtures of inorganic and organic materials (Andy Sutton et al., 2011). Surface area, chemical functionalities and other properties can be very different, resulting in different sorption profiles.

Other materials that can be taken advantage of include wood panels, lime plaster, clay plaster, gypsum, or other wall renders. Some additives can be added to such products, such as hemp or v/VOC degrading nanoparticles. Such materials were investigated along with insulation products as part of the Eco-innovative, Safe and Energy Efficient wall panels and materials for a healthier indoor environment (ECO-SEE) project (Peter Walker, 2017). A combined effort of multiple materials, each of which can be modified to optimise this effect, is likely to have a more significant effect on sorption of the wide range of v/VOCs.

8.4 Other future work

8.4.1 Sorption profiles

Adding more features to the experimental set-up to simulate real life scenarios would be helpful. For example, studying the effect of the addition of moisture or both polar and non-polar v/VOCs simultaneously to the flow fibres are exposed to would highlight competitive and preferential sorption patterns. The use of other v/VOCs which polarities are in between the ones already studied, such as an alcohol or a ketone, would bridge the gap and give an enhanced understanding of the link between the v/VOC polarity spectrum and sorption. In addition, desorption profiles of the v/VOCs would enhance the conclusions made about structure-sorption relationships and clarify if these fibres are able to buffer the atmosphere, keeping v/VOC concentrations at low levels, rather than getting saturated quickly and providing no long-term sorption benefits. The effect of the modifications with regards to desorption would be equally of interest.

To better understand the dynamic nature of the 18-MEA lipid layer of wool fibres, a DVS analysis of the total sorption capacity of non-polar VOCs would be essential. If, unlike the case of formaldehyde, one cycle is enough to reach the maximum sorption capacity, then it can be concluded that the sorption of non-polar VOCs does not trigger any molecular surface movement. Such an observation would be in line with the statement made concerning the preferential sorption of non-polar VOCs, as was seen in the case of Light Herdwick wool when exposed to different concentration levels of the different v/VOCs. It also would be interesting

to examine if this preference holds true for other wool types such as Blackface, which exhibits lower sorption characteristics of non-polar VOCs.

The explanation of the dynamic movement of the surface lipid layer and its correlation with experimental results can be further confirmed. Inverse gas chromatography may shed more light on the subject. Also, sorption tests can be conducted on fibres that have undergone progressive damaging and removing of their lipid layer, by using hydrogen peroxide (Jovančić et al., 2001) or modified proteases (Jus et al., 2007). If such mechanical action does effect sorption, custom made fibres with specialised surface functional groups may be synthesised to optimise selective gaseous sorption and perhaps aid in gaseous separation and purification of mixtures.

In addition, it would be of real interest to link this dynamic behaviour with literature findings. For example, it is well known and reported that wool fibres swell when subjected to a wet atmosphere (Speakman, 1931; Warburton, 1947). Keeping that in mind, would it be correct to say that the movement is done by the lipids themselves, or is the underlying protein matrix the component actually doing the movement whilst the lipid layer allows itself to sink-in?

8.4.2 Modifications and additives

It is worth checking if enhanced sorption can be achieved by coating scoured wool fibres with purified lanolin. This may provide industrial challenges though, as it is not possible to process wool fibres without scouring for fear of biological hazards. Coating fibres on an individual level with lanolin would prove uneconomic on large scale, but coating the surfaces of products may be a viable and sufficient method of v/VOC sorption enhancement. The investigation of other economic material as additives is of interest, with the carbon resulting from paper mill sewage sludge carbonisation being a promising one worth investigating for v/VOC capture. However, as is the case with other additives, incorporating it with wool fibres or products needs consideration.

Regrettably, total formaldehyde sorption capacity of control and ball-milled wool were not tested due to time constraints and the availability of the DVS apparatus. The data on a control sample can clarify the effect that the presence of larger mesopores combined with the lessening of the bound surface lipid layer have on sorption capacity. Adding to that, if ball milling increases formaldehyde's sorption capacity, then mechanically increasing fibre surface area would be able to provide both enhanced sorption of low levels of VOCs and total sorption capacity, at least of formaldehyde's, simultaneously. Also of interest to conclude through the use of DVS analysis is whether formaldehyde gas exhibit a clustering effect as it is being sorbed onto the fibre surface, which would clarify the behaviour seen in its sorption by

chemically modified fibres having polar surface functionalities introduced (see section 7.4.2, Figure 7.5).

Chemical modification methods can be varied to introduce more functionalities than those permitted by using anhydrides. Enzymatic derivatisation, mainly acylation, is one such method that is reported in the literature (see section 6.3.2). Using the anhydride method can be enhanced through several means, such as by the use of supercritical CO₂ as a reaction medium. This would eliminate the need to remove the solvent from the fibres by extraction, as the CO₂ can be depressurised and vented out. Also, if several functionalities are intended to be introduced to the fibre surface, one-pot reactions with several anhydrides may be possible, although reaction rates and compatibilities should be investigated.

In the case of modification using DDSA, it might be of benefit to know if the polar carboxylic acid function that is introduced with it would aid with the dynamic movement of the whole of the non-polar functionality along the fibre surface as the surrounding environment changes (see section 7.4.1). In other words, if high concentrations of non-polar VOCs are introduced into the environment surrounding the modified fibres, and then cycles of a polar gaseous environment is alternated between exposures to the non-polar VOCs – in a reverse manner of formaldehyde total sorptive capacity tests - would an increase in the sorption capacity of non-polar VOCs be noticed? The comparison between fibres modified with DDSA and fibres chemically modified to have a large non-polar chain attached to the surface without the carboxylic group would provide the answer.

The combination of a chemical modification and addition of chitosan does the unexpected and results in a decrease in surface area and cumulative pore volume. This should be further investigated to check if the result is simply coincidental, as sheep wool fibres vary – even on the visible scale – in the same batch. Also, as previously mentioned, a more comprehensive and stringent experimental procedure would shed more light on the seemingly small effects that modification and additives have on the thermal conductivity of the fibres.

Finally, as efficient as carbon fibre is at sorbing non-polar VOCs, its total sorption capacity and desorption potential should be taken into account to check if their sorption potential is short-lived or not. Also, whether the sorption of polar v/VOCs by wool would be reduced when carbon fibre is present as an additive would certainly be worth checking.

References

- Adgate, J.L., Church, T.R., Ryan, A.D., Ramachandran, G., Fredrickson, A.L., Stock, T.H., Morandi, M.T., Sexton, K., 2004. Outdoor, Indoor, and Personal Exposure to VOCs in Children. *Environ. Health Perspect.* 112, 1386–1392. <https://doi.org/10.1289/ehp.7107>
- Adger, W.N., Eakin, H., Winkels, A., 2009. Nested and teleconnected vulnerabilities to environmental change. *Front. Ecol. Environ.* 7, 150–157. <https://doi.org/10.1890/070148>
- Akubuiro, E.C., 1993. Potential mechanistic routes for the oxidative disintegration of ketones on carbon adsorbents. *Ind. Eng. Chem. Res.* 32, 2960–2968. <https://doi.org/10.1021/ie00024a002>
- Allwörden, I.K., 1916. The nature of sheep's wool and a new research method for the chemical identification of damaged wool. *Z Angew Chem* 29, 77–78.
- Aluigi, A., Vineis, C., Tonin, C., Tonetti, C., Varesano, A., Mazzuchetti, G., 2009. Wool Keratin-Based Nanofibres for Active Filtration of Air and Water. *J. Biobased Mater. Bioenergy* 3, 311–319. <https://doi.org/10.1166/jbmb.2009.1039>
- Aluigi, A., Zoccola, M., Vineis, C., Tonin, C., Ferrero, F., Canetti, M., 2007. Study on the structure and properties of wool keratin regenerated from formic acid. *Int. J. Biol. Macromol.* 41, 266–273. <https://doi.org/10.1016/j.ijbiomac.2007.03.002>
- Anastas, P.T.A., Warner, J.C.A., 2000. *Green Chemistry: Theory and Practice*. Oxford University Press.
- Andar Ltd, 2016. Textiles - Andar Ltd [WWW Document]. Text. - Andar Ltd. URL <http://andar.co.nz/textiles/> (accessed 11.30.16).
- Anderson, S.E., Jackson, L.G., Franko, J., Wells, J.R., 2010. Evaluation of Dicarbonyls Generated in a Simulated Indoor Air Environment Using an In Vitro Exposure System. *Toxicol. Sci.* 115, 453–461. <https://doi.org/10.1093/toxsci/kfq067>
- Ando, H., Adachi, M., Umeda, K., Matsuura, A., Nonaka, M., Uchio, R., Tanaka, H., Motoki, M., 1989. Purification and Characteristics of a Novel Transglutaminase Derived from Microorganisms. *Agric. Biol. Chem.* 53, 2613–2617.
- Andy Sutton, Daniel Black, Peter Walker, 2011. *Hemp Lime: An introduction to low-impact building materials (Information paper)*. BRE and University of Bath.
- Arai, T., Freddi, G., Innocenti, R., Kaplan, D.L., Tsukada, M., 2001. Acylation of silk and wool with acid anhydrides and preparation of water-repellent fibers. *J. Appl. Polym. Sci.* 82, 2832–2841. <https://doi.org/10.1002/app.2137>
- Aruoma, O.I., Murcia, A., Butler, J., Halliwell, B., 1993. Evaluation of the antioxidant and prooxidant actions of gallic acid and its derivatives. *J. Agric. Food Chem.* 41, 1880–1885. <https://doi.org/10.1021/jf00035a014>

- Asquith, R.S., Otterburn, M.S., Buchanan, J.H., Cole, M., Fletcher, J.C., Gardner, K.L., 1970. The identification of ϵ N-(γ -l-glutamyl)-l-lysine cross-links in native wool keratins. *Biochim. Biophys. Acta BBA - Protein Struct.* 221, 342–348. [https://doi.org/10.1016/0005-2795\(70\)90274-6](https://doi.org/10.1016/0005-2795(70)90274-6)
- Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB), 2012. A contribution to the Construction Products Directive: Health-related Evaluation Procedure for Volatile Organic Compounds Emissions (VOC and SVOC) from Building Products. Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB).
- Australian Wool Exchange, 2015. Australian Wool Exchange [WWW Document]. AWEX. URL <http://www.awex.com.au/about-awex.html> (accessed 11.7.13).
- Australian Wool Innovation [WWW Document], 2016. URL <http://www.wool.com/> (accessed 7.1.16).
- Báez, A., Padilla, H., García, R., Torres, M. de. C., Rosas, I., Belmont, R., 2003. Carbonyl levels in indoor and outdoor air in Mexico City and Xalapa, Mexico. *Sci. Total Environ.* 302, 211–226. [https://doi.org/10.1016/S0048-9697\(02\)00344-3](https://doi.org/10.1016/S0048-9697(02)00344-3)
- Bahi, A., Jones, J.T., Carr, C.M., Ulijn, R.V., Shao, J., 2007. Surface Characterization of Chemically Modified Wool. *Text. Res. J.* 77, 937–945. <https://doi.org/10.1177/0040517507083520>
- Bailey, P.L., Pocalyko, D.J., Richardson, N.K., Schilling, K.M., 1996. Covalent bonding of active agents to skin, hair or nails. US5490980 A.
- Bamford, S., Ellis, J., Huddleston, K.M., 1998. Method for the treatment of wool. US5755827 A.
- Bandosz, T.J., 2006. Air treatment - VOC and odor removal, in: *Activated Carbon Surfaces in Environmental Remediation*. Academic Press, pp. 399–419.
- Barba, C., Martí, M., Carilla, J., Manich, A.M., Coderch, L., 2013. Moisture sorption/desorption of protein fibres. *Thermochim. Acta* 552, 70–76. <https://doi.org/10.1016/j.tca.2012.11.001>
- Barguil, S., Moullec, Y.L., Person, A., Laurent, A.-M., Festy, B., 1990. Chemical characterization of indoor air quality in Parisian homes. *Aerobiologia* 6, 28–31. <https://doi.org/10.1007/BF02539038>
- Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951a. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* 73, 373–380. <https://doi.org/10.1021/ja01145a126>
- Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951b. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* 73, 373–380. <https://doi.org/10.1021/ja01145a126>

- Bartolotta, A., Carini, G., Carini, G., Di Marco, G., Tripodo, G., 2010. Subglass Cooperative Mechanical Relaxations and Activation Entropy in Heterocyclic Polymer Networks. *Macromolecules* 43, 4798–4804. <https://doi.org/10.1021/ma100137w>
- Beck, M.I., Tomka, I., 1997. Effects of the degree of substitution in ethyl cellulose on the clustering of sorbed water. *J. Macromol. Sci. Part B* 36, 19–39. <https://doi.org/10.1080/00222349708220413>
- Benson, R.E., Fahnestock, S.R., Hamilton, P., O'Brien, J.P., Wang, H., 2012. Hair binding peptides and peptide-based hair reagents for personal care. US8273337 B2.
- Berglund, B., Berglund, U., Lindvall, T., 1984. Characterization of indoor air quality and sick buildings. *ASHRAE Trans.* 90, 1045–1055.
- Bernhard, C.A., Kirchner, S., Knutti, R., Lagoudi, A., 1995. Volatile organic compounds in 56 European office buildings, in: *Proceedings of Healthy Buildings*. pp. 1347–1352.
- Beynon, R.J., Bond, J.S., 1989. *Proteolytic enzymes: a practical approach*. IRL Press at Oxford University Press.
- Bikov, A., Paschalaki, K., Logan-Sinclair, R., Horváth, I., Kharitonov, S.A., Barnes, P.J., Usmani, O.S., Paredi, P., 2013. Standardised exhaled breath collection for the measurement of exhaled volatile organic compounds by proton transfer reaction mass spectrometry. *BMC Pulm. Med.* 13, 43. <https://doi.org/10.1186/1471-2466-13-43>
- Bizzozero, O.A., 1995a. Chemical analysis of acylation sites and species. *Methods Enzymol.* 250, 361–379.
- Bizzozero, O.A., 1995b. Chemical analysis of acylation sites and species. *Methods Enzymol.* 250, 361–379.
- Black Mountain Insulation, 2012. *Black Mountain Natural Insulation Installation Guide*.
- Blount, B.C., Kobelski, R.J., McElprang, D.O., Ashley, D.L., Morrow, J.C., Chambers, D.M., Cardinali, F.L., 2006. Quantification of 31 volatile organic compounds in whole blood using solid-phase microextraction and gas chromatography–mass spectrometry. *J. Chromatogr. B* 832, 292–301. <https://doi.org/10.1016/j.jchromb.2006.01.019>
- Blout, E.R., Stahman, M.A., 1962. *Polyamino acids, polypeptides and proteins*. Univ. Wis. Press 275.
- Bluyssen, P.M., De Oliveira Fernandes, E., Groes, L., Clausen, G., Fanger, P.O., Valbjørn, O., Bernhard, C.A., Roulet, C.A., 1996. European Indoor Air Quality Audit Project in 56 Office Buildings. *Indoor Air* 6, 221–238. <https://doi.org/10.1111/j.1600-0668.1996.00002.x>
- Bonès, R.M., Sikorski, J., 1967. The Histological Structure of Wool Fibres and Their Plasticity. *J. Text. Inst.* 58, 521–532. <https://doi.org/10.1080/00405006708659949>

- Bornehag, C.-G., Stridh, C.-G., 2000. Volatile organic compounds (VOC) in the Swedish housing stock, in: *Proceedings of Healthy Buildings 2000*, Vol. 2. Helsinki, Finland, pp. 437–442.
- Bornehag, C.G., Sundell, J., Bonini, S., Custovic, A., Malmberg, P., Skerfving, S., Sigsgaard, T., Verhoeff, A., 2004. Dampness in buildings as a risk factor for health effects, EUROEXPO: a multidisciplinary review of the literature (1998–2000) on dampness and mite exposure in buildings and health effects. *Indoor Air* 14, 243–257. <https://doi.org/10.1111/j.1600-0668.2004.00240.x>
- Bozzi, A., Yuranova, T., Kiwi, J., 2005. Self-cleaning of wool-polyamide and polyester textiles by TiO₂-rutile modification under daylight irradiation at ambient temperature. *J. Photochem. Photobiol. Chem.* 172, 27–34. <https://doi.org/10.1016/j.jphotochem.2004.11.010>
- Bradbury, J., Chapman, G., 1964. The Chemical Composition of Wool I. The Separation and Microscopic Characterization of Components Produced. *Aust. J. Biol. Sci.* 17, 960–972.
- Bradbury, J., Chapman, G., King, N., 1965. The Chemical Composition of Wool II. Analysis of the Major Histological Components Produced by Ultrasonic Disintegration. *Aust. J. Biol. Sci.* 18, 353–364.
- Bradbury, J., King, N., 1967. The Chemical Composition of Wool IV. The Quantity of Each Histological Component. *Aust. J. Chem.* 20, 2803–2807.
- Bradbury, J., Leeder, J., 1972. Keratin Fibres VI. Mechanism of the Allwörden Reaction. *Aust. J. Biol. Sci.* 25, 133–138.
- Bradbury, J., Ley, K., 1972. The Chemical Composition of Wool XI. Separation and Analysis of Exocuticle and Endocuticle. *Aust. J. Biol. Sci.* 25, 1235–1248.
- Bradbury, J., O'shea, J., 1969. Keratin Fibres II. Separation and Analysis of Medullary Cells. *Aust. J. Biol. Sci.* 22, 1205–1216.
- Bradbury, J.H., 1974. The Structure and Chemistry of Keratin Fibers, in: *Advances in Protein Chemistry*. Academic Press, pp. 111–200.
- Bradbury, J.H., Chapman, G.V., 1963. An investigation by light microscopy of the swelling of wool fibers. *Text. Res. J.* 33, 666–668.
- Bradbury, J.H., Kulkarni, V.G., 1975. The Chemical Composition of Wool XIII. Separation and Analysis of Microfibrils. *Text. Res. J.* 45, 79–83. <https://doi.org/10.1177/004051757504500114>
- Bradbury, J.H., Leeder, J.D., Watt, I.C., 1971. Cell membrane complex of wool, in: *Applied Polymer Symposia*.

- Bradbury, J.H., Peters, D.E., 1972. The Chemical Composition of Wool IX. Separation and Analysis of Macrofibrils. *Text. Res. J.* 42, 471–474. <https://doi.org/10.1177/004051757204200807>
- Brasche, S., Bullinger, M., Morfeld, M., Gebhardt, H.J., Bischof, W., 2001. Why do Women Suffer from Sick Building Syndrome more often than Men? – Subjective Higher Sensitivity versus Objective Causes. *Indoor Air* 11, 217–222. <https://doi.org/10.1034/j.1600-0668.2001.110402.x>
- Braun, R.C., Wilson, M.J.G., 1970. The removal of atmospheric sulphur by building stones. *Atmospheric Environ.* 1967 4, 371–378. [https://doi.org/10.1016/0004-6981\(70\)90082-X](https://doi.org/10.1016/0004-6981(70)90082-X)
- Breakspear, S., Smith, J.R., Luengo, G., 2005. Effect of the covalently linked fatty acid 18-MEA on the nanotribology of hair's outermost surface. *J. Struct. Biol.* 149, 235–242. <https://doi.org/10.1016/j.jsb.2004.10.003>
- BREEAM [WWW Document], 2018. . BREEAM. URL <https://www.breeam.com/> (accessed 1.12.18).
- Brinke, J.T., Selvin, S., Hodgson, A.T., Fisk, W.J., Mendell, M.J., Koshland, C.P., Daisey, J.M., 1998. Development of New Volatile Organic Compound (VOC) Exposure Metrics and their Relationship to “Sick Building Syndrome” Symptoms. *Indoor Air* 8, 140–152. <https://doi.org/10.1111/j.1600-0668.1998.t01-1-00002.x>
- British Wool Marketing Board, 2015a. British Sheep Breeds and Their Wool [WWW Document]. Br. Wool Mark. Board. URL <http://www.britishwool.org.uk/british-sheep-breeds.php> (accessed 2.11.15).
- British Wool Marketing Board, 2015b. British Sheep Breeds and Their Wool [WWW Document]. Br. Wool Mark. Board. URL <http://www.britishwool.org.uk/british-sheep-breeds.php> (accessed 2.11.15).
- British Wool Marketing Board [WWW Document], 2016. URL <http://www.britishwool.org.uk/> (accessed 7.1.16).
- Brown, S.K., 2007. Occurrence of Volatile Organic Compounds in Indoor Air, in: Salthammer, T. (Ed.), *Organic Indoor Air Pollutants*. Wiley-VCH Verlag GmbH, pp. 170–184.
- Brown, S.K., Sim, M.R., Abramson, M.J., Gray, C.N., 1994. Concentrations of Volatile Organic Compounds in Indoor Air – A Review. *Indoor Air* 4, 123–134. <https://doi.org/10.1111/j.1600-0668.1994.t01-2-00007.x>
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* 60, 309–319. <https://doi.org/10.1021/ja01269a023>
- BSI, 2013. CEN/TS 16516 Construction products. Assessment of release of dangerous substances. Determination of emissions into indoor air.

- Cal, M.P., Rood, M.J., Larson, S.M., 1996. Removal of VOCs from humidified gas streams using activated carbon cloth. *Gas Sep. Purif.* 10, 117–121. [https://doi.org/10.1016/0950-4214\(96\)00004-7](https://doi.org/10.1016/0950-4214(96)00004-7)
- Camoni, I., Mucci, N., Foa, V., 1998. Advice of the Italian Cctn on the Health Risk Assessment Relative to Exposure to Automobile Emissions (No. PB-99-117798/XAB; SERIE RELAZIONI--98/3). Istituto Superiore di Sanita, Lab. di Tossicologia Applicata, Roma (Italy); ISPESL, Dipt. di Medicina del Lavoro, Rome (Italy); Milan Univ., Clinica del Lavoro Luigi Devoto (Italy).
- Cardamone, J.M., Yao, J., Nuñez, A., 2004. Controlling Shrinkage in Wool Fabrics: Effective Hydrogen Peroxide Systems. *Text. Res. J.* 74, 887–898. <https://doi.org/10.1177/004051750407401008>
- Carneiro, J.O., Teixeira, V., Portinha, A., Magalhães, A., Coutinho, P., Tavares, C.J., Newton, R., 2007. Iron-doped photocatalytic TiO₂ sputtered coatings on plastics for self-cleaning applications. *Mater. Sci. Eng. B* 138, 144–150. <https://doi.org/10.1016/j.mseb.2005.08.130>
- Carrer, P., Maroni, M., Alcini, D., Cavallo, D., Fustinoni, S., Lovato, L., Visigalli, F., 2000. Assessment through Environmental and Biological Measurements of Total Daily Exposure to Volatile Organic Compounds of Office Workers in Milan, Italy. *Indoor Air* 10, 258–268. <https://doi.org/10.1034/j.1600-0668.2000.010004258.x>
- Carslaw, N., Hathway, A., Fletcher, L., Hamilton, J., Ingham, T., Noakes, C., 2013. Chemical versus biological contamination indoors: trade-offs versus win–win opportunities for improving indoor air quality. *Indoor Air* 23, 173–174. <https://doi.org/10.1111/ina.12030>
- Cassie, A.B.D., 1945. Absorption of water by wool. *Trans Faraday Soc* 41, 458–464.
- Chan, C.-C., Spengler, J.D., Özkaynak, H., Lefkopoulou, M., 1991. Commuter Exposures to VOCs in Boston, Massachusetts. *J. Air Waste Manag. Assoc.* 41, 1594–1600. <https://doi.org/10.1080/10473289.1991.10466955>
- Chapman, G.V., Bradbury, J.H., 1968a. The Chemical Composition of Wool VII. Separation and Analysis of Orthocortex and Paracortex. *Arch. Biochem. Biophys.* 127, 157–163. [https://doi.org/10.1016/0003-9861\(68\)90212-9](https://doi.org/10.1016/0003-9861(68)90212-9)
- Chapman, G.V., Bradbury, J.H., 1968b. The Chemical Composition of Wool VII. Separation and Analysis of Orthocortex and Paracortex. *Arch. Biochem. Biophys.* 127, 157–163. [https://doi.org/10.1016/0003-9861\(68\)90212-9](https://doi.org/10.1016/0003-9861(68)90212-9)
- Chen, T., Kumar, G., Harris, M.T., Smith, P.J., Payne, G.F., 2000. Enzymatic grafting of hexyloxyphenol onto chitosan to alter surface and rheological properties. *Biotechnol. Bioeng.* 70, 564–573. [https://doi.org/10.1002/1097-0290\(20001205\)70:5<564::AID-BIT11>3.0.CO;2-W](https://doi.org/10.1002/1097-0290(20001205)70:5<564::AID-BIT11>3.0.CO;2-W)

- Chen, Y.-S., Liu, H.-S., 2002. Absorption of VOCs in a Rotating Packed Bed. *Ind. Eng. Chem. Res.* 41, 1583–1588. <https://doi.org/10.1021/ie010752h>
- Chi, C., Chen, W., Guo, M., Weng, M., Yan, G., Shen, X., 2016. Law and features of TVOC and Formaldehyde pollution in urban indoor air. *Atmos. Environ.* 132, 85–90. <https://doi.org/10.1016/j.atmosenv.2016.02.043>
- Chiang, Y.-C., Chiang, P.-C., Huang, C.-P., 2001. Effects of pore structure and temperature on VOC adsorption on activated carbon. *Carbon* 39, 523–534. [https://doi.org/10.1016/S0008-6223\(00\)00161-5](https://doi.org/10.1016/S0008-6223(00)00161-5)
- Claeson, A.-S., Levin, J.-O., Blomquist, G., Sunesson, A.-L., 2002. Volatile metabolites from microorganisms grown on humid building materials and synthetic media. *J Env. Monit* 4, 667–672. <https://doi.org/10.1039/B202571J>
- Claeson, A.-S., Nordin, S., Sunesson, A.-L., 2009. Effects on perceived air quality and symptoms of exposure to microbially produced metabolites and compounds emitted from damp building materials. *Indoor Air* 19, 102–112. <https://doi.org/10.1111/j.1600-0668.2008.00566.x>
- Claeson, A.-S., Sandström, M., Sunesson, A.-L., 2007. Volatile organic compounds (VOCs) emitted from materials collected from buildings affected by microorganisms. *J Env. Monit* 9, 240–245. <https://doi.org/10.1039/B614766F>
- Clarisse, B., Laurent, A.M., Seta, N., Le Moullec, Y., El Hasnaoui, A., Momas, I., 2003. Indoor aldehydes: measurement of contamination levels and identification of their determinants in Paris dwellings. *Environ. Res.* 92, 245–253. [https://doi.org/10.1016/S0013-9351\(03\)00039-2](https://doi.org/10.1016/S0013-9351(03)00039-2)
- Clauder, L., Mansour, E., Ormondroyd, G., Pfriend, A., 2015. Emissions from bio-based building products, in: *European Conference on Wood Modification*. Presented at the European Conference on Wood Modification 2015, Helsinki, Finland.
- Cometto-Muñiz, J.E., Cain, W.S., Abraham, M.H., 2004. Detection of single and mixed VOCs by smell and by sensory irritation. *Indoor Air* 14, 108–117. <https://doi.org/10.1111/j.1600-0668.2004.00297.x>
- Cometto-Muñiz, J.E., Cain, W.S., Hudnell, H.K., 1997. Agonistic sensory effects of airborne chemicals in mixtures: Odor, nasal pungency, and eye irritation. *Percept. Psychophys.* 59, 665–674. <https://doi.org/10.3758/BF03206014>
- Cortez, J., Bonner, P.L.R., Griffin, M., 2004. Application of transglutaminases in the modification of wool textiles. *Enzyme Microb. Technol.* 34, 64–72. <https://doi.org/10.1016/j.enzmictec.2003.08.004>
- Costa, N.A., Pereira, J., Ferra, J., Cruz, P., Martins, J., Magalhães, F.D., Mendes, A., Carvalho, L.H., 2013. Scavengers for achieving zero formaldehyde emission of wood-

- based panels. *Wood Sci. Technol.* 47, 1261–1272. <https://doi.org/10.1007/s00226-013-0573-4>
- Couto, S.R., Toca Herrera, J.L., 2006. Industrial and biotechnological applications of laccases: A review. *Biotechnol. Adv.* 24, 500–513. <https://doi.org/10.1016/j.biotechadv.2006.04.003>
- Coward, S., Llewellyn, J., Raw, G., Brown, V., Crump, D., Ross, D., 2001. Indoor air quality in homes in England (No. BR 433). BRE Centre for Safety, Health and Environment, London.
- CSIRO, 2011. Wool fibre structure - CSIROpedia [WWW Document]. CSIROpedia. URL <http://www.csiropedia.csiro.au/display/CSIROPedia/Wool+fibre+structure> (accessed 11.13.13).
- Curling, S.F., Loxton, C., Ormondroyd, G.A., 2012. A rapid method for investigating the absorption of formaldehyde from air by wool. *J. Mater. Sci.* 47, 3248–3251. <https://doi.org/10.1007/s10853-011-6163-7>
- Daoud, W.A., Xin, J.H., 2005. Synthesis of single-phase anatase nanocrystallites at near room temperatures. *Chem. Commun.* 2110–2112. <https://doi.org/10.1039/B418821G>
- Daoud, W.A., Xin, J.H., 2004. Nucleation and Growth of Anatase Crystallites on Cotton Fabrics at Low Temperatures. *J. Am. Ceram. Soc.* 87, 953–955. <https://doi.org/10.1111/j.1551-2916.2004.00953.x>
- Darling, E.K., Cros, C.J., Wargocki, P., Kolarik, J., Morrison, G.C., Corsi, R.L., 2012. Impacts of a clay plaster on indoor air quality assessed using chemical and sensory measurements. *Build. Environ.* 57, 370–376. <https://doi.org/10.1016/j.buildenv.2012.06.004>
- David, H.G., 1968. Studies of the Variability of Some Characteristics of Australian Wool (awb Types 413 and 40) in Auction Lots. *J. Text. Inst.* 59, 513–522. <https://doi.org/10.1080/00405006808660013>
- Davis, E.M., Elabd, Y.A., 2013. Water Clustering in Glassy Polymers. *J. Phys. Chem. B* 117, 10629–10640. <https://doi.org/10.1021/jp405388d>
- De Bortoli, M., Knöppel, H., Pecchio, E., Peil, A., Rogora, L., Schauenburg, H., Schlitt, H., Vissers, H., 1986. Concentrations of selected organic pollutants in indoor and outdoor air in Northern Italy. *Environ. Int.* 12, 343–350. [https://doi.org/10.1016/0160-4120\(86\)90048-6](https://doi.org/10.1016/0160-4120(86)90048-6)
- de Jong, J.I., de Jonge, J., 1952. The reaction of urea with formaldehyde. *Recl. Trav. Chim. Pays-Bas* 71, 643–660. <https://doi.org/10.1002/recl.19520710704>
- de Kluizenaar, Y., Roda, C., Dijkstra, N.E., Fossati, S., Mandin, C., Mihucz, V.G., Hänninen, O., de Oliveira Fernandes, E., Silva, G.V., Carrer, P., Bartzis, J., Bluysen, P.M., 2016.

- Office characteristics and dry eye complaints in European workers—The OFFICAIR study. *Build. Environ.* 102, 54–63. <https://doi.org/10.1016/j.buildenv.2016.03.013>
- Demiruren, A., Burns, R.H., 1955. Resilience of Scoured Wool. *Text. Res. J.* 25, 665–675. <https://doi.org/10.1177/004051755502500801>
- DGNB, 2012. DGNB criteria: environmental quality. Germany.
- Dimitriades, B., 1999. Scientific Basis of an Improved EPA Policy on Control of Organic Emissions for Ambient Ozone Reduction. *J. Air Waste Manag. Assoc.* 49, 831–838. <https://doi.org/10.1080/10473289.1999.10463852>
- Dingle, P., Franklin, P., 2002. Formaldehyde Levels and the Factors Affecting These Levels in Homes in Perth, Western Australia. *Indoor Built Environ.* 11, 111–116. <https://doi.org/10.1177/1420326X0201100206>
- Dong, Y., Bai, Z., Zhang, L., Liu, R., Zhu, T., 2006. Finishing of cotton fabrics with aqueous nano-titanium dioxide dispersion and the decomposition of gaseous ammonia by ultraviolet irradiation. *J. Appl. Polym. Sci.* 99, 286–291. <https://doi.org/10.1002/app.22476>
- Downes, J.G., Mackay, B.H., 1958. Sorption kinetics of water vapor in wool fibers. *J. Polym. Sci.* 28, 45–67. <https://doi.org/10.1002/pol.1958.1202811605>
- Du, A., Koo, D., Theryo, G., Hillmyer, M.A., Cairncross, R.A., 2012. Water transport and clustering behavior in homopolymer and graft copolymer polylactide. *J. Membr. Sci.* 396, 50–56. <https://doi.org/10.1016/j.memsci.2011.12.030>
- Dubey, P.K., Mohiuddin, S.G., Ramesh, D., 1997. Reactions of phthalic anhydride with alcohols. *Asian J. Chem.* 9, 379.
- Dumont, E., Darracq, G., Couvert, A., Couriol, C., Amrane, A., Thomas, D., Andrès, Y., Le Cloirec, P., 2010. Determination of partition coefficients of three volatile organic compounds (dimethylsulphide, dimethyldisulphide and toluene) in water/silicone oil mixtures. *Chem. Eng. J.* 162, 927–934. <https://doi.org/10.1016/j.cej.2010.06.045>
- Dunn, L.A., Weatherall, I.L., 1992. Longitudinal variation in the stress–strain properties of wool fibers. *J. Appl. Polym. Sci.* 44, 1275–1279. <https://doi.org/10.1002/app.1992.070440717>
- Duran, N., Duran, M., 2000. Enzyme applications in the textile industry. *Rev. Prog. Color. Relat. Top.* 30, 41–44. <https://doi.org/10.1111/j.1478-4408.2000.tb03779.x>
- EEA, 2013. Air quality in Europe — 2013 report (No. 9/2013). European Environment Agency, Denmark.
- EPA, 1991. Formaldehyde (CASRN 50-00-0) [WWW Document]. URL <http://www.epa.gov/iris/subst/0419.htm> (accessed 10.14.13).
- European Respiratory Society, 2013. European Lung White book [WWW Document]. ERS - Respir. Health Dis. Eur. URL <http://www.erswhitebook.org/> (accessed 9.6.13).

- Evans, D.J., Denning, R.J., Church, J.S., 2002. Interface of keratin fibres with their environment, in: *Encyclopedia of Surface and Colloid Science*. pp. 2628–2642.
- Evans, D.J., Leeder, J.D., Rippon, J.A., Rivett, D.E., 1985. Separation and analysis of the surface lipids of the wool fiber. *Int. Wool Text. Res. Conf. Proc.* 135–142.
- Every breath we take: the lifelong impact of air pollution, 2016. . The Royal College of Physicians, London.
- Extrand, C.W., 2002. Model for Contact Angles and Hysteresis on Rough and Ultraphobic Surfaces. *Langmuir* 18, 7991–7999. <https://doi.org/10.1021/la025769z>
- Fairbairn, A.S., Reid, D.D., 1958. Air pollution and other local factors in respiratory disease. *Br. J. Prev. Soc. Med.* 12, 94–103.
- Farran, L., Ennos, A.R., Starkie, M., Eichhorn, S.J., 2009. Tensile and shear properties of fingernails as a function of a changing humidity environment. *J. Biomech.* 42, 1230–1235. <https://doi.org/10.1016/j.jbiomech.2009.03.020>
- Favre, E., Clément, R., Nguyen, Q.T., Schaetzel, P., Néel, J., 1993. Sorption of organic solvents into dense silicone membranes. Part 2.—Development of a new approach based on a clustering hypothesis for associated solvents. *J. Chem. Soc. Faraday Trans.* 89, 4347–4353. <https://doi.org/10.1039/FT9938904347>
- Federal Public Service Of Health, Food Chain Safety And Environment, 2012. Royal Decree establishing threshold levels for the emissions to the indoor environment from construction products for certain intended uses.
- Fellin, P., Otson, R., 1994. Assessment of the influence of climatic factors on concentration levels of volatile organic compounds (VOCs) in canadian homes. *Atmos. Environ.* 28, 3581–3586. [https://doi.org/10.1016/1352-2310\(94\)00204-X](https://doi.org/10.1016/1352-2310(94)00204-X)
- Feng, X., Patterson, D.A., Balaban, M., Emanuelsson, E.A.C., 2013. Enabling the utilization of wool as an enzyme support: Enhancing the activity and stability of lipase immobilized onto woolen cloth. *Colloids Surf. B Biointerfaces* 102, 526–533. <https://doi.org/10.1016/j.colsurfb.2012.08.037>
- Finnimore, E.D., Wortmann, F.-J., 1980. A Rapid Method for Determining the Sorption Characteristics of Textile Materials 1. *Text. Res. J.* 50, 659–661. <https://doi.org/10.1177/004051758005001104>
- Finnish Society of Indoor Air Quality and Climate, 2010. Classification of Indoor Environment 2008: Target Values, Design Guidance, and Product Requirements.
- Fisk, W.J., Rosenfeld, A.H., 1997. Estimates of Improved Productivity and Health from Better Indoor Environments. *Indoor Air* 7, 158–172. <https://doi.org/10.1111/j.1600-0668.1997.t01-1-00002.x>
- Folk, J.E., 1977. The epsilon-(gamma-glutamyl) lysine crosslink and the catalytic role of transglutaminase, in: *Advances in Protein Chemistry*. pp. 1–120.

- Franchi, M., Carrer, P., Kotzias, D., Rameckers, E.M. a. L., Seppänen, O., Van Bronswijk, J.E.M.H., Viegi, G., Gilder, J.A., Valovirta, E., 2006. Working towards healthy air in dwellings in Europe. *Allergy* 61, 864–868. <https://doi.org/10.1111/j.1398-9995.2006.01106.x>
- Freddi, G., Tsukada, M., Shiozaki, H., 1999. Chemical modification of wool fibers with acid anhydrides. *J. Appl. Polym. Sci.* 71, 1573–1579. [https://doi.org/10.1002/\(SICI\)1097-4628\(19990307\)71:10<1573::AID-APP5>3.0.CO;2-A](https://doi.org/10.1002/(SICI)1097-4628(19990307)71:10<1573::AID-APP5>3.0.CO;2-A)
- Fuertes, A.B., Marbán, G., Nevskaja, D.M., 2003. Adsorption of volatile organic compounds by means of activated carbon fibre-based monoliths. *Carbon* 41, 87–96. [https://doi.org/10.1016/S0008-6223\(02\)00274-9](https://doi.org/10.1016/S0008-6223(02)00274-9)
- Fujishima, A., Zhang, X., 2006. Titanium dioxide photocatalysis: present situation and future approaches. *Comptes Rendus Chim.* 9, 750–760. <https://doi.org/10.1016/j.crci.2005.02.055>
- Ghosh, A., Collie, S.R., 2014. Keratinous Materials as Novel Absorbent Systems for Toxic Pollutants. *Def. Sci. J.* 64, 209–221. <https://doi.org/10.14429/dsj.64.7319>
- Gilli, G., Scursatone, E., Bono, R., 1994. Benzene, toluene and xylenes in air, geographical distribution in the Piedmont region (Italy) and personal exposure. *Sci. Total Environ.* 148, 49–56. [https://doi.org/10.1016/0048-9697\(94\)90373-5](https://doi.org/10.1016/0048-9697(94)90373-5)
- Girman, J.R., Hadwen, G.E., Burton, L.E., Womble, S.E., McCarthy, J.F., 1999a. Individual volatile organic compound prevalence and concentrations in 56 buildings of the building assessment survey and evaluation (BASE) study. *Indoor Air* 99, 460–465.
- Girman, J.R., Hadwen, G.E., Burton, L.E., Womble, S.E., McCarthy, J.F., 1999b. Individual volatile organic compound prevalence and concentrations in 56 buildings of the building assessment survey and evaluation (BASE) study. *Indoor Air* 99, 460–465.
- Gold, L.S., Sawyer, C.B., Magaw, R., Backman, G.M., De Veciana, M., Levinson, R., Hooper, N.K., Havender, W.R., Bernstein, L., Peto, R., Pike, M.C., Ames, B.N., 1984. A carcinogenic potency database of the standardized results of animal bioassays. *Environ. Health Perspect.* 58, 9–319.
- Gorry, P.A., 1990. General least-squares smoothing and differentiation by the convolution (Savitzky-Golay) method. *Anal. Chem.* 62, 570–573.
- Grace, J.M., Gerenser, L.J., 2003. Plasma Treatment of Polymers. *J. Dispers. Sci. Technol.* 24, 305–341. <https://doi.org/10.1081/DIS-120021793>
- Grosjean, D., Williams, E.L., Grosjean, E., Andino, J.M., Seinfeld, J.H., 1993. Atmospheric oxidation of biogenic hydrocarbons: reaction of ozone with .beta.-pinene, D-limonene and trans-caryophyllene. *Environ. Sci. Technol.* 27, 2754–2758. <https://doi.org/10.1021/es00049a014>

- Guo, H., Lee, S., Chan, L., Li, W., 2004. Risk assessment of exposure to volatile organic compounds in different indoor environments. *Environ. Res.* 94, 57–66. [https://doi.org/10.1016/S0013-9351\(03\)00035-5](https://doi.org/10.1016/S0013-9351(03)00035-5)
- H. A. Barnes, J. F. Hutton, K. Walters, 1989. *An introduction to rheology*. Elsevier Science Publishers, Amsterdam.
- Haly, A.R., Snaith, J.W., 1968. Specific heat studies of various wool–water systems. *Biopolymers* 6, 1355–1377. <https://doi.org/10.1002/bip.1968.360060910>
- Harding, A.W., Foley, N.J., Norman, P.R., Francis, D.C., Thomas, K.M., 1998. Diffusion Barriers in the Kinetics of Water Vapor Adsorption/Desorption on Activated Carbons. *Langmuir* 14, 3858–3864. <https://doi.org/10.1021/la971317o>
- Hartwell, T.D., Pellizzari, E.D., Perritt, R.L., Whitmore, R.W., Zelon, H.S., Sheldon, L.S., Sparacino, C.M., Wallace, L., 1987. Results from the Total Exposure Assessment Methodology (TEAM) study in selected communities in Northern and Southern California. *Atmospheric Environ.* 1967 21, 1995–2004. [https://doi.org/10.1016/0004-6981\(87\)90161-2](https://doi.org/10.1016/0004-6981(87)90161-2)
- Hearle, J.W.S., 2000. A critical review of the structural mechanics of wool and hair fibres. *Int. J. Biol. Macromol.* 27, 123–138. [https://doi.org/10.1016/S0141-8130\(00\)00116-1](https://doi.org/10.1016/S0141-8130(00)00116-1)
- Heine, E., Höcker, H., 1995. Enzyme treatments for wool and cotton. *Rev. Prog. Color. Relat. Top.* 25, 57–70. <https://doi.org/10.1111/j.1478-4408.1995.tb00104.x>
- Helen Briggs BBC, 2014. Air pollution linked to seven million deaths globally [WWW Document]. BBC News. URL <http://www.bbc.co.uk/news/health-26730178> (accessed 4.5.16).
- Hill, C.A.S., 2008. The reduction in the fibre saturation point of wood due to chemical modification using anhydride reagents: A reappraisal. *Holzforschung* 62, 423–428. <https://doi.org/10.1515/HF.2008.078>
- Hill, C.A.S., Keating, B.A., Jalaludin, Z., Mahrtdt, E., 2011. A rheological description of the water vapour sorption kinetics behaviour of wood invoking a model using a canonical assembly of Kelvin-Voigt elements and a possible link with sorption hysteresis. *Holzforschung* 66, 35–47. <https://doi.org/10.1515/HF.2011.115>
- Hill, C.A.S., Norton, A., Newman, G., 2010. The water vapor sorption behavior of flax fibers— Analysis using the parallel exponential kinetics model and determination of the activation energies of sorption. *J. Appl. Polym. Sci.* 116, 2166–2173. <https://doi.org/10.1002/app.31819>
- Hill, C.A.S., Xie, Y., 2011. The dynamic water vapour sorption properties of natural fibres and viscoelastic behaviour of the cell wall: is there a link between sorption kinetics and hysteresis? *J. Mater. Sci.* 46, 3738–3748. <https://doi.org/10.1007/s10853-011-5286-1>

- Hodgson, A.T., Beal, D., McIlvaine, J.E.R., 2002. Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air* 12, 235–242. <https://doi.org/10.1034/j.1600-0668.2002.01129.x>
- Hoffmann, K., Krause, C., Seifert, B., Ullrich, D., 2000. The German Environmental Survey 1990/92 (GerES II): sources of personal exposure to volatile organic compounds. *J. Expo. Anal. Environ. Epidemiol.* 10, 115–125.
- Holcomb, L.C., Seabrook, B.S., 1995. Review: Indoor Concentrations of Volatile Organic Compounds: Implications for Comfort, Health and Regulation. *Indoor Built Environ.* 4, 7–26. <https://doi.org/10.1177/1420326X9500400103>
- Hossain, K.M.G., González, M.D., Lozano, G.R., Tzanov, T., 2009. Multifunctional modification of wool using an enzymatic process in aqueous–organic media. *J. Biotechnol.* 141, 58–63. <https://doi.org/10.1016/j.jbiotec.2009.02.011>
- Huang, H., Haghghat, F., Blondeau, P., 2006. Volatile organic compound (VOC) adsorption on material: influence of gas phase concentration, relative humidity and VOC type. *Indoor Air* 16, 236–247. <https://doi.org/10.1111/j.1600-0668.2005.00421.x>
- Huson, M., Evans, D., Church, J., Hutchinson, S., Maxwell, J., Corino, G., 2008. New insights into the nature of the wool fibre surface. *J. Struct. Biol.* 163, 127–136.
- Ingham, P.E., Causer, S.M., McMillan, R.C., 1994. The role of wool carpets in controlling indoor air pollution. Presented at the Textile Institute Conference, UK.
- ISO, 2011a. ISO 16000-6:2011 - Indoor air -- Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID (Standard). ISO.
- ISO, 2011b. ISO 16000-3:2011 - Indoor air -- Part 3: Determination of formaldehyde and other carbonyl compounds in indoor air and test chamber air -- Active sampling method (Standard). ISO.
- ISO, 2007. ISO 16000-5:2007 - Indoor air -- Part 5: Sampling strategy for volatile organic compounds (VOCs) (Standard). ISO.
- Jeffries, R., 1960. Part I. The sorption of water by celluloses below 100°C. *J. Text. Inst. Trans.* 51, T340–T374. <https://doi.org/10.1080/19447026008659778>
- Johnson, N.A.G., Russell, I., 2008. Advances in wool spinning technology, in: *Advances in Wool Technology*. Elsevier, pp. 86–105.
- Johnsson, B., Roffael, E., Behn, C., 2014. Assessment of lowering formaldehyde release of particleboards using urea as a scavenger by chamber, perforator and flask method. *Int. Wood Prod. J.* 5, 50–54. <https://doi.org/10.1179/2042645313Y.0000000049>
- Jonas, K., Mark, W., Leo, B., 1947. Shrinkproofing and feltproofing of keratinous textile fibers. US2427097 A.

- Jovančić, P., Jocić, D., Molina, R., Juliá, M.R., Erra, P., 2001. Shrinkage Properties of Peroxide-Enzyme-Biopolymer Treated Wool. *Text. Res. J.* 71, 948–953. <https://doi.org/10.1177/004051750107101103>
- Jurvelin, J., Vartiainen, M., Jantunen, M., Pasanen, P., 2001. Personal Exposure Levels and Microenvironmental Concentrations of Formaldehyde and Acetaldehyde in the Helsinki Metropolitan Area, Finland. *J. Air Waste Manag. Assoc.* 51, 17–24. <https://doi.org/10.1080/10473289.2001.10464251>
- Jus, S., Kokol, V., Guebitz, G.M., 2008. Tyrosinase-catalysed coupling of functional molecules onto protein fibres. *Enzyme Microb. Technol.* 42, 535–542. <https://doi.org/10.1016/j.enzmictec.2008.02.012>
- Jus, S., Schroeder, M., Guebitz, G.M., Heine, E., Kokol, V., 2007. The influence of enzymatic treatment on wool fibre properties using PEG-modified proteases. *Enzyme Microb. Technol.*, Selected papers from the 4th International Conference on Textile Biotechnology INTB06 40, 1705–1711. <https://doi.org/10.1016/j.enzmictec.2006.10.001>
- Kan, C.W., Chan, K., Yuen, C.W.M., Miao, M.H., 1998. Surface properties of low-temperature plasma treated wool fabrics. *J. Mater. Process. Technol.* 83, 180–184. [https://doi.org/10.1016/S0924-0136\(98\)00060-0](https://doi.org/10.1016/S0924-0136(98)00060-0)
- Kane, L.E., Alarie, Y., 1978a. Evaluation of sensory irritation from acrolein-formaldehyde mixtures. *Am. Ind. Hyg. Assoc. J.* 39, 270–274. <https://doi.org/10.1080/0002889778507758>
- Kane, L.E., Alarie, Y., 1978b. Sensory Irritation of Select Experimental Photochemical Oxidants. *Arch. Environ. Health Int. J.* 33, 244–250. <https://doi.org/10.1080/00039896.1978.10667343>
- Karus, M., Kaup, M., 2002. Natural Fibres in the European Automotive Industry. *J. Ind. Hemp* 7, 119–131. https://doi.org/10.1300/J237v07n01_10
- Keating, B.A., Hill, C.A.S., Sun, D., English, R., Davies, P., McCue, C., 2013. The water vapor sorption behavior of a galactomannan cellulose nanocomposite film analyzed using parallel exponential kinetics and the Kelvin–Voigt viscoelastic model. *J. Appl. Polym. Sci.* 129, 2352–2359. <https://doi.org/10.1002/app.39132>
- Kilburn, D., Claude, J., Mezzenga, R., Dlubek, G., Alam, A., Ubbink, J., 2004. Water in Glassy Carbohydrates: Opening It Up at the Nanolevel. *J. Phys. Chem. B* 108, 12436–12441. <https://doi.org/10.1021/jp048774f>
- Kim, S.R., Halden, R.U., Buckley, T.J., 2007. Volatile Organic Compounds in Human Milk: Methods and Measurements. *Environ. Sci. Technol.* 41, 1662–1667. <https://doi.org/10.1021/es062362y>

- King, G., Cassie, A.B.D., Baxter, S., 1940. Propagation of temperature changes through textiles in humid atmospheres. *Trans. Faraday Soc.* 35, 445–465. <https://doi.org/10.1039/TF9403500445>
- King, J., Kupferthaler, A., Frauscher, B., Hackner, H., Unterkofler, K., Teschl, G., Hinterhuber, H., Amann, A., Högl, B., 2012. Measurement of endogenous acetone and isoprene in exhaled breath during sleep. *Physiol. Meas.* 33, 413. <https://doi.org/10.1088/0967-3334/33/3/413>
- King, N., Bradbury, J., 1968. The Chemical Composition of Wool V. The Epicuticle. *Aust. J. Biol. Sci.* 21, 375–384.
- Kinney, T., 2014. Wool : master's design thesis (Thesis).
- Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., Engelmann, W.H., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J. Expo. Anal. Environ. Epidemiol.* 11, 231–252.
- Klepeis, N.E., Tsang, A.M., Behar, J.V., 1996. Analysis of the National Human Activity Pattern Survey (NHAPS) respondents from a standpoint of exposure assessment. Final Rpt EPA.
- Knowlton, B.R., Elgarhy, Y., 1991. Method of enhancing the soil- and stain-resistance characteristics of polyamide and wool fabrics, the fabrics so treated, and treating compositions. US5073442 A.
- Knudsen, H.N., Kjaer, U.D., Nielsen, P.A., Wolkoff, P., 1999. Sensory and chemical characterization of VOC emissions from building products: impact of concentration and air velocity. *Atmos. Environ.* 33, 1217–1230. [https://doi.org/10.1016/S1352-2310\(98\)00278-7](https://doi.org/10.1016/S1352-2310(98)00278-7)
- Kohler, R., Dück, R., Ausperger, B., Alex, R., 2003. A numeric model for the kinetics of water vapor sorption on cellulosic reinforcement fibers. *Compos. Interfaces* 10, 255–276. <https://doi.org/10.1163/156855403765826900>
- Koistinen, K., Kotzias, D., Kephelopoulos, S., Schlitt, C., Carrer, P., Jantunen, M., Kirchner, S., McLaughlin, J., Mølhav, L., Fernandes, E.O., Seifert, B., 2008. The INDEX project: executive summary of a European Union project on indoor air pollutants. *Allergy* 63, 810–819. <https://doi.org/10.1111/j.1398-9995.2008.01740.x>
- Krabbenhoft, K., Damkilde, L., 2004. A model for non-fickian moisture transfer in wood. *Mater. Struct.* 37, 615–622. <https://doi.org/10.1007/BF02483291>
- Kreplak, L., Doucet, J., Dumas, P., Briki, F., 2004. New Aspects of the α -Helix to β -Sheet Transition in Stretched Hard α -Keratin Fibers. *Biophys. J.* 87, 640–647. <https://doi.org/10.1529/biophysj.103.036749>

- Krimm, S., 1960. Infrared spectra of high polymers, in: Fortschritte Der Hochpolymeren-Forschung, Advances in Polymer Science. Springer Berlin Heidelberg, pp. 51–172.
- Krzyzanowski, M., Quackenboss, J.J., Lebowitz, M.D., 1990. Chronic respiratory effects of indoor formaldehyde exposure. *Environ. Res.* 52, 117–125. [https://doi.org/10.1016/S0013-9351\(05\)80247-6](https://doi.org/10.1016/S0013-9351(05)80247-6)
- Kubo, I., Masuoka, N., Xiao, P., Haraguchi, H., 2002. Antioxidant Activity of Dodecyl Gallate. *J. Agric. Food Chem.* 50, 3533–3539. <https://doi.org/10.1021/jf011250h>
- Kulkarni, V., Bradbury, J., 1974. The Chemical Composition of Wool XII. Further Studies on Cortical Cells and Macrofibrils. *Aust. J. Biol. Sci.* 27, 383–396.
- Lantto, R., Ellis, J., Fatarella, E., Cortez, J., 2012. Influence of different pretreatments on the accessibility of transglutaminase and tyrosinase to wool fibre proteins. *J. Text. Inst.* 103, 55–63. <https://doi.org/10.1080/00405000.2010.544103>
- LaTorre, C., Bhushan, B., 2006. Investigation of scale effects and directionality dependence on friction and adhesion of human hair using AFM and macroscale friction test apparatus. *Ultramicroscopy* 106, 720–734. <https://doi.org/10.1016/j.ultramic.2005.11.010>
- Lawson, R.B., Adams, C.D., 1999. Enhanced VOC Absorption Using the Ozone/Hydrogen Peroxide Advanced Oxidation Process. *J. Air Waste Manag. Assoc.* 49, 1315–1323. <https://doi.org/10.1080/10473289.1999.10463959>
- LEED | USGBC [WWW Document], 2017. URL <https://new.usgbc.org/leed> (accessed 1.12.18).
- LEED v4 for Homes and Midrise, 2013.
- Levenberg, K., 1944. A method for the solution of certain non-linear problems in least squares. *Q. Appl. Math.* 2, 164–168.
- Li, F.B., Li, X.Z., Ao, C.H., Lee, S.C., Hou, M.F., 2005. Enhanced photocatalytic degradation of VOCs using Ln³⁺-TiO₂ catalysts for indoor air purification. *Chemosphere* 59, 787–800. <https://doi.org/10.1016/j.chemosphere.2004.11.019>
- Li, J., Li, Y., Li, L., Mak, A.F.T., Ko, F., Qin, L., 2009. Preparation and biodegradation of electrospun PLLA/keratin nonwoven fibrous membrane. *Polym. Degrad. Stab.* 94, 1800–1807. <https://doi.org/10.1016/j.polymdegradstab.2009.06.004>
- Li, W.-H., Yue, Q.-Y., Gao, B.-Y., Ma, Z.-H., Li, Y.-J., Zhao, H.-X., 2011. Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions. *Chem. Eng. J.* 171, 320–327. <https://doi.org/10.1016/j.cej.2011.04.012>
- Li, Y., Nguyen, Q.T., Fatyeyeva, K., Marais, S., 2014. Water Sorption Behavior in Different Aromatic Ionomer Composites Analyzed with a “New Dual-Mode Sorption” Model. *Macromolecules* 47, 6331–6342. <https://doi.org/10.1021/ma501097k>

- Liuxue, Z., Xiulian, W., Peng, L., Zhixing, S., 2007. Photocatalytic activity of anatase thin films coated cotton fibers prepared via a microwave assisted liquid phase deposition process. *Surf. Coat. Technol.* 201, 7607–7614. <https://doi.org/10.1016/j.surfcoat.2007.02.004>
- Lizzie Parry Mail Online, 2015. How the AIR in your home could increase your risk of heart disease [WWW Document]. Mail Online. URL <http://www.dailymail.co.uk/health/article-2920391/How-AIR-house-making-ill-drying-washing-using-gas-cooker-15-million-homes-affected-Toxic-Home-Syndrome-increases-risk-heart-disease-cancer.html> (accessed 4.5.16).
- Lorimier, C., Subrenat, A., Le Coq, L., Le Cloirec, P., 2005. Adsorption of Toluene onto Activated Carbon Fibre Cloths and Felts: Application to Indoor Air Treatment. *Environ. Technol.* 26, 1217–1230. <https://doi.org/10.1080/09593332608618600>
- Lstiburek, J., 2002. Residential ventilation and latent loads. *ASHRAE J.* 44, 18.
- Lu, D., 2013a. Evaluating Wool Curtain's Ability to Remove Indoor Formaldehyde: A Full Scale Proof of Concept. University of Texas at Austin.
- Lu, D., 2013b. Evaluating Wool Curtain's Ability to Remove Indoor Formaldehyde: A Full Scale Proof of Concept. University of Texas at Austin.
- Mahal, G.S., Johnston, A., Burns, R.H., 1951. Types and Dimensions of Fiber Scales from the Wool Types of Domestic Sheep and Wild Life. *Text. Res. J.* 21, 83–93. <https://doi.org/10.1177/004051755102100205>
- Maiphetho, L., 2007. Contact dermatitis in the textile industry: allergies in the workplace. *Curr. Allergy Clin. Immunol.* 20, 28–35.
- Makinson, K.R., 1979. Shrinkproofing of wool. M. Dekker.
- Mansour, E., Loxton, C., Elias, R.M., Ormondroyd, G.A., 2014. Assessment of health implications related to processing and use of natural wool insulation products. *Environ. Int.* 73, 402–412. <https://doi.org/10.1016/j.envint.2014.08.004>
- Marchand, C., Bulliot, B., Le Calvé, S., Mirabel, P., 2006. Aldehyde measurements in indoor environments in Strasbourg (France). *Atmos. Environ.* 40, 1336–1345. <https://doi.org/10.1016/j.atmosenv.2005.10.027>
- Marmur, A., 2004. The Lotus Effect: Superhydrophobicity and Metastability. *Langmuir* 20, 3517–3519. <https://doi.org/10.1021/la036369u>
- Marshall, J.G., 1964. A process for the preparation of permono sulphuric acid. GB967951 (A).
- Martí, M., Ramírez, R., Manich, A.M., Coderch, L., Parra, J.L., 2007. Thermal analysis of merino wool fibres without internal lipids. *J. Appl. Polym. Sci.* 104, 545–551. <https://doi.org/10.1002/app.25586>
- Matsuoka, S., 1992. Relaxation Phenomena in Vitrifying Polymers and Molecular Liquids. Hanser Publishers, Munich.

- Matsuoka, S., Hale, A., 1997. Cooperative relaxation processes in polymers. *J. Appl. Polym. Sci.* 64, 77–93. [https://doi.org/10.1002/\(SICI\)1097-4628\(19970404\)64:1<77::AID-APP7>3.0.CO;2-O](https://doi.org/10.1002/(SICI)1097-4628(19970404)64:1<77::AID-APP7>3.0.CO;2-O)
- Maxwell, J.M., Huson, M.G., 2005. Scanning probe microscopy examination of the surface properties of keratin fibres. *Micron* 36, 127–136. <https://doi.org/10.1016/j.micron.2004.10.001>
- McCann, J., Horn, L., Girman, J., Nero, A.V., 1986. Potential Risks from Exposure to Organic Carcinogens in Indoor Air (No. LBL-22474; CONF-8610446-1). Lawrence Berkeley Lab., CA (USA).
- McNeil, S., 2011. Removal of Indoor Air Contaminants by Wool Carpet. AgResearch Lincoln, New Zealand.
- Mead, K., Brylewski, R., 2011. *Passivhaus:Passivhaus Primer: Introduction - An aid to understanding the key principles of the Passivhaus Standard*. BRE Trust.
- Meilert, K.T., Laub, D., Kiwi, J., 2005. Photocatalytic self-cleaning of modified cotton textiles by TiO₂ clusters attached by chemical spacers. *J. Mol. Catal. Chem.* 237, 101–108. <https://doi.org/10.1016/j.molcata.2005.03.040>
- Metz, S.J., van de Ven, W.J.C., Potreck, J., Mulder, M.H.V., Wessling, M., 2005. Transport of water vapor and inert gas mixtures through highly selective and highly permeable polymer membranes. *J. Membr. Sci.* 251, 29–41. <https://doi.org/10.1016/j.memsci.2004.08.036>
- Meyer, B., Boehme, C., 1997. Formaldehyde emission from solid wood. *For. Prod. J.* 47, 45–48.
- Ministère De L'écologie, Du Développement Durable, Des Transports Et Du Logement, 2011. Décret no 2011-321 du 23 mars 2011 relatif à l'étiquetage des produits de construction ou de revêtement de mur ou de sol et des peintures et vernis sur leurs émissions de polluants volatils.
- Mirabedini, S.M., Rahimi, H., Hamedifar, S., Mohsen Mohseni, S., 2004. Microwave irradiation of polypropylene surface: a study on wettability and adhesion. *Int. J. Adhes. Adhes.* 24, 163–170. <https://doi.org/10.1016/j.ijadhadh.2003.09.004>
- Missia, D.A., Demetriou, E., Michael, N., Tolis, E.I., Bartzis, J.G., 2010. Indoor exposure from building materials: A field study. *Atmos. Environ.* 44, 4388–4395. <https://doi.org/10.1016/j.atmosenv.2010.07.049>
- Modelski, S., Kołtuniewicz, A., Witek-Krowiak, A., 2011. Kinetics of VOC absorption using capillary membrane contactor. *Chem. Eng. J.* 168, 1016–1023. <https://doi.org/10.1016/j.cej.2011.01.075>
- Mølhave, L., 1991. Volatile Organic Compounds, Indoor Air Quality and Health. *Indoor Air* 1, 357–376. <https://doi.org/10.1111/j.1600-0668.1991.00001.x>

- Montazer, M., Seifollahzadeh, S., 2011. Enhanced Self-cleaning, Antibacterial and UV Protection Properties of Nano TiO₂ Treated Textile through Enzymatic Pretreatment. *Photochem. Photobiol.* 87, 877–883. <https://doi.org/10.1111/j.1751-1097.2011.00917.x>
- Murphy, R.J., Norton, A., 2008. Life cycle assessments of natural fibre insulation materials. *Natl. Non-Food Crops Cent.-NNFCC* 79.
- Müssig, J., 2010a. Insulation Materials Based on Natural Fibres, in: *Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications*. John Wiley & Sons.
- Müssig, J., 2010b. *Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications*. John Wiley & Sons.
- Müssig, J., Graupner, N., 2010. Technical Applications of Natural Fibres: An Overview, in: *Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications*. John Wiley & Sons.
- National Academy of Sciences, 2004. *Damp Indoor Spaces and Health*. National Academies Press, Washington, D.C.
- NatuHemp - Natural Hemp Insulation [WWW Document], 2018. . Black Mt. Nat. Insul. URL <https://www.blackmountaininsulation.com/products/natuhemp> (accessed 1.23.18).
- Navarri, P., Marchal, D., Ginestet, A., 2001. Activated carbon fibre materials for VOC removal. *Filtr. Sep.* 38, 33–40. [https://doi.org/10.1016/S0015-1882\(01\)80150-6](https://doi.org/10.1016/S0015-1882(01)80150-6)
- Negri, A.P., Cornell, H.J., Rivett, D.E., 1993. A Model for the Surface of Keratin Fibers. *Text. Res. J.* 63, 109–115. <https://doi.org/10.1177/004051759306300207>
- Nesocell Bio [WWW Document], 2018. URL <http://www.nesocell.com/bio.html> (accessed 1.23.18).
- Newns, A.C., 1956. The sorption and desorption kinetics of water in a regenerated cellulose. *Trans. Faraday Soc.* 52, 1533–1545. <https://doi.org/10.1039/TF9565201533>
- Nolte, H., Bishop, D.P., Höcker, 1996. Effects of Proteolytic and Lipolytic Enzymes on Untreated and Shrink-resist-treated Wool. *J. Text. Inst.* 87, 212–226. <https://doi.org/10.1080/00405009608659069>
- Nordon, P., Mackay, B.H., Downes, J.G., McMahon, G.B., 1960. Sorption Kinetics of Water Vapor in Wool Fibers: Evaluation of Diffusion Coefficients and Analysis of Integral Sorption. *Text. Res. J.* 30, 761–770. <https://doi.org/10.1177/004051756003001003>
- NWGA - The National Wool Growers Association [WWW Document], 2016. URL <http://www.nwga.co.za/> (accessed 7.1.16).
- Oh, W.S., Xu, C., Kim, D.Y., Goodman, D.W., 1997. Preparation and characterization of epitaxial titanium oxide films on Mo(100). *J. Vac. Sci. Technol. A* 15, 1710–1716. <https://doi.org/10.1116/1.580925>

- Okubayashi, S., Griesser, U.J., Bechtold, T., 2004. A kinetic study of moisture sorption and desorption on lyocell fibers. *Carbohydr. Polym.* 58, 293–299. <https://doi.org/10.1016/j.carbpol.2004.07.004>
- Ormondroyd, G.A., 2007. An investigation of novel wood protection methods (Ph.D.). University of Wales, Bangor,.
- Ormondroyd, G.A., Curling, S.F., Mansour, E., Hill, C.A.S., 2016. The water vapour sorption characteristics and kinetics of different wool types. *J. Text. Inst.* 108, 1198–1210. <https://doi.org/10.1080/00405000.2016.1224442>
- Otto, D., Molhave, L., Rose, G., Hudnell, H.K., House, D., 1990. Neurobehavioral and sensory irritant effects of controlled exposure to a complex mixture of volatile organic compounds. *Neurotoxicol. Teratol.* 12, 649–652. [https://doi.org/10.1016/0892-0362\(90\)90079-R](https://doi.org/10.1016/0892-0362(90)90079-R)
- Papadopoulos, A.M., 2005. State of the art in thermal insulation materials and aims for future developments. *Energy Build.* 37, 77–86. <https://doi.org/10.1016/j.enbuild.2004.05.006>
- Parida, S.K., Dash, S., Patel, S., Mishra, B.K., 2006. Adsorption of organic molecules on silica surface. *Adv. Colloid Interface Sci.* 121, 77–110. <https://doi.org/10.1016/j.cis.2006.05.028>
- Park, S., Seo, J., 2016. Optimum Installation of Sorptive Building Materials Using Contribution Ratio of Pollution Source for Improvement of Indoor Air Quality. *Int. J. Environ. Res. Public Health* 13, 396. <https://doi.org/10.3390/ijerph13040396>
- Parthasarathy, S., Maddalena, R.L., Russell, M.L., Apte, M.G., 2011. Effect of Temperature and Humidity on Formaldehyde Emissions in Temporary Housing Units. *J. Air Waste Manag. Assoc.* 61, 689–695. <https://doi.org/10.3155/1047-3289.61.6.689>
- Parvinzadeh, M., 2007a. Effect of proteolytic enzyme on dyeing of wool with madder. *Enzyme Microb. Technol.* 40, 1719–1722. <https://doi.org/10.1016/j.enzmictec.2006.10.026>
- Parvinzadeh, M., 2007b. Effect of proteolytic enzyme on dyeing of wool with madder. *Enzyme Microb. Technol.*, Selected papers from the 4th International Conference on Textile Biotechnology INTB06 40, 1719–1722. <https://doi.org/10.1016/j.enzmictec.2006.10.026>
- Patkowska-Sokola, B., Dobrzański, Z., Osman, K., Bodkowski, R., Zygadlik, K., 2009. The content of chosen chemical elements in wool of sheep of different origins and breeds. *Arch Tierz* 52, 410–418.
- Pauling, L., Corey, R.B., 1951. The Pleated Sheet, a New Layer Configuration of Polypeptide Chains. *Proc. Natl. Acad. Sci. U. S. A.* 37, 251–256.
- Periolatto, M., Ferrero, F., Migliavacca, G., 2014. Low temperature dyeing of wool fabric by acid dye after UV irradiation. *J. Text. Inst.* 0, 1–7. <https://doi.org/10.1080/00405000.2013.872324>

- Peter Walker, 2017. Eco-innovative, Safe and Energy Efficient wall panels and materials for a healthier indoor environment (Final project report). University of Bath.
- Peters, D., Bradbury, J., 1976. The Chemical Composition of Wool XV. The Cell Membrane Complex. *Aust. J. Biol. Sci.* 29, 43–56.
- Peters, D., Bradbury, J., 1972. The Chemical Composition of Wool X. Material Digested by Trypsin From Fibres and Cortical Cells. *Aust. J. Biol. Sci.* 25, 1225–1234.
- Petralia, S.A., Vena, J.E., Freudenheim, J.L., Dosemeci, M., Michalek, A., Goldberg, M.S., Brasure, J., Graham, S., 1999. Risk of premenopausal breast cancer in association with occupational exposure to polycyclic aromatic hydrocarbons and benzene. *Scand. J. Work. Environ. Health* 25, 215–221.
- Pierlot, A.P., 1999. Water in Wool. *Text. Res. J.* 69, 97–103. <https://doi.org/10.1177/004051759906900204>
- Poddar, T.K., Majumdar, S., Sirkar, K.K., 1996. Membrane-based absorption of VOCs from a gas stream. *AIChE J.* 42, 3267–3282. <https://doi.org/10.1002/aic.690421127>
- Popa, J., Haghghat, F., 2002. Characterization of the sink effect of VOCs on building materials, with specific emphasis on painted surfaces, in: *Proceedings of 9th Int Conference Indoor Air Qual Climate Monterey CA*. pp. 558–563.
- Popescu, C.-M., Hill, C.A.S., 2013. The water vapour adsorption–desorption behaviour of naturally aged *Tilia cordata* Mill. wood. *Polym. Degrad. Stab.* 98, 1804–1813. <https://doi.org/10.1016/j.polymdegradstab.2013.05.021>
- Popescu, C.-M., Hill, C.A.S., Kennedy, C., 2015. Variation in the sorption properties of historic parchment evaluated by dynamic water vapour sorption. *J. Cult. Herit.* <https://doi.org/10.1016/j.culher.2015.06.001>
- Qi, K., Daoud, W.A., Xin, J.H., Mak, C.L., Tang, W., Cheung, W.P., 2006. Self-cleaning cotton. *J. Mater. Chem.* 16, 4567–4574. <https://doi.org/10.1039/B610861J>
- Quijano, G., Couvert, A., Amrane, A., Darracq, G., Couriol, C., Le Cloirec, P., Paquin, L., Carrié, D., 2011. Potential of ionic liquids for VOC absorption and biodegradation in multiphase systems. *Chem. Eng. Sci.* 66, 2707–2712. <https://doi.org/10.1016/j.ces.2011.01.047>
- Ramshaw, C., Mallinson, R.H., 1981. Mass transfer process. US4283255 A.
- Ranjbar-Mohammadi, M., Arami, M., Bahrami, H., Mazaheri, F., Mahmoodi, N.M., 2010a. Grafting of chitosan as a biopolymer onto wool fabric using anhydride bridge and its antibacterial property. *Colloids Surf. B Biointerfaces* 76, 397–403. <https://doi.org/10.1016/j.colsurfb.2009.11.014>
- Ranjbar-Mohammadi, M., Arami, M., Bahrami, H., Mazaheri, F., Mahmoodi, N.M., 2010b. Grafting of chitosan as a biopolymer onto wool fabric using anhydride bridge and its

- antibacterial property. *Colloids Surf. B Biointerfaces* 76, 397–403.
<https://doi.org/10.1016/j.colsurfb.2009.11.014>
- Reddie, R.N., Nicholls, C.H., 1971. Absorption of Formaldehyde by Wool. *Text. Res. J.* 41, 303–311. <https://doi.org/10.1177/004051757104100403>
- Reiss, R., Ryan, P.B., Tibbetts, S.J., Koutrakis, P., 1995. Measurement of Organic Acids, Aldehydes, and Ketones in Residential Environments and Their Relation to Ozone. *J. Air Waste Manag. Assoc.* 45, 811–822.
<https://doi.org/10.1080/10473289.1995.10467411>
- Reitzig, M., Mohr, S., Heinzow, B., Knöppel, H., 1998. VOC Emissions after Building Renovations: Traditional and Less Common Indoor Air Contaminants, Potential Sources, and Reported Health Complaints. *Indoor Air* 8, 91–102.
<https://doi.org/10.1111/j.1600-0668.1998.t01-2-00004.x>
- Research and Markets, 2011. Natural Fiber Composites Market Trend and Forecast 2011 - 2016: Trend, Forecast and Opportunity Analysis. Research and Markets.
- Riva, A., Algaba, I., Prieto, R., 2002. Dyeing kinetics of wool fabrics pretreated with a protease. *Color. Technol.* 118, 59–63. <https://doi.org/10.1111/j.1478-4408.2002.tb00138.x>
- Roger, J.A., 1989. Acylation of viral and eukaryotic proteins. *Biochem J* 258, 625–638.
- Rogers, G.E., 1959. Electron Microscope Studies of Hair and Wool. *Ann. N. Y. Acad. Sci.* 83, 378–399. <https://doi.org/10.1111/j.1749-6632.1960.tb40914.x>
- Rogers, G.E., Bawden, C.S., 2008. The protein structure of wool and its relation to physical properties, in: *Advances in Wool Technology*. Elsevier, pp. 10–13.
- Rohr, A.C., Shore, S.A., Spengler, J.D., 2008. Repeated Exposure to Isoprene Oxidation Products Causes Enhanced Respiratory Tract Effects in Multiple Murine Strains [WWW Document]. URL <http://informahealthcare.com/doi/abs/10.1080/08958370390229870> (accessed 12.9.13).
- Roux, P.L. le, Speakman, J.B., 1957. The Plasticity of Wool Part III: The Physical and Chemical Causes of Variation. *Text. Res. J.* 27, 1–7.
<https://doi.org/10.1177/004051755702700101>
- RT News, 2016. Smell of death: 99K Europeans die each year from toxic household fumes, study says [WWW Document]. RT Int. URL <https://www.rt.com/news/333311-air-freshener-pollution-study/> (accessed 4.5.16).
- Ryder, M.L., 1984. Medieval Sheep and Wool Types. *Agric. Hist. Rev.* 32, 14–28.
- Sack, T.M., Steele, D.H., Hammerstrom, K., Remmers, J., 1992. A survey of household products for volatile organic compounds. *Atmospheric Environ. Part Gen. Top.* 26, 1063–1070. [https://doi.org/10.1016/0960-1686\(92\)90038-M](https://doi.org/10.1016/0960-1686(92)90038-M)

- Sanongraj, W., Chen, Y., Crittenden, J.C., Destailats, H., Hand, D.W., Perram, D.L., Taylor, R., 2007. Mathematical Model for Photocatalytic Destruction of Organic Contaminants in Air. *J. Air Waste Manag. Assoc.* 57, 1112–1122. <https://doi.org/10.3155/1047-3289.57.9.1112>
- Santayanon, R., Wootthikanokkhan, J., 2003. Modification of cassava starch by using propionic anhydride and properties of the starch-blended polyester polyurethane. *Carbohydr. Polym.* 51, 17–24. [https://doi.org/10.1016/S0144-8617\(02\)00109-1](https://doi.org/10.1016/S0144-8617(02)00109-1)
- Schlossman, M.L., McCarthy, J.P., 1978. Lanolin and its derivatives. *J. Am. Oil Chem. Soc.* 55, 447–450. <https://doi.org/10.1007/BF02911911>
- Schmenger, J., Schmitt, M., 2012. Hair coloring compositions with a non-ammonia alkalizing agent. EP2476405 A1.
- Schroeder, M., Schweitzer, M., Lenting, H.B.M., Guebitz, G.M., 2004. Chemical modification of proteases for wool cuticle scale removal. *Biocatal. Biotransformation* 22, 299–305. <https://doi.org/10.1080/10242420400025794>
- Schultz, A.M., Henderson, L.E., Oroszlan, S., 1988. Fatty Acylation of Proteins. *Annu. Rev. Cell Biol.* 4, 611–647. <https://doi.org/10.1146/annurev.cb.04.110188.003143>
- Schumacher, K., Heine, E., Höcker, H., 2001. Extremozymes for improving wool properties. *J. Biotechnol., Biotechnology in the Textile Industry - Perspectives for the New Millennium* 89, 281–288. [https://doi.org/10.1016/S0168-1656\(01\)00314-5](https://doi.org/10.1016/S0168-1656(01)00314-5)
- Sean Poulter Mail Online, 2016. Air fresheners and scented candles “to blame for pollution in home” [WWW Document]. Mail Online. URL <http://www.dailymail.co.uk/news/article-3457368/Air-fresheners-scented-candles-blame-pollution-home-kills-40-000-year.html> (accessed 4.5.16).
- Seifert, B., 1992. Regulating Indoor Air, in: Knöppel, H., Wolkoff, P. (Eds.), *Chemical, Microbiological, Health and Comfort Aspects of Indoor Air Quality — State of the Art in SBS*, Eurocourses: Chemical and Environmental Science. Springer Netherlands, pp. 311–320.
- Seo, J., Kato, S., Ataka, Y., Chino, S., 2009. Performance test for evaluating the reduction of VOCs in rooms and evaluating the lifetime of sorptive building materials. *Build. Environ.* 44, 207–215. <https://doi.org/10.1016/j.buildenv.2008.02.013>
- Seo, J., Kato, S., Ataka, Y., Yang, J.-H., 2010. Influence of Environmental Factors on Performance of Sorptive Building Materials. *Indoor Built Environ.* 19, 413–421. <https://doi.org/10.1177/1420326X10367298>
- Sexton, K., Adgate, J.L., Church, T.R., Ashley, D.L., Needham, L.L., Ramachandran, G., Fredrickson, A.L., Ryan, A.D., 2005. Children’s Exposure to Volatile Organic Compounds as Determined by Longitudinal Measurements in Blood. *Environ. Health Perspect.* 113, 342–349. <https://doi.org/10.1289/ehp.7412>

- Shamblin, S.L., Hancock, B.C., Zografis, G., 1998. Water vapor sorption by peptides, proteins and their formulations. *Eur. J. Pharm. Biopharm.* 45, 239–247.
- Sharratt, V., Hill, C.A.S., Zaihan, J., Kint, D.P.R., 2010. Photodegradation and weathering effects on timber surface moisture profiles as studied using dynamic vapour sorption. *Polym. Degrad. Stab.* 95, 2659–2662. <https://doi.org/10.1016/j.polymdegradstab.2010.07.011>
- Shen, J., Rushforth, M., Cavaco-Paulo, A., Guebitz, G., Lenting, H., 2007. Development and industrialisation of enzymatic shrink-resist process based on modified proteases for wool machine washability. *Enzyme Microb. Technol.*, Selected papers from the 4th International Conference on Textile Biotechnology INTB06 40, 1656–1661. <https://doi.org/10.1016/j.enzmictec.2006.07.034>
- Shi, J., Han, X., Kelu, Y., 2014. A novel bio-functional finishing agent for wool based on waterborne polyurethane mixed with chitosan. *Text. Res. J.* 40517513517969. <https://doi.org/10.1177/0040517513517969>
- Shurtleff, W., 1933. Method and Apparatus for Purifying. 1937483.
- Sigma-Aldrich, 2017. Molecular Sieves - Technical Information Bulletin [WWW Document]. Sigma-Aldrich. URL <http://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins/al-1430/molecular-sieves.html> (accessed 7.30.17).
- Silva, C.J.S.M., Prabakaran, M., Guebitz, G., Cavaco-Paulo, A., 2005. Treatment of wool fibres with subtilisin and subtilisin-PEG. *Enzyme Microb. Technol.* 36, 917–922. <https://doi.org/10.1016/j.enzmictec.2005.01.017>
- Simoni, M., Lombardi, E., Berti, G., Rusconi, F., Grutta, S.L., Piffer, S., Petronio, M.G., Galassi, C., Forastiere, F., Viegi, G., 2005. Mould/dampness exposure at home is associated with respiratory disorders in Italian children and adolescents: the SIDRIA-2 Study. *Occup. Environ. Med.* 62, 616–622. <https://doi.org/10.1136/oem.2004.018291>
- Skorski, M.R., Esenther, J.M., Ahmed, Z., Miller, A.E., Hartings, M.R., 2016. The chemical, mechanical, and physical properties of 3D printed materials composed of TiO₂-ABS nanocomposites. *Sci. Technol. Adv. Mater.* 17, 89–97. <https://doi.org/10.1080/14686996.2016.1152879>
- Smith, E., Schroeder, M., Guebitz, G., Shen, J., 2010. Covalent bonding of protease to different sized enteric polymers and their potential use in wool processing. *Enzyme Microb. Technol.* 47, 105–111. <https://doi.org/10.1016/j.enzmictec.2010.05.011>
- Smith, M.T., 2010. Advances in Understanding Benzene Health Effects and Susceptibility. *Annu. Rev. Public Health* 31, 133–148. <https://doi.org/10.1146/annurev.publhealth.012809.103646>

- Speakman, J.B., 1944. An analysis of the water adsorption isotherm of wool. *Trans. Faraday Soc.* 40, 6–10.
- Speakman, J.B., 1931. The micelle structure of the wool fibre. *Proc. R. Soc. Lond. Ser. A* 132, 167–191.
- Speakman, J.B., 1929. The rigidity of wool and its change with adsorption of water vapour. *Trans. Faraday Soc.* 25, 92–103. <https://doi.org/10.1039/TF9292500092>
- Speakman, J.B., Stott, M.E., 1936. Part II—The Influence of Drying Conditions on the Affinity of Wool for Water. *J. Text. Inst. Trans.* 27, T186–T190. <https://doi.org/10.1080/19447023608661681>
- Steinemann, A.C., MacGregor, I.C., Gordon, S.M., Gallagher, L.G., Davis, A.L., Ribeiro, D.S., Wallace, L.A., 2011. Fragranced consumer products: Chemicals emitted, ingredients unlisted. *Environ. Impact Assess. Rev.* 31, 328–333. <https://doi.org/10.1016/j.eiar.2010.08.002>
- Stephens, E.R., Darley, E.F., Taylor, O.C., Scott, W.E., 1961. Photochemical reaction products in air pollution. *Int J Air Water Pollut* 4, 100.
- Stewart, R.G., 1988. *Woolscouring and Allied Technology*. Wool Research Organisation of New Zealand.
- Subrenat, A.S., Le Cloirec, P.A., 2006. Volatile Organic Compound (voc) Removal by Adsorption Onto Activated Carbon Fiber Cloth and Electrothermal Desorption: An Industrial Application. *Chem. Eng. Commun.* 193, 478–486. <https://doi.org/10.1080/00986440500191768>
- Sundell, J., Lonnberg, G., Wall, S., Stenberg, B., Zingmark, P.A., 1990. The office illness project in northern Sweden. Part III: A case-referent study of sick building syndrome (SBS) in relation to building. *Indoor Air* 167, 63–638.
- Swift, J.A., Smith, J.R., 2001. Microscopical investigations on the epicuticle of mammalian keratin fibres. *J. Microsc.* 204, 203–211. <https://doi.org/10.1046/j.1365-2818.2001.00957.x>
- Tancrède, M., Wilson, R., Zeise, L., Crouch, E.A.C., 1987. The carcinogenic risk of some organic vapors indoors: A theoretical survey. *Atmospheric Environ.* 1967 21, 2187–2205. [https://doi.org/10.1016/0004-6981\(87\)90351-9](https://doi.org/10.1016/0004-6981(87)90351-9)
- Tappler, P., 2014. *Lüftung 3.0 Bewohnergesundheit und Raumluftqualität in neu errichteten, energieeffizienten Wohnhäusern (Project report No. 819037)*. Österreichisches Institut für Baubiologie und Bauökologie, Austria.
- Technical Committee CEN/TC 351, 2012. *Construction products — Assessment of emissions of regulated dangerous substances from construction products — Determination of emissions into indoor air*.
- Thermafleece, 2013. *Installing Thermafleece in roofs*.

- Thermafleece NatraHemp Insulation [WWW Document], 2018. URL <http://www.thermafleece.com/product/thermafleece-natrahemp> (accessed 1.23.18).
- Thomé, S., 2006. Untersuchungen zur Sorption von Innenraum-Luftschadstoffen durch Wolle (Text.Thesis.Doctoral). RWTH Aachen University.
- Towler, D.A., Gordon, J.I., Adams, S.P., Glaser, L., 1988. The Biology and Enzymology of Eukaryotic Protein Acylation. *Annu. Rev. Biochem.* 57, 69–97. <https://doi.org/10.1146/annurev.bi.57.070188.000441>
- Tsatsaroni, E., Liakopoulou-Kyriakides, M., Eleftheriadis, I., 1998. Comparative study of dyeing properties of two yellow natural pigments—Effect of enzymes and proteins. *Dyes Pigments* 37, 307–315. [https://doi.org/10.1016/S0143-7208\(97\)00069-7](https://doi.org/10.1016/S0143-7208(97)00069-7)
- Tung, W.S., Daoud, W.A., 2011. Self-cleaning fibers via nanotechnology: a virtual reality. *J. Mater. Chem.* 21, 7858. <https://doi.org/10.1039/c0jm03856c>
- UK Government, 2013. Green Deal Framework (Amendment) Regulations 2013.
- University of Western Macedonia, 2006. Prioritization of building materials as indoor pollution sources (BUMA) [WWW Document]. URL <http://www.uowm.gr/bumaproject/> (accessed 10.28.13).
- US Department of Energy, 2014. ASHRAE Standard 62.2. Ventilation and Acceptable Indoor Air Quality in Low-Rise Residential Buildings (Standard). U.S.A.
- US EPA, O., 2012. An Introduction to Indoor Air Quality: Volatile Organic Compounds (VOCs) [WWW Document]. URL <http://www.epa.gov/iaq/voc.html#Standards> (accessed 11.6.13).
- Vachoud, L., Chen, T., Payne, G.F., Vazquez-Duhalt, R., 2001. Peroxidase catalyzed grafting of gallate esters onto the polysaccharide chitosan. *Enzyme Microb. Technol.* 29, 380–385. [https://doi.org/10.1016/S0141-0229\(01\)00404-5](https://doi.org/10.1016/S0141-0229(01)00404-5)
- Vaizoğlu, S.A., Aycan, S., Devenci, M.A., Tuğ, Acer, B., Bulut, B., Bayraktar, U.D., Akyollu, B., Çelik, M., Arslan, U., Akpınar, F., Baris, Z., Arslan, S., Deniz, A., Evci, E.D., Güler, Ç., 2003. Determining Domestic Formaldehyde Levels in Ankara, Turkey. *Indoor Built Environ.* 12, 329–336. <https://doi.org/10.1177/142032603035546>
- Van Der Wal, J.F., Hoogeveen, A.W., Van Leeuwen, L., 1998. A Quick Screening Method for Sorption Effects of Volatile Organic Compounds on Indoor Materials. *Indoor Air* 8, 103–112. <https://doi.org/10.1111/j.1600-0668.1998.t01-2-00005.x>
- Vardoulakis, S., Heaviside, C., 2012. Health Effects of Climate Change in the UK 2012. London: Health Protection Agency.
- Velikov, V., Borick, S., Angell, C.A., 2001. The Glass Transition of Water, Based on Hyperquenching Experiments. *Science* 294, 2335–2338. <https://doi.org/10.1126/science.1061757>
- Ventilation: Approved Document F, 2010.

- von Pettenkofer, M., 1858. *Besprechung allgemeiner auf die Ventilation bezüglicher Fragen.* Cotta, Munich.
- Vrentas, J.S., Vrentas, C.M., 1996. Hysteresis Effects for Sorption in Glassy Polymers. *Macromolecules* 29, 4391–4396. <https://doi.org/10.1021/ma950969I>
- Vrentas, J.S., Vrentas, C.M., 1991. Sorption in glassy polymers. *Macromolecules* 24, 2404–2412. <https://doi.org/10.1021/ma00009a043>
- Waggoner, J.R., Stachnik, M., Weston, T.A., Bryner, M.A., 2002. Construction membrane. US6355333 B1.
- Wainman, T., Zhang, J., Weschler, C.J., Liroy, P.J., 2000. Ozone and Limonene in Indoor Air: A Source of Submicron Particle Exposure. *Environ. Health Perspect.* 108, 1139–1145. <https://doi.org/10.2307/3434825>
- Wålander, R., Ernstgård, L., Johanson, G., Norbäck, D., Venge, P., Wieslander, G., 2005. Acute Effects of a Fungal Volatile Compound. *Environ. Health Perspect.* 113, 1775–1778.
- Wallace, L.A., 2001. Human Exposure to Volatile Organic Pollutants: Implications for Indoor Air Studies. *Annu. Rev. Energy Environ.* 26, 269–301. <https://doi.org/10.1146/annurev.energy.26.1.269>
- Wallace, L.A., 1991. Comparison of risks from outdoor and indoor exposure to toxic chemicals. *Environ. Health Perspect.* 95, 7–13.
- Wallace, L.A., 1989. The exposure of the general population to benzene. *Cell Biol. Toxicol.* 5, 297–314. <https://doi.org/10.1007/BF01795358>
- Wallace, L.A., Ott, W.R., 1982. Personal Monitors: A State-of-the-Art Survey. *J. Air Pollut. Control Assoc.* 32, 601–610. <https://doi.org/10.1080/00022470.1982.10465435>
- Wallace, L.A., Pellizzari, E.D., Hartwell, T.D., Sparacino, C., Whitmore, R., Sheldon, L., Zelon, H., Perritt, R., 1987. The TEAM (Total Exposure Assessment Methodology) Study: personal exposures to toxic substances in air, drinking water, and breath of 400 residents of New Jersey, North Carolina, and North Dakota. *Environ. Res.* 43, 290–307.
- Wallace, L.A., Pellizzari, E.D., Hartwell, T.D., Whitmore, R., Sparacino, C., Zelon, H., 1986. Total exposure assessment methodology (team) study: Personal exposures, indoor-outdoor relationships, and breath levels of volatile organic compounds in New Jersey. *Environ. Int.* 12, 369–387. [https://doi.org/10.1016/0160-4120\(86\)90051-6](https://doi.org/10.1016/0160-4120(86)90051-6)
- Wallace, L., Nelson, W., Ziegenfus, R., Pellizzari, E., Michael, L., Whitmore, R., Zelon, H., Hartwell, T., Perritt, R., Westerdahl, D., 1991. The Los Angeles TEAM Study: personal exposures, indoor-outdoor air concentrations, and breath concentrations of 25 volatile organic compounds. *J. Expo. Anal. Environ. Epidemiol.* 1, 157–192.

- Wang, Q., Fan, X., Hu, Y., Yuan, J., Cui, L., Wang, P., 2009. Antibacterial functionalization of wool fabric via immobilizing lysozymes. *Bioprocess Biosyst. Eng.* 32, 633–639. <https://doi.org/10.1007/s00449-008-0286-5>
- Warburton, F.L., 1947. A Direct Measurement of the Transverse Swelling of Wool Fibres in Water Vapour. *J. Text. Inst. Trans.* 38, T65–T72. <https://doi.org/10.1080/19447024708659290>
- Ward, R.J., Willis, H.A., George, G.A., Guise, G.B., Denning, R.J., Evans, D.J., Short, R.D., 1993. Surface Analysis of Wool by X-Ray Photoelectron Spectroscopy and Static Secondary Ion Mass Spectrometry. *Text. Res. J.* 63, 362–368. <https://doi.org/10.1177/004051759306300609>
- Wargocki, P., Wyon, D.P., Baik, Y.K., Clausen, G., Fanger, P.O., 1999. Perceived Air Quality, Sick Building Syndrome (SBS) Symptoms and Productivity in an Office with Two Different Pollution Loads. *Indoor Air* 9, 165–179. <https://doi.org/10.1111/j.1600-0668.1999.t01-1-00003.x>
- Watt, I.C., 1980. Adsorption-Desorption Hysteresis in Polymers. *J. Macromol. Sci. Part - Chem.* 14, 245–255. <https://doi.org/10.1080/00222338008066635>
- Watt, I.C., 1960a. Kinetic Studies of the Wool-Water System Part I: The Influence of Water Concentration. *Text. Res. J.* 30, 443–450. <https://doi.org/10.1177/004051756003000605>
- Watt, I.C., 1960b. Kinetic Study of the Wool-Water System Part II: The Mechanisms of Two-Stage Absorption. *Text. Res. J.* 30, 644–651. <https://doi.org/10.1177/004051756003000902>
- Watt, I.C., Algie, J.E., 1961. Kinetic Studies of the Wool -Water System Part III: The Mechanism of Sorption at High Water Concentrations. *Text. Res. J.* 31, 793–799. <https://doi.org/10.1177/004051756103100905>
- Watt, I.C., D'Arcy, R.L., 1979. 26—Water-Vapour Adsorption Isotherms of Wool. *J. Text. Inst.* 70, 298–307. <https://doi.org/10.1080/00405007908658854>
- Watt, I.C., D'Arcy, R.L., 1976. Hydration of biopolymers. *J. Polym. Sci. Polym. Symp.* 55, 155–166. <https://doi.org/10.1002/polc.5070550117>
- Wei, W., Ramalho, O., Mandin, C., 2015. Indoor air quality requirements in green building certifications. *Build. Environ.* 92, 10–19. <https://doi.org/10.1016/j.buildenv.2015.03.035>
- Wells, W.F., 1943. Air Disinfection in Day Schools. *Am. J. Public Health Nations Health* 33, 1436–1443.
- Weschler, C.J., 2000. Ozone in Indoor Environments: Concentration and Chemistry. *Indoor Air* 10, 269–288. <https://doi.org/10.1034/j.1600-0668.2000.010004269.x>

- Weschler, C.J., Hodgson, A.T., Wooley, J.D., 1992. Indoor chemistry: ozone, volatile organic compounds, and carpets. *Environ. Sci. Technol.* 26, 2371–2377. <https://doi.org/10.1021/es00036a006>
- Weschler, C.J., Shields, H.C., 1999. Indoor ozone/terpene reactions as a source of indoor particles. *Atmos. Environ.* 33, 2301–2312. [https://doi.org/10.1016/S1352-2310\(99\)00083-7](https://doi.org/10.1016/S1352-2310(99)00083-7)
- WHO, 2013. Health risks of air pollution in Europe – HRAPIE project. Recommendations for concentration–response functions for cost–benefit analysis of particulate matter, ozone and nitrogen dioxide.
- WHO, 2000. The right to healthy indoor air (Report on WHO Meeting No. Bilthoven, Netherlands). WHO.
- Wilson, J.H., Counce, R.M., Lucero, A.J., Jennings, H.L., Singh, S.P., 1992. Air Stripping and Emissions Control Technologies: Field Testing of Countercurrent Packings, Rotary Air Stripping, Catalytic Oxidation, and Adsorption Materials.
- Wissenbach, D.K., Winkler, B., Otto, W., Kohajda, T., Roeder, S., Müller, A., Hoeke, H., Matysik, S., Schlink, U., Borte, M., Herbarth, O., Lehmann, I., von-Bergen, M., 2016. Long-term indoor VOC concentrations assessment a trend analysis of distribution, disposition, and personal exposure in cohort study samples. *Air Qual. Atmosphere Health* 1–10. <https://doi.org/10.1007/s11869-016-0396-1>
- Wojciechowska, E., Włochowicz, A., Weselucha-Birczyńska, A., 1999. Application of Fourier-transform infrared and Raman spectroscopy to study degradation of the wool fiber keratin. *J. Mol. Struct.* 511–512, 307–318. [https://doi.org/10.1016/S0022-2860\(99\)00173-8](https://doi.org/10.1016/S0022-2860(99)00173-8)
- Wolkoff, P., 1999. How to measure and evaluate volatile organic compound emissions from building products. A perspective. *Sci. Total Environ.* 227, 197–213. [https://doi.org/10.1016/S0048-9697\(99\)00019-4](https://doi.org/10.1016/S0048-9697(99)00019-4)
- Wolkoff, P., Clausen, P.A., Jensen, B., Nielsen, G.D., Wilkins, C.K., 1997. Are We Measuring the Relevant Indoor Pollutants? *Indoor Air* 7, 92–106. <https://doi.org/10.1111/j.1600-0668.1997.t01-2-00003.x>
- Wolkoff, P., Clausen, P.A., Larsen, K., Hammer, M., Larsen, S.T., Nielsen, G.D., 2008a. Acute airway effects of ozone-initiated d-limonene chemistry: Importance of gaseous products. *Toxicol. Lett.* 181, 171–176. <https://doi.org/10.1016/j.toxlet.2008.07.018>
- Wolkoff, P., Clausen, P.A., Larsen, K., Hammer, M., Larsen, S.T., Nielsen, G.D., 2008b. Acute airway effects of ozone-initiated d-limonene chemistry: Importance of gaseous products. *Toxicol. Lett.* 181, 171–176. <https://doi.org/10.1016/j.toxlet.2008.07.018>

- Wolkoff, P., Clausen, P.A., Larsen, S.T., Hammer, M., Nielsen, G.D., 2012a. Airway effects of repeated exposures to ozone-initiated limonene oxidation products as model of indoor air mixtures. *Toxicol. Lett.* 209, 166–172. <https://doi.org/10.1016/j.toxlet.2011.12.008>
- Wolkoff, P., Clausen, P.A., Larsen, S.T., Hammer, M., Nielsen, G.D., 2012b. Airway effects of repeated exposures to ozone-initiated limonene oxidation products as model of indoor air mixtures. *Toxicol. Lett.* 209, 166–172. <https://doi.org/10.1016/j.toxlet.2011.12.008>
- Wolkoff, P., Larsen, S.T., Hammer, M., Kofoed-Sørensen, V., Clausen, P.A., Nielsen, G.D., 2007. Respiratory effects of some key ozone-initiated terpene reaction products. *Technology* 43, 3561–3568.
- Wolkoff, P., Nielsen, G.D., 2001. Organic compounds in indoor air—their relevance for perceived indoor air quality? *Atmos. Environ.* 35, 4407–4417. [https://doi.org/10.1016/S1352-2310\(01\)00244-8](https://doi.org/10.1016/S1352-2310(01)00244-8)
- Wolkoff, P., Wilkins, C.K., Clausen, P.A., Nielsen, G.D., 2006. Organic compounds in office environments – sensory irritation, odor, measurements and the role of reactive chemistry. *Indoor Air* 16, 7–19. <https://doi.org/10.1111/j.1600-0668.2005.00393.x>
- Wools of New Zealand [WWW Document], 2016. . Laneve Wools N. Z. URL <http://www.wools-nz.co.uk/index.html> (accessed 7.1.16).
- World Health Organization, 1989. Indoor air quality: Organic pollutants. *Environ. Technol. Lett.* 10, 855–858. <https://doi.org/10.1080/09593338909384805>
- World Health Organization, Regional Office for Europe, 2010. Selected pollutants: WHO guideline for indoor air quality.
- Wortmann, F.-J., Jong, S.D., 1985. Analysis of the Humidity-Time Superposition for Wool Fibers. *Text. Res. J.* 55, 750–756. <https://doi.org/10.1177/004051758505501207>
- Xiao, X., Hu, J., 2016. Influence of Sodium Bisulfite and Lithium Bromide Solutions on the Shape Fixation of Camel Guard Hairs in Slenderization Process. *Int. J. Chem. Eng.* 2016, 1–11. <https://doi.org/10.1155/2016/4803254>
- Xie, Y., Hill, C.A.S., Jalaludin, Z., Curling, S.F., Anandjiwala, R.D., Norton, A.J., Newman, G., 2010. The dynamic water vapour sorption behaviour of natural fibres and kinetic analysis using the parallel exponential kinetics model. *J. Mater. Sci.* 46, 479–489. <https://doi.org/10.1007/s10853-010-4935-0>
- Xie, Y., Hill, C.A.S., Jalaludin, Z., Sun, D., 2011. The water vapour sorption behaviour of three celluloses: analysis using parallel exponential kinetics and interpretation using the Kelvin-Voigt viscoelastic model. *Cellulose* 18, 517–530. <https://doi.org/10.1007/s10570-011-9512-4>
- Xu, W., Ke, G., Wu, J., Wang, X., 2006. Modification of wool fiber using steam explosion. *Eur. Polym. J.* 42, 2168–2173. <https://doi.org/10.1016/j.eurpolymj.2006.03.026>

- Yang, D.K., Koros, W.J., Hopfenberg, H.B., Stannett, V.T., 1985. Sorption and transport studies of water in Kapton polyimide. I. *J. Appl. Polym. Sci.* 30, 1035–1047. <https://doi.org/10.1002/app.1985.070300313>
- Yao, J., Liu, Y., Yang, S., Liu, J., 2008. Characterization of secondary structure transformation of stretched and slenderized wool fibers with FTIR spectra. *J. Eng. Fibers Fabr.* 3, 47.
- Yu, C., Crump, D., 1998. A review of the emission of VOCs from polymeric materials used in buildings. *Build. Environ.* 33, 357–374. [https://doi.org/10.1016/S0360-1323\(97\)00055-3](https://doi.org/10.1016/S0360-1323(97)00055-3)
- Yu, J.-W., Neretnieks, I., 1993. The Effect Of A Passive Adsorption Sheet On Reducing Organic Pollutants In Indoor Air. *Indoor Air* 3, 12–19. <https://doi.org/10.1111/j.1600-0668.1993.t01-3-00003.x>
- Zhang, J., Liou, P.J., He, Q., 1994. Characteristics of aldehydes: concentrations, sources, and exposures for indoor and outdoor residential microenvironments. *Environ. Sci. Technol.* 28, 146–152. <https://doi.org/10.1021/es00050a020>
- Zhao, X.S., Ma, Q., Lu, G.Q. (Max), 1998. VOC Removal: Comparison of MCM-41 with Hydrophobic Zeolites and Activated Carbon. *Energy Fuels* 12, 1051–1054. <https://doi.org/10.1021/ef980113s>
- Zheng, Y., Gao, X., Jiang, L., 2007. Directional adhesion of superhydrophobic butterfly wings. *Soft Matter* 3, 178–182. <https://doi.org/10.1039/B612667G>
- Zimm, B.H., 1953. Simplified Relation Between Thermodynamics and Molecular Distribution Functions for a Mixture. *J. Chem. Phys.* 21, 934–935. <https://doi.org/10.1063/1.1699065>
- Zimm, B.H., Lundberg, J.L., 1956. Sorption of vapors by high polymers. *J. Phys. Chem.* 60, 425–428.
- Zweers, T., Preller, L., Brunekreef, B., Boleij, J. s. m., 1992. Health and Indoor Climate Complaints of 7043 office Workers in 61 Buildings in the Netherlands. *Indoor Air* 2, 127–136. <https://doi.org/10.1111/j.1600-0668.1992.00001.x>