Chapter 21
An Investigation of the Degradation of Polymeric Grave Goods in Soil Environments

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Abstract Plastic materials are a source of items that may be located in clandestine grave sites. Knowledge of their type and state of preservation or deterioration may provide a valuable resource for the identification of a victim or perpetrator. This study involves an examination of the effect of the nature of the soil environment on the structural properties of two common polymers, poly(vinyl chloride) and nylon, over a period of 18 months. These polymers represent common types of plastic sheeting and carpet material that may be used to wrap a body. Infrared spectroscopy and scanning electron microscopy have been used to monitor the structural changes that occur to these polymers in a soil environment and degradation mechanisms are proposed.

21.1 Introduction

A clandestine burial may be accompanied by materials such as clothing, other textile material, tools, weapons or even plastic or paper products. Such items may provide valuable information that establishes the identity of a victim or a perpetrator. The nature of a burial environment affects the state of preservation of grave goods (Janaway 1996, 2008). Such materials may be exposed to a variety of conditions, such as differing soil types, climate or exposure to body fluids. The environment to which these materials are exposed may be responsible for the varying degrees of preservation or the rate at which materials degrade in a burial environment. The acceleration or inhibition of the material degradation processes affects the interpretation of a burial site. There have been relatively few reported forensic studies about how the structure of various material types may be specifically affected by soil burial, with much of the reported work involving physical descriptions of the degraded materials.

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Synthetic polymers are used for a variety of purposes and for this study two examples of polymers that might potentially be found at a clandestine burial site are examined. Polymers is in sheet form may be used to wrap a body prior to disposal or burial and a number of case studies have reported the use of plastic shower curtains as a means of covering a body. Shower curtains are commonly manufactured using the polymer poly(vinyl chloride) (PVC). Carpets manufactured using synthetic polymer fibres also provide an example of material used for the disposal of human remains. Nylon is the most common synthetic material used in the manufacture of carpet with nylon 6 and nylon 6,6 being the particular structural types of this polyamide that are widely used for carpet production (Anton and Baird 2005).

For the current study, the effects of various environmental factors on the structural and chemical properties of polymers that can be encountered as grave goods are being investigated. Buried materials have been systematically exhumed from model soil environments, with parameters including soil type and moisture content being controlled. Analytical techniques, including infrared spectroscopy and scanning electron microscopy are being employed to examine the exhumed specimens.

21.2 Materials and Methods

Model soil environments were prepared in sealed polyethylene boxes with ventilation holes inserted above soil level. Five environments were prepared for the current study: loam soil, a 50:50 clay: loam soil mixture, sand, wet soil and dry soil. Commercially obtained loam soil, builder's clay and river sand were used to produce the model environments. The reference soil environment was established using loam soil at pH 7 and 'as received' moisture content. The wet soil environment was created by the addition of distilled water and this was monitored using a moisture meter with additional portions of distilled water been added when necessary. The dry soil environment was established by placing loam soil in a vacuum oven at 60 °C for 12 h. Commercial plasticised PVC sheeting of 70 μm thickness was cut into 5 × 20 cm pieces and buried in each soil environment. A preliminary study of nylon carpet (comprised of 0.4 mm × 10 mm fibre bundles) was carried out on the burial of 5 × 20 cm pieces in a wet environment. All specimens were buried at a depth of 5 cm below the surface (total depth 10 cm). The boxes were stored at room temperature in the dark. Sampling was carried out on a 3 month basis for a period of 18 months. Exhume specimens were rinsed with distilled water to remove residual soil. Following air-drying, the specimens were stored in polyethylene bags prior to analysis.

PVC specimens were analysed using a Nicolet Magna IR 6700 Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector. The specimens were examined using an attenuated total reflectance (ATR) sampling accessory. The spectra were recorded over a range of 4000–500 cm^{-1} and 128 scans were collected with a resolution of 4 cm^{-1}. Samples were repeated in duplicate. Nylon samples were analysed using a Cary 630 Fourier transform infrared spectrometer and sampled using a diamond ATR accessory. The spectra were recorded over a range of 4000–600 cm^{-1} and 32 scans were collected with a resolution of 2 cm^{-1}. Samples were repeated in duplicate.

A FEI Quanta 200 ESEM and a Zeiss Evo SEM was used for the qualitative analysis of the surface morphology of the polymer specimens. Specimens were secured onto the sample holder using a carbon tab. Both instruments had an accelerating voltage of 20 kV using H_2O as the chamber gas. The FEI Quanta 200 was used with a spot size of 4.0 and pressure of 130 Pa while the Zeiss Evo was used with a spot size of 5.0 and pressure of 105 Pa.

21.3 Results and Discussion

21.3.1 Poly(Vinyl Chloride)

Figure 21.1a illustrates the infrared spectrum of the PVC film prior to burial. The spectrum shows representative bands associated with the polymer itself, as well as distinctive bands associated with the plasticiser content. Typically PVC sheeting contains about 10–30 % plasticiser content in order to introduce flexibility into the polymer. The spectrum shows bands associated with bis(2-ethylhexyl) phthalate, a common phthalate ester plasticiser. Characteristic plasticiser bands are observed at 1070, 1120, 1465, 1578 and 1595 cm^{-1} and a strong band due to C=O stretching at 1720 cm^{-1} (Marcilla et al. 2008; ASTM Standard D2124 2011; Muralisrinivarasan 2012). Infrared analysis of an extract of the plasticiser from the PVC into tetrahydrofuran was used to confirm the identity of the plasticiser as bis(2-ethylhexyl) phthalate as observed in Fig. 21.1b. The fingerprint region of the plasticised PVC spectrum below 1500 cm^{-1} is complex with overlapping plasticiser and polymer bands,

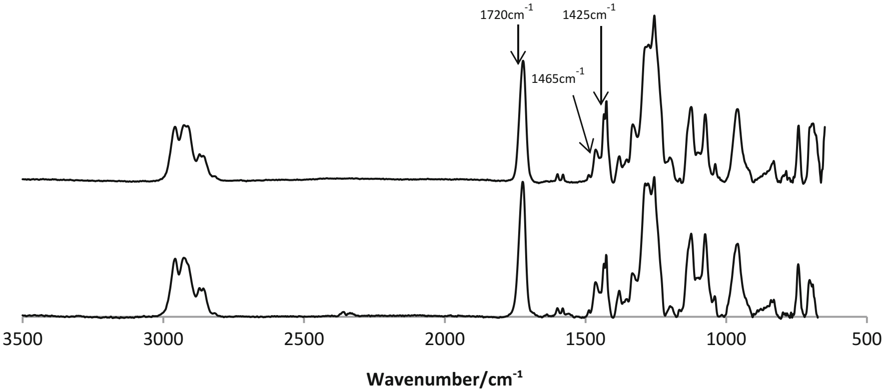

Fig. 21.1a FTIR spectra of PVC prior to burial (*bottom*) and after burial in a wet soil environment for 12 months (*top*)

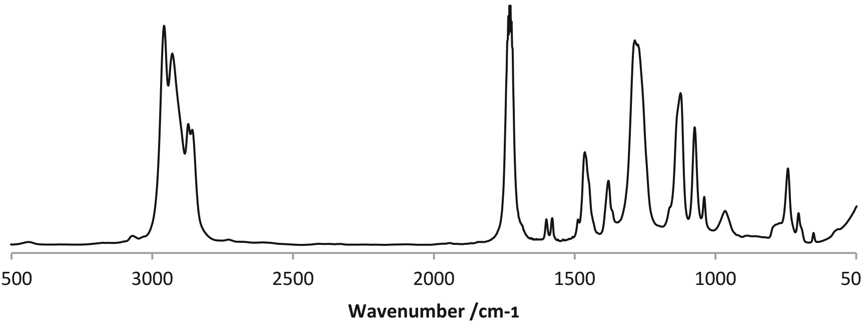

Fig. 21.1b FTIR spectra of bis(2-ethylhexyl) phthalate plasticizer in PVC

but there are bands at 955 and 1425 cm^{-1} that may be assigned to the polymer structure (Ramesh et al. 2007; Marcilla et al. 2008; Muralisrinivarasan 2012) Weak bands are also observed near 2300 cm^{-1} in the spectrum of the PVC sheeting prior to burial. These may be attributed to a phosphate ester, which are commonly used in PVC formulations as flame retardants (Berard et al. 2005). These bands are not observed in the PVC after burial.

Inspection of the spectra collected for different burial environments reveals changes to the plasticiser bands as a function of burial duration. An example spectrum is illustrated in Fig. 21.1a, showing the spectrum of PVC buried in wet soil for 12 months. The ratio of the absorbance of the 1720 cm^{-1} plasticiser band relative to the 1425 cm^{-1} PVC band decreases with burial time in each environment (Fig. 21.2). The principal plasticiser bands at 1720 and 1465 cm^{-1} have been referenced to a 1425 cm^{-1} polymer band as these bands are relatively clear of overlap with adjacent bands. However, the slopes obtained for each plot do vary according to environment and the results are summarised in Table 21.1. The slopes for the 1720/1425 plots for the wet, clay and sand environments indicate a sharper decline in plasticiser content compared to the reference and dry environments. The presence of water in the soil appears responsible for the loss of at least surface plasticiser (ATR spectroscopy samples the sample to a micrometre level), with the rate of removal more than doubled compared to the reference soil as determined from the relative slopes of the decrease in the 1720 cm^{-1} band with time. The plasticiser is not water soluble so is not being dissolved in the moisture present in the soil environment – further experimentation is required to determine the nature of the loss mechanism (e.g. enhanced microbial activity). The clay and sand environments, which also show a greater rate of reduction in the plasticiser content, are potentially capable of retaining a greater degree of moisture than the reference soil, so water is connected to the mechanism responsible for the removal of surface plasticiser. The dry environment with moisture removed shows similar behaviour to the reference soil.

There is also an indication that the 1465/1425 cm^{-1} ratios decrease with burial time and are similarly dependent on soil environment, although the changes to this ratio are less distinct than those observed for the 1720/1425 ratio. The 1465/1425

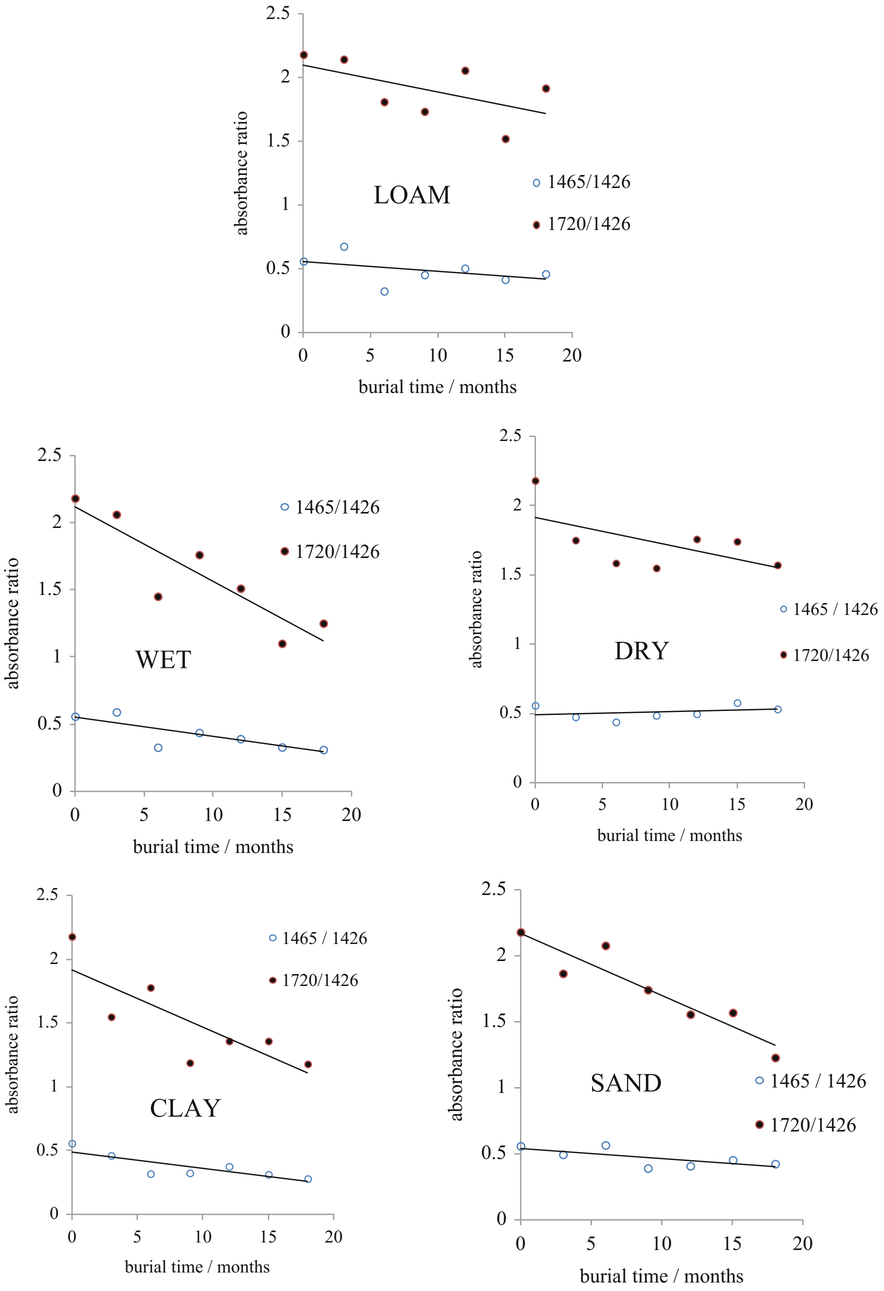

Fig. 21.2 Infrared absorbance ratios as a function of burial time for PVC specimens

Table 21.1 Slopes of absorbance ratios versus burial time plots for PVC specimens

Burial environment	1720/1426 cm^{-1} ratio	1465/1426 cm^{-1} ratio
Loam	−0.021	−0.008
Wet	−0.055	−0.014
Dry	−0.020	0.002
Clay	−0.045	−0.013
Sand	−0.047	−0.008

ratio plots are also shown in Fig. 21.2 and the slopes calculated for each plot are listed in Table 21.1. It is noted that the slopes produced by the different ratio calculations differ in each environment, but this is likely to be a consequence of the measurement of different penetration depths at the 1720 and 1495 cm^{-1} bands in the ATR spectra: there is a greater penetration depth at 1495 cm^{-1}. The observation of different slopes may provide an indication that there is a higher concentration of plasticiser at the polymer surface.

The loss of plasticiser is recognised as a PVC degradation process known to occur due to an increase in temperature (Murase et al. 1994; Jakubowicz et al. 1999). The process has been shown to be linear with time when the process is due to evaporation. It is noted that there is no indication of the other main degradation process associated with PVC, in particular, dehydrochlorination. Such a mechanism involves the loss of chlorine and the formation of C=C bonds (Singh and Sharma (2008). No changes in the 1680 cm^{-1} region due to the appearance of the C=C bond in the spectra obtained in the current study were observed so there is no indication of dehydrochlorination in these environments in the time frame studied.

Changes to the surface morphology of the polymer surface have been examined using SEM. A typical micrograph of the PVC prior to burial is shown in Fig. 21.3. The surface appears smooth with minimal variation in texture across the surface. A micrograph is also shown in Fig. 21.3 of the surface of PVC after burial in clay soil for 18 months. A notable change in surface texture is observed, with variation illustrated by patches if lighter regions distributed across the surface of the polymer. These regions may correlate with areas of plasticiser loss at the surface as loss of this additive is likely to result in a change in surface texture. The presence of very small bright spots is believed to be residual particles remaining from soil contact.

21.3.2 Nylon

A preliminary investigation of the effect on nylon carpet fibres of burial in wet soil has been carried out. Figure 21.4 illustrates SEM images obtained for a nylon fibre prior to burial and one exposed to wet soil for 18 months. The fibre prior to burial is smooth and even in texture. After wet burial, regions of polymer surface with an apparently rougher texture are observed to be distributed on the fibre surface. Such regions are indicative of surface modification and similar changes have been

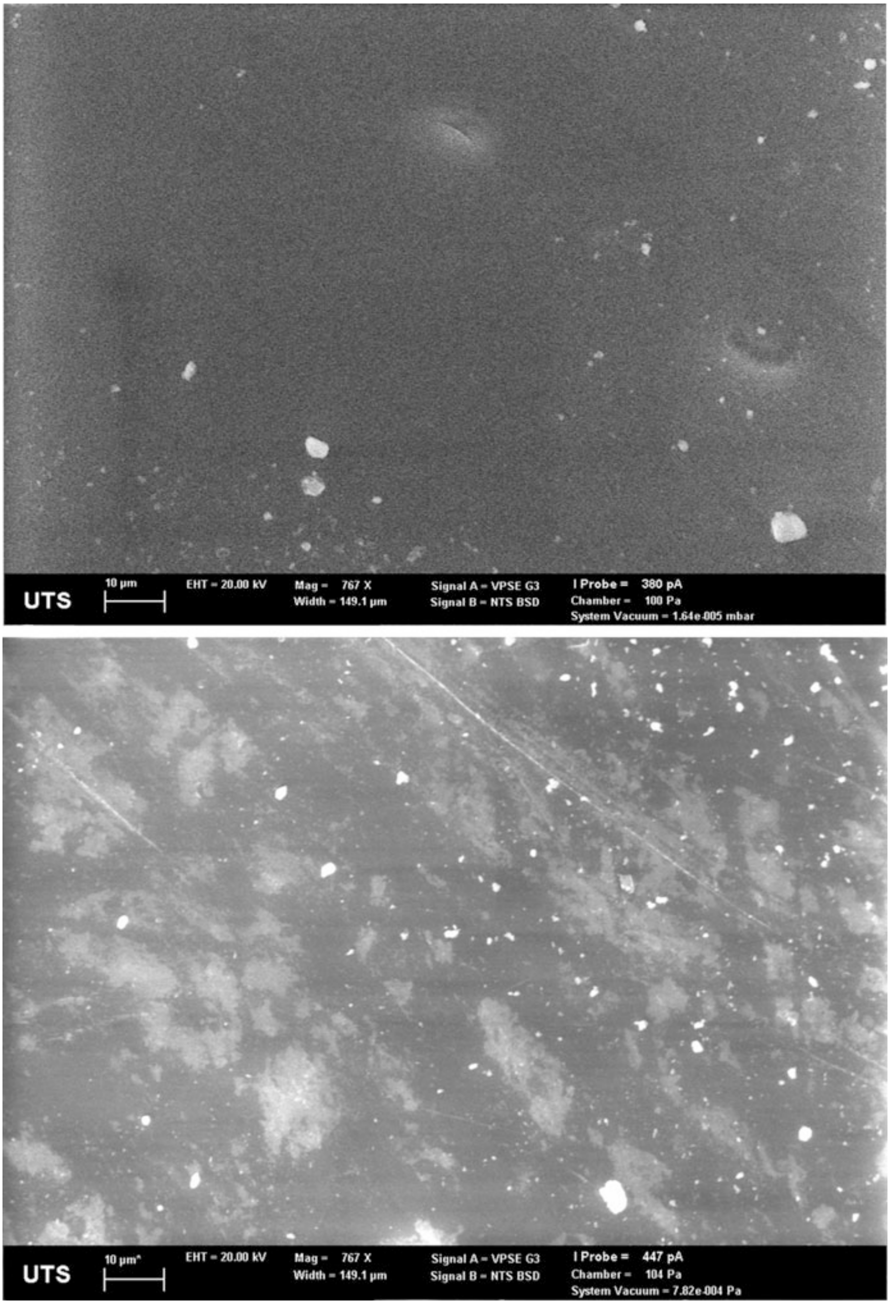

Fig. 21.3 Scanning electron micrographs (767x magnification, horizontal field width of 149 µm) of PVC fibre prior to burial (*top*) and after burial in a clay environment for 18 months (*bottom*)

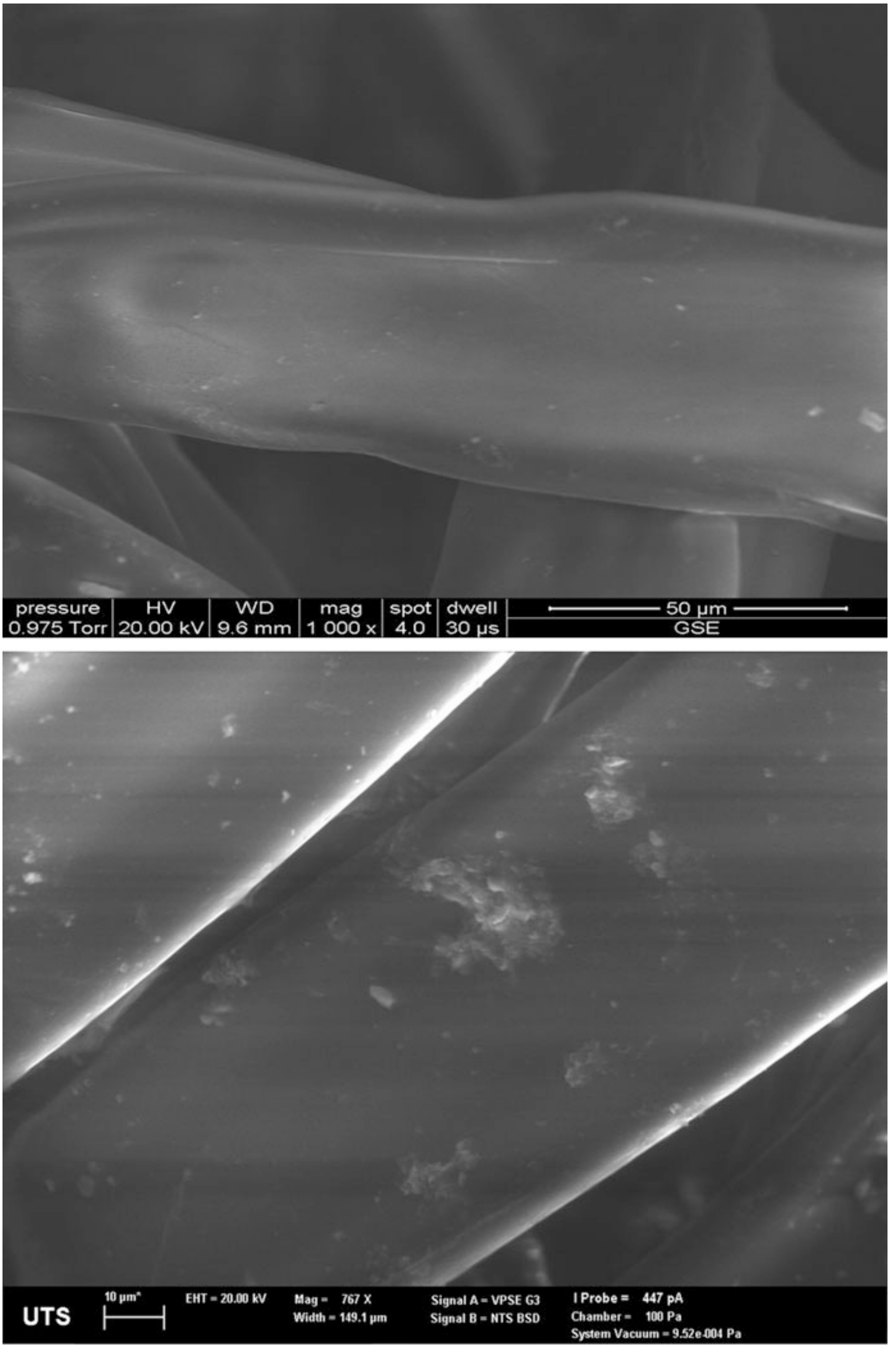

Fig. 21.4 Scanning electron micrographs of nylon fibre prior to burial (*top*; 1000x magnification, horizontal field width of 149 μm) and after burial in a wet environment for 18 months (*bottom*; 767x magnification, horizontal field width of 149 μm)

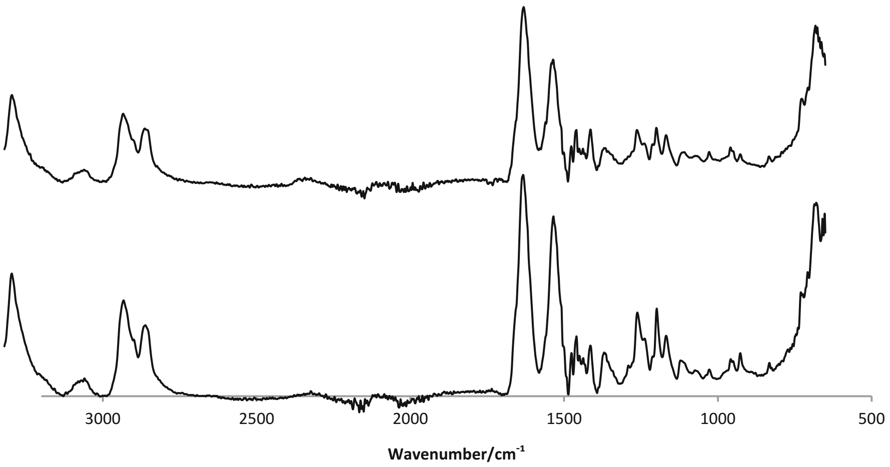

Fig. 21.5 FTIR spectra of nylon fibres prior to burial (*bottom*) and after burial in wet soil for 18 months (*top*)

reported for degraded nylon resulting from exposure to proteolytic enzymes (Parvinzadeh et al. 2009).

The FTIR spectrum of nylon after exposure to 18 months burial in wet soil, as well as the spectrum for nylon prior to burial, is illustrated in Fig. 21.5. There are some minor changes to the spectrum after exposure to wet soil. There are decreases in the intensity of bands at 1370, 1180 and 1140 cm^{-1} that are attributed to C-N-H, CH_2-NH and C-O deformations, respectively (Goncalves et al. 2007). A decrease in intensity of the combination band (N-H deformation and C-N stretching) at 3080 cm^{-1} is also observed after burial. Such spectral changes have been associated with the oxidation of the nylon structure via the amide nitrogen (Mikolajewski et al. 1964; Goncalves et al. 2007). It is also noted that the ratio of the intensities of the amide I (predominantly C=O stretching) and II (N-H bending and C-N stretching) bands at 1630 and 1535 cm^{-1}, respectively, changes after exposure to the wet soil environment. A change to this ratio has been associated to changes in the nature of the hydrogen bonding in nylon (Iwamoto and Murase 2003). It is noted that a band near 1680 cm^{-1} is not noted in the spectrum of the buried nylon. Observation of such a band is known to indicate nylon oxidation (Colin et al. 1981).

The changes observed to the nylon carpet fibres remain relatively minor after 18 months exposure to wet soil. Although nylon is known to absorb water after long term exposure to moisture, consideration should be given to the surface treatment of the fibres during manufacture. Nylon carpets are chemically treated to promote stain resistance as, despite this polymer's attractive physical properties for use in carpets, they are susceptible to staining. The stainblockers used are typically formaldehyde polycondensates of sulfonated, substituted phenols or naphthols (Burkinshaw and Son 2008). The presence of such agents may be responsible for inhibiting the changes to the nylon structure and the nature of pre-treatments will be considered in further studies.

21.4 Conclusions

This study has demonstrated the potential of infrared spectroscopy as a technique for characterising and monitoring the changes to polymer based materials buried in a variety of soil environments. For the time frame studied, the main mechanism for change to buried PVC is the loss of plasticiser and the rate of loss appears to be associated with nature of soil environment (i.e. wet or dry, loam, clay or sand). A more detailed statistical study is being carried out in order to test the validity of these trends. A preliminary study of nylon exposed a wet soil environment has indicated that long term burial can result in an oxidation process that can be monitored by infrared spectroscopy. The burial of nylon in a wider range of environments is also being investigated. Other analytical techniques including thermal analysis are also being employed to gain more a more complete picture of the changes to the polymers as a result of burial.

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