A preliminary study of non-woven fabrics for forensic identification purposes

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Abstract

While traditional woven textiles have been the subject of many forensic investigations, non-woven fabrics have received minimal attention thus far. Given the expansion of commercial applications of non-woven fabrics, a preliminary investigation of household wipes has been carried out to characterise the compositions of these widely available non-woven fabrics. Infrared spectroscopy and thermogravimetric analysis were employed to identify the fibre type and additives of three types of commercial wipes. Polyester and/or viscose fibres were found to be the main components and, along with the identification of binders, enable source types to be differentiated. The predicted different sensitivities of the fibre types to biodeterioration highlights the importance of future environmental studies for the correct characterisation of non-woven fabrics in evidence.

Keywords: non-woven fibres; infrared spectroscopy; thermogravimetric analysis; polyester; viscose.

1. Introduction

Textile materials regularly contribute to evidence collected from crime scenes. Although traditional woven textiles have been more commonly examined for forensic purposes, limited investigations of non-woven fabrics have been carried out to date. While conventional textile fabrics are produced by the weaving of fibres, non-woven fabrics are cost effective web materials that are produced by the bonding of assembled individual fibres[1-4]. Non-woven materials find use in a wide range of household, industrial and medical applications[1,3,5], so there is an increasing likelihood of finding this class of material as physical evidence.

A non-woven material in the form of a household wipe contributed to the physical evidence in the Khandalyce Pearce murder case in Australia[6-8]. In 2015 the skeletal remains of a young child were discovered in a suitcase on the side of a highway in South Australia. Fragments of a household wipe were recovered from the child's mouth and these were shown to be consistent with household wipes purchased by the offender responsible for the death of Khandalyce Pearce. For this case, the originally purchased cloth was identified by the manufacturer as a polyester/viscose blend and it was predicted that the viscose component of the cloth had deteriorated by the time of recovery. The composition of this mixed cloth type demonstrates that an understanding of this material class is important when examining this evidence type.

A broad range of non-woven fabric types are manufactured, depending on the specific end use[1-4]. Natural and synthetic fibres are used to produce commercial non-woven fabrics and the choice of fibre is based on the potential end use. There is a variety of web formation processes, with the choice of process influencing the product performance. Three methods of web formation are commonly used: dry-laid (fibres are mechanically separated and oriented), wet-laid (fibres are mixed with chemicals in water then drained) and spun-laid (also known as polymer-laid, a molten polymer is extruded and cooled to form a web). Bonding methods are commonly used to provide strength and there are three basic types: chemical, mechanical and thermal bonding. Chemical bonding involves the application of a polymer latex or solution to the web that is then thermally cured. During mechanical bonding, friction between entangled fibres provides strength and can be achieved via a variety of approaches, including a hydroentanglement process where high pressure jets of water cause the fibres to interlace (also known as spunlacing). Thermal bonding uses heat to bond suitable fibres or a thermoplastic binder.

For the current study, three varieties of household cleaning wipes were chosen as suitable non-woven fabrics for investigation. Biodegradable and antibacterial versions are marketed in addition to the traditional absorbent clothes. Fabric samples were examined with infrared spectroscopy using attenuated total reflectance (ATR) sampling. Infrared spectroscopy is an established standard technique for the forensic examination of fibres and enables the specific fibre types to be identified as well as simultaneously identifying the presence of many additives or agents used in the manufacturing process[9]. Thermogravimetric analysis (TGA) was also employed in this study to provide supporting compositional analysis. TGA is used to distinguish mass loss steps that correspond to the decomposition of the different material components, thus enabling fibres and any additives to be confirmed.

2. Materials and methods

2.1. Materials

Three types of household cleaning cloths were investigated for this study. Chux Original Superwipes cleaning cloths (Clorox Australia Pty Ltd, Australia) were chosen to represent the 'original' standard composition of this type of commercial product. These cloths were reported by the manufacturer to contain a viscose polyester blend. Chux Biodegradable Superwipes cloths (Clorox Australia Pty Ltd, Australia) were chosen to represent 'biodegradable' cloths and were reported by the manufacturer to be comprised of 97% natural viscose cellulose fibres and 3% synthetic binder. Glitz Antibacterial Wipes (Pascoes Pty Ltd, Australia) were used for the investigation of 'antibacterial' cloth and are reported by the manufacturer to contain the ingredients of regenerated cellulose, poly(ethylene terephthalate) and triclosan, with concentrations for the components not specified. Images of the as received fabrics are shown in Figure 1.

2.2. Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Magna-IR 6700 spectrometer (Thermo Scientific, USA) with an ATR accessory comprised of a diamond crystal with a 45° angle of incidence. The spectra were recorded over a range of 4000-400 cm^{-1}, with a spectral resolution of 4 cm^{-1} and averaged over 128 scans. A minimum of three replicates from different locations on the fabric were collected for each sample.

2.4. Thermogravimetric analysis

TGA was carried out using a Netzsch STA 449 F5 thermobalance configured in TG mode. Samples (6-9 mg) of fabric were cut into 5 mm discs and placed in platinum crucibles. The samples were then heated in a helium purge flowing at 40 mL/min from 40 to 600°C at a heating rate of 2 °C/min.

3. Results and discussion

3.1. Characterisation of biodegradable non-woven fabric

A representative ATR spectrum obtained for the as received biodegradable fabric is illustrated in Figure 2. An inspection of the spectra showed reproducibility for the as received fabrics. The active sampling area for the ATR crystal employed was of the order of 1-2 mm and able to encompass multiple components. The spectrum in Figure 2 shows bands typical of viscose (also commonly referred to as rayon or viscose rayon), a regenerated cellulose fibre[10-13]. A broad band centred at 3330 cm^{-1} is associated with O-H stretching and C-H stretching bands occur in the 3000-2800 cm^{-1} region. The band near 1650 cm^{-1} is an O-H bending mode due to water absorbed by cellulose. Characteristic viscose C-H bending and C-O stretching modes are also observed in the 1500-1200 and 1200-850 cm^{-1} regions, respectively.

Although the biodegradable cloths examined were described by the manufacturer as being comprised of 'natural viscose cellulose fibres', the detail regarding the source of the cellulose was not provided. Viscose is generally produced using soft woods as a source of cellulose. Bamboo has more recently emerged as a cellulose source for viscose production and products made from bamboo are often labelled as 'biodegradable'[14-15]. However, viscose produced from bamboo has been shown to be indistinguishable from that produced using soft woods. As cellulose extracted from all sources is dissolved in sodium hydroxide and carbon disulfide during a standard viscose process, the final product is chemically the same[14-15]. As such, the source of cellulose used in viscose production for non-woven fabrics do not provide a means of distinguishing viscose fabrics.

A carbonyl band at 1730 cm^{-1} is also observed in the biodegradable fabric spectrum and this is attributed to the presence of binder. The band is relatively weak, but as the binder is stated by the manufacturer as representing 3% of the material composition, the observation of weaker bands associated with the binder is as expected. The presence of the carbonyl band indicates that the binder is likely to be an acrylic resin (polymers and copolymers of acrylic and methacrylic acids)[16-17]. Acrylic binders, such as polyacrylate copolymers, are the most popular class as a wide range of compositions are available to produce a broad range of physical properties[4,18].

TGA data collected for the fabrics is presented in Figure 3. The biodegradable fabric produces two mass loss steps in the temperature ranges of 250-350°C and 350-400°C. The associated derivative thermogravimetric (DTG) curve shows two peaks centred at 326 and 375°C. The 326°C peak can be attributed to the degradation of cellulose[19-22]. The thermal decomposition of cellulose in an inert atmosphere involves a complex series of reaction including dehydration, fragmentation, elimination and condensation processes[23-24]. The identification of cellulose supports the presence of viscose as the main component of the biodegradable fabric. The smaller peak observed with a maximum at 375°C can be attributed to an acrylic binder, supporting the prediction of this binder type from the spectroscopic data. Previous studies have demonstrated that a mass loss at this temperature is associated with a main chain degradation of an acrylic binder, including polyacrylate copolymers (e.g. butyl acrylate / methyl methacrylate)[25-26].

3.2. Characterisation of antibacterial non-woven fabric

An ATR spectrum for the as received antibacterial fabric is shown in Figure 4 and is characteristic of a polyester fibre. A strong C=O stretching band at 1710 cm^{-1} and a strong C-H rocking band at 725 cm^{-1}, as well as characteristic patterns of C-O stretching and C-H bending contributions in the 1300-1000 cm^{-1} and 1500-1400 cm^{-1} regions, respectively, demonstrate that the antibacterial fibre is polyester-based[10,27-28]. This observation is in agreement with the manufacturer's stated ingredient of poly(ethylene terephthalate) (PET), the most widely used polyester fibre, reported in the product safety data sheet[29].

Although the manufacturer states that the antibacterial fabric contains regenerated cellulose, the spectra obtained do not provide evidence of the presence of any type of regenerated cellulose, particularly due to a notable lack of characteristic O-H stretching bands in the 3500-3000 cm^{-1} region of the spectrum[10-11]. The percentage compositions of the individual ingredients are not specified by the manufacturer in the associated safety data and the manufacturer describes the chemical nature of the material as a non-woven polyester fabric within the same documentation[29].

The antibacterial fabric is also reported by the manufacturer to contain triclosan, a chlorinated aromatic compound used as an antibacterial agent[30-31]. Previous studies of triclosan on polymer fibres have reported the use of infrared spectroscopy to determine the presence of this agent on surfaces, and report that it is difficult to identify triclosan given the strong overlap with polymer bands, particularly in the fingerprint region of the spectrum[32-33]. Additionally, the low concentration of triclosan means that contributing bands appear relatively weak in the overall spectrum.

The spectrum obtained for the antibacterial fabric and the lack of an additional carbonyl band contribution near 1730 cm^{-1} appearing in the spectrum indicates that this material does not contain a binder. Thus, the antibacterial fabric appears to have been mechanically bonded, rather than chemically bonded[2-3]. Mechanical bonding methods, such as hydroentanglement, enable a non-woven fibre to be produced without the need for chemical binders.

The TG curve for the antibacterial fabric shows a single mass loss between 350-450°C (Figure 3). The DTG curve shows a peak maximum at 405°C. These observations correlate with a decomposition of polyester fibres[34-36]. Polyesters undergo thermal decomposition mainly via both the formation of intramolecular reactions and chain scission. No other processes are observed, confirming a simple composition of polyester fibre.

3.3. Characterisation of original non-woven fabric

Figure 5 illustrates an ATR spectrum obtained for the as received 'original' fabric. The original fabric is comprised of a combination of viscose and polyester[10-12]. Infrared bands that are strong bands in the polyester spectrum, such as the carbonyl band at 1710 cm^{-1}, are observed to be relatively weak compared to the viscose contribution to the original fabric spectrum, indicating that the major component of the fabric is viscose. Such commercial household wipes are generally comprised of approximately 70 w% viscose and 30 w% polyester fibre, however, this ratio can vary depending on the manufacturer. The 1710 cm^{-1} carbonyl band of the polyester in Figure 5 appears as a shoulder on the stronger 1727 cm^{-1} band, attributed to the presence of an acrylic binder[16-17]. Due to the relatively low intensity of the polyester carbonyl band contribution compared to the binder contribution, a polyester contribution of less than 30 w% to the original fabric is likely.

The TG data collected for the original fabric show evidence of three mass loss steps during decomposition (Figure 3). The first mass loss (12%) is observed up to a temperature of 250°C and is attributed to the evaporation of residual absorbed water and/or volatilisation of volatile matter[37-39]. A second mass loss of 48% with a peak of maximum at 326°C is very similar to that observed for the biodegradable fabric and is due to the breakdown of cellulose in the viscose component of the original fabric. The third mass loss step (33%) ranging from 350 to 450°C with a peak maximum at 402°C is attributed to the decomposition of polyester. As this latter peak shows asymmetry, the breakdown of both the acrylic binder and the polyester fibres in the original fabric appear to contribute to this peak. Although it is not possible to obtain an exact quantitative analysis of the original fabric from the thermal data due to the overlap of decomposition processes, it does confirm that viscose is the major component of this fabric type.

3.4 Fibre comparison

A challenge associated with the correct identification of fibre evidence is the potential changes that fibres can undergo as result of ageing and environmental exposure. Commercial non-woven fabrics marketed as 'biodegradable' are, by their very nature, designed to degrade at a faster rate than the traditional counterparts. The use of viscose fibre in the biodegradable fabric under study means an earlier deterioration of this type of fabric compared to synthetic fibre is predicted. The use of viscose fibres provides a suitable medium for the growth of microorganisms[15,40-42].

The antibacterial fabric examined contains only polyester fibres. Polyester fibres are known to be resistant to biodeterioration[40]. PET is comprised of a stable linear aromatic polyester structure that undergoes a very slow biodeterioration process. The nature of the chemical structure inhibits biodeterioration by preventing hydrolytic enzymes produced by microorganisms from attacking the polymer chain[40,43]. In addition, polyester fibres are hydrophobic in nature and the lack of moisture on the fabric surface also inhibits the growth of microorganisms[40,44]. The inclusion of an antibacterial agent into the commercial antibacterial fabric under study is predicted to further delay biodeterioration through the inhibition of bacterial growth on the polyester fabric.

As the original fabric contains both viscose and polyester fibres, longer term changes will impact the identification of the fabric when exposed to environmental factors. In biodegrading environments, the viscose component is predicted deteriorate first, leaving the more stable polyester component over a period of time.

4. Conclusions

This study has demonstrated that variation exists in the material composition of non-woven fabrics that are used to produce readily available commercial household wipes. Infrared spectroscopy is an effective tool for the rapid identification of the main components of non-woven fabrics. Viscose and polyester are the two fibre types identified in household wipes and are readily discriminated. The presence or absence of binders also provide a potential means of discrimination. The many uses of non-woven fibres, ranging from personal wipes to agricultural applications, means that there is an increasing probability of encountering the materials as evidence and a more extensive survey of the fabrics from different manufacturers will provide a beneficial resource.

The identification of polyester and/or viscose components has implications for the longer-term stability of this evidence type. Viscose is more susceptible to degradation compared to the more stable polyester fibres. This differential deterioration of the fabric needs to be considered when identifying the source of non-woven fabrics as evidence. A longitudinal study of non-woven fabrics exposed to outdoor environmental conditions is currently being undertaken to determine the stability of viscose and polyester based non-woven fabrics in order to understand how these factors influence the identification of non-woven fabric evidence.

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Declaration of interest statement

The authors declare no conflicts of interest

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References

1. Albrecht W, Fuchs H, Kittelmann W. Nonwoven fabrics: Raw materials, manufacture, applications, characteristics, testing processes. Weinheim: Wiley-VCH; 2003.

2. Bhat G, Rong H. Biodegradable non-wovens. In Blackburn RS, editor. Biodegradable and sustainable fibres. Cambridge: Woodhead Publishing; 2005. p 310-342.

3. Chapman RA, editor. Applications of nonwovens in technical textiles. Oxford: Woodhead Publishing; 2010.

4. Fahrbach E, Schaut G, Weghmann A. Nonwoven fabrics. In Ley C, editor. Ullmann's encyclopedia of industrial chemistry volume 24. Weinheim: Wiley-VCH; 2012. p 585-608.

5. Chapman R. Nonwoven fabrics, staple fibres. In: Seidel A, editor. Kirk-Othmer encyclopedia of chemical technology. New York: Wiley; 2005.

6. Regina v Holdom (2018) NSWSC 1677.

7. Benny-Morrison A. The lost girls. Sydney: Harper-Collins Publishers; 2019.

8. Cormack L. Gruesome details revealed into how mother and daughter died at the hands of Daniel Holdom. The Sydney Morning Herald. 2018 Sept 28.

9. ASTM Standard E2224-19. Standard guide for forensic analysis of fibres by infrared spectroscopy. West Conshohocken: ASTM International; 2019.

10. Peets P, Kaupmees K, Vahur S, Leito I. Reflectance FT-IR spectroscopy as a viable option for textile fiber identification. Herit Sci 2019;7:93.

11. Colom X, Carrillo F. Crystallinity changes in lyocell and viscose-type fibres by caustic treatment. Eur Polym J 2002;38(11):2225-2230.

12. Carrillo F, Colom X, Suñol JJ, Saurina J. Structural FTIR analysis and thermal characterisation of lyocell and viscose-type fibres. Eur Polym J. 2004;40:2229-2234.

13. Woodings C. Fibres, regenerated cellulose. In: Seidel A, editor. Kirk-Othmer encyclopedia of chemical technology. New York: Wiley; 2003.

14. Nayak L, Mishra SP. Prospect of bamboo as a renewable textile fiber, historical overview, labeling, controversies and regulation. Fash Text 2016;3:2.

15. Brinsko KM. Optical characterisation of some modern "eco-friendly" fibers. J Forensic Sci. 2010;55(4):915-23.

16. Chércoles Asensio R, San Andrés Moya M, de la Roja JM, Gómez M. Analytical characterisation of polymers used in conservation and restoration by ATR-FTIR spectroscopy. Anal Bioanal Chem. 2009;395(7):2081-96.

17. Wiesinger R, Pagnin L, Anghelone M, Moretto LM, Orsega EF, Schreiner M. Pigment and binder concentrations in modern paint samples determined by IR and Raman spectroscopy. Angew. Chem. Int. Ed. 2018;201857:7401-7407.

18. Slone RV. Acrylic ester polymers. In: Seidel A, editor. Kirk-Othmer encyclopedia of chemical technology. New York: Wiley; 2003.

19. Zhou H, Long Y, Meng A, Li Q, Zhang Y. The pyrolysis simulation of five biomass species by hemi-cellulose, cellulose and lignin based on thermogravimetric curves. Thermochim. Acta. 2013;566:36-43.

20. Rojo E, Alonso MV, Dominguez JC, Del Saz-Orozco B, Oliet M, Rodriguez F. Alkali treatment of viscose cellulosic fibers from eucalyptus wood: Structural, morphological, and thermal analysis. J Appl Polym Sci. 2013;130:2198–2204.

21. Liu Q, Lv C, Yang Y, He F, Ling L. Study on the pyrolysis of wood-derived rayon fibre by thermogravimetry–mass spectrometry. J Mol Struct. 2005;733(1–3):193-202.

22. Karacan I, Soy T. Enhancement of oxidative stabilisation of viscose rayon fibres impregnated with ammonium sulfate prior to carbonisation and activation steps. J Appl Polym Sci. 2013;128:1239-1249.

23. Khelfa A, Finqueneisel G, Auber M, Weber JV. Influence of some minerals on the cellulose thermal degradation mechanisms. J Therm Anal Calorim. 2008;92:7957-99.

24. Rajan R, Rainosalo E, Ramamoorthy SK, Thomas SP, Zavašnik J, Vuorinen J, Skrifvars M. Mechanical, thermal and burning properties of viscose fabric composites: Influence of epoxy resin modification. J Appl Polym Sci. 2018;135:46673.

25. Rodrigues LDA, Guerrini LM, Oliveira MP. Thermal and mechanical properties of cationic starch-graft-poly(butyl acrylate-co-methyl methacrylate) latex film obtained by semi-continuous emulsion polymerisation for adhesive application. J Therm Anal Calorim. 2021;146:143–152.

26. Drevelle C, Duquesne S, Le Bras M, Lefebvre J, Delobel R, Castrovinci A, Magniez C, Vouters M. Influence of ammonium polyphosphate on the mechanism of thermal degradation of an acrylic binder resin. J Appl Polym Sci. 2004;94:717-729.

27. Chen Z, Hay JN, Jenkins MJ. FTIR spectroscopic analysis of poly(ethylene terephthalate) on crystallisation. Eur Polym J. 2012;48(9):1586-1610.

28. Chen Z, Hay JN, Jenkins MJ. The thermal analysis of poly(ethylene terephthalate) by FTIR spectroscopy. Thermochim Acta. 2013;552:123-130.

29. Pascoes Pty Ltd, https://www.pascoes.com.au/wp-content/uploads/2019/12/Glitz-Antibacterial-Wipes-ANZ.pdf (accessed August 29, 2022).

30. Morais DS, Guedes RM, Lopes MA. Antimicrobial approaches for textiles: From research to market. Materials. 2016;9(6):498.

31. Chatha SAS, Asgher M, Asgher R, Hussain AI, Iqbal Y, Hussain SM, Bilal M, Saleem F, Iqbal HMN. Environmentally responsive and anti-bugs textile finishes - Recent trends, challenges, and future perspectives. Sci Total Environ. 2019;690:667-682.

32. Orhan M. Triclosan applications for biocidal functionalisation of polyester and cotton surfaces. J. Eng. Fibers Fabr. 2020;15:1-11.

33. Orhan M, Kut D, Gunesoglu C. Improving the antibacterial property of polyethylene terephthalate by cold plasma treatment. Plasma Chem. 2012;32:293-304.

34. Alongi J, Ciobanu M, Tata J, Carosio F, Malucelli G. Thermal stability and flame retardancy of polyester, cotton and relative blend textile fabrics subjected to sol-gel treatments. J Appl Polym Sci. 2011;119(4):1961-1969.

35. Pan Y, Liu L, Song L, Hu Y, Wang W, Zhao H. Durable flame retardant treatment of polyethylene terephthalate (PET) fabric with cross-linked layer-by-layer assembled coating. Polym Degrad Stab. 2019;165:145-152.

36. Cionek CA, Nunes C, Freitas A, Homem N, Muniz E, Amorim T. Degradation study of polyester fibre in swimming pool water. Text Res J. 2021;91(1-2):51-61.

37. Sefain MZ, El-Kalyoubi SF. Thermogravimetric studies of different celluloses. Thermochim Acta. 1984;75(1–2):107-113.

38. Khasbaatar AD, Chun YJ, Choi US. Synthesis and thermal study on viscose rayon succinate coupled with metals and viscose rayon succinic silane. J Ind Eng Chem. 2007;13(7):1109-1116.

39. Mironova M, Makarov I, Golova L, Vinogradov M, Shandryuk G, Levin I. Improvement in carbonisation efficiency of cellulosic fibres using silylated acetylene and alkoxysilanes. Fibers. 2019;7(10):84.

40. Tomsic B, Klemenčič D, Simoncic B, Orel B. Influence of antimicrobial finishes on the biodeterioration of cotton and cotton/polyester fabrics: Leaching versus bio-barrier formation. Polym Degrad Stabil. 2011;96:1286-1296.

41. Szostak-Kotowa J. Biodeterioration of textiles. Int Biodeterior Biodegrad. 2004;53(3):165-170.

42. Park CH, Kang YK, Im SS. Biodegradability of cellulose fabrics. J Appl Polym Sci. 2004;94:248-253.

43. Marten E, Müller RJ, Deckwer WD. Studies on the enzymatic hydrolysis of polyesters. II. Aliphatic-aromatic copolyesters. Polym Degrad Stabil. 2005;88(3):371-381.

44. Montegut D, Indictor N, Koestler RJ. Fungal deterioration of cellulosic textiles: a review. Int Biodeterior. 1991;28(1–4):209-226.

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