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# Fourier transform infrared analysis of poly(ester-urethanes) at low temperature *in-situ* by using a newly constructed liquid nitrogen cooled sample stage

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The design and use of an apparatus intended to cool samples for *in-situ* Fourier transform infrared (FTIR) spectroscopy study is described. Using liquid nitrogen as the cooling medium, a working sample temperature of $-165\,^{\circ}$C was achieved. The combination of the cooling stage and FTIR spectroscopy allowed us to study the hydrogen bonding in polyurethanes at very low temperatures *in-situ*. Experimental results in the N–H and carbonyl absorption regions as a function of temperature are compared.

## 1. Introduction

The analysis of polymers by spectroscopic means has had a great impact on the development of specific structure–property relationships in materials. Many spectroscopic techniques are now applied to the structural characterization of polymers. In this study, the structure of polyesterurethanes was investigated using Fourier transform infrared spectroscopy (FTIR) and an attempt was made to perform an *in-situ* study on the effect of low temperature on the structure of polyurethane.

Although other characterization methods have been used, infrared spectroscopy seems to be uniquely appropriate for analysing the complex chemical and morphological structures that make up polyurethanes.

Analysis of characteristic group frequencies in a spectrum allows qualitative estimates of chemical composition in polymers and co-polymers. Structural factors such as branching or crosslinking can also be measured. IR analysis yields further structural information, concerning steric and conformational order in a polymer chain. In addition, the nature and quantity of any additives in a polyurethane can also be determined. These techniques have been extensively applied and the broad scope of infrared applications to polymeric materials has been expanded with the introduction of Fourier transform infrared spectroscopy [1, 2].

The behaviour of most of the polymeric materials is determined by the characteristic viscoelastic responses of the families of linear and amorphous, semicrystalline and crosslinked polymer materials. These families are well documented by their modulus versus temperature profiles [3, 4]. Polymers have different properties above and below the transition temperature ($T_g$). Polyurethanes are extensively hydrogen bonded and have been widely studied and thus appear to be an ideal material to obtain spectral information on hydrogen bonding at low temperatures. Polyurethanes are segmented block co-polymers, composed of alternating soft and hard blocks, that have different transition temperatures which results in versatile physical properties. This versatility is mainly due to the varying amounts of hydrogen bonding present within the polyurethanes. A number of investigators have studied hydrogen bonding using FTIR spectroscopy at high temperature but no similar low temperature data has been reported in the literature [3–14].

In this study, the polyurethanes have been *in-situ* analysed in the transmittance mode at low temperature.

## 2. Experimental procedure

A cooling sample stage was designed and constructed which was intended to cool thin film samples *in-situ*. Using liquid nitrogen as the cooling medium, a working sample temperature of at least $-100\,^{\circ}$C was expected, although a temperature as low as $-150\,^{\circ}$C was thought to be possible.

### 2.1. The liquid nitrogen sampling stage

The design of the cooling stage hinges around the basic idea that heat will be removed from a sample by conduction when it is in contact with a block of liquid nitrogen cooled aluminium. To cool the aluminium, part of the sample block is extended into the liquid nitrogen reservoir. This was accomplished by inverting a small Dewar flask and fabricating a sample block so

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that together with a silicone plug, it sealed the reservoir. The reservoir is filled and vented through two pipes machined to pass through the sample block and then rise to the top of the reservoir. These pipes are connected with two flexible tubes that pass to the top of the stage.

When the stage is in position on the bench the sample block hangs down into the path of the infrared beam, which passes through the sample block by means of a 17 mm diameter hole drilled horizontally through it. This hole is intersected by a thin vertical slot designed to accept a sample slide, so that a sample film may be placed in the beam path.

The entire arrangement especially the sample block is insulated by a 20–30 mm layer of styrene foam. The outer case was made by vacuum forming 3 mm Acrylonitrile butadiene styrene, ABS, over a suitable form and it supports both the filling and venting tube ends. The sample holder, the slide, was fabricated in aluminium and has a hole drilled through it matching that in the sample block. The slide was made in two halves between which the thin film sample is mounted. A type T thermocouple and a digital thermometer were used to monitor the temperature.

## 2.2. Sample preparation

A poly(ester-urethane) based on poly(tetramethylene adipate) glycol (PTAG) as the soft segment, biphenyl methane diisocyanate (MDI) and butane diol (BD) as the hard block were used in this study. The procedure for the synthesis of polyurethane has been described elsewhere [5]. Thin films, (0.05–0.07 mm thick) were prepared by casting from a 3 wt% solution of the polymer in tetrahydrofuran (THF). Films were cast onto glass slides (25 × 75 mm) which had been previously cleaned and deactivated by washing in a detergent, rinsing in distilled water, then wiping with THF solvent to remove any further contamination. The polymer solution was applied to the glass slides using a glass micropipette. Each slide was flooded with approximately equal amounts of solution, so that the resulting films would have a similar thickness. Once a slide had been flooded, it was covered with a glass petri dish to allow a slow rate of THF evaporation to occur. At least 36 h were required for evaporation of most of the solvent. The polymer films were removed from the slides by simple peeling or by flotation over distilled water. After removal all films were dried under vacuum at room temperature over silica gel for a period of at least one week (7–10 days).

## 2.3. Test procedure

Prior to fitting the cooling stage into the optical bench, the film sample is placed in the sample slide-holder which is then pushed into position. The thermocouple is adjusted so that it makes contact with the surface of the sample. With external dimensions of 160 × 300 × 110 mm the infrared cooling stage is easy to handle and locates firmly and positively in the open window on the top of bench's door.

Fourier Transform Infrared analysis was carried out using a Nicolet 800 FTIR instrument, purged with compressed, filtered and carbon dioxide free air and equipped with a Mercury cadmium telluride, MCT, type detector. Spectra were obtained in transmission mode on all the cast films using 32 scans with a 4 $\mathrm{cm}^{-1}$ resolution, a gain of 1 and a velocity of 30 $\mathrm{mm\,s}^{-1}$.

# 3. Results and discussion

## 3.1. Performance and thermal profile

The results of a number of tests were combined to produce a thermal profile (Fig. 1). The cooling stage was filled until liquid nitrogen was seen to be coming out of the vent tube (this used just over 0.5 l). The sample immediately started to cool down, with it's temperature dropping quite rapidly at 33 $^\circ\mathrm{C\,min}^{-1}$ from the controlled laboratory temperature of 20 °C to − 80 °C in 3 min. At this point the stage was topped up with a further 0.5 l of liquid nitrogen and although the rate slowed slightly, at 8 min the sample temperature had reached − 145 °C. The addition of a further 0.5 l of liquid nitrogen helped to push the sample temperature down to − 160 °C. No more liquid nitrogen was added, and as the sample temperature began to rise, the system passed through four distinct phases.

(1) A rapid temperature gain to about − 145 °C.

(2) The sample stabilized at − 145 °C and whilst liquid nitrogen remained in the reservoir the sample gained only approximately 0.1 $^\circ\mathrm{C\,min}^{-1}$.

(3) After about 90 min the temperature started to rise more rapidly with the sample temperature increasing at a rate of over 2 $^\circ\mathrm{C\,min}^{-1}$.

(4) At about − 50 °C the heating up rate slowed down and the sample gained 0.1 $^\circ\mathrm{C\,min}^{-1}$, reaching zero after approximately 3 h.

The obtained thermal profile (Fig. 1) provided an excellent opportunity to obtain spectra over a wide range of temperatures. Before the effect of low temperature on the FTIR spectra of polyurethane was

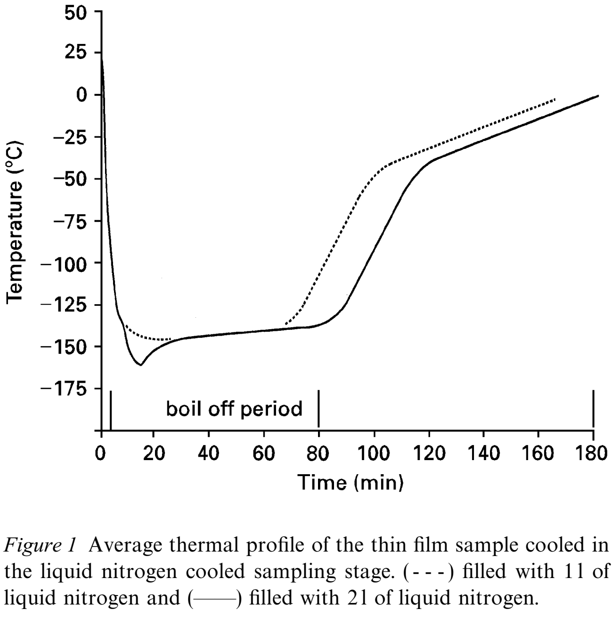

*Figure 1* Average thermal profile of the thin film sample cooled in the liquid nitrogen cooled sampling stage. (- - -) filled with 1 l of liquid nitrogen and (——) filled with 2 l of liquid nitrogen.

studied, it was important to assign and identify the peaks observed at ambient temperatures.

Spectra of the polymers are presented in Figs 2–5. The assignment of the major absorption bands observed in these spectra was effected by comparison with model compounds given in the literature [6–13].

The N–H bond in polyurethanes has several spectral bands and these were observed in the region of 3460–3220 $\mathrm{cm}^{-1}$ (NH stretching). In addition the NH stretching frequency will shift depending on the conformation of the urethane linkages with respect to one another. The assignments of hydrogen bonded and non-hydrogen bonded absorption bands to specific molecular groupings in polyurethanes were made with the aid of spectra reported in the literature. The bands at 3325, and 3313 $\mathrm{cm}^{-1}$ were assigned to NH/carbonyl hydrogen bonding and the band at 3440, and 3451 $\mathrm{cm}^{-1}$ could be assigned to free NH (non-hydrogen bonded) groups. A broad and well defined peak was observed for the hydrogen bonded NH region while the free (non bonded) was only detectable as a shoulder (Fig. 2). Trifan and Terenzi [14] have reported that hydrogen bonding causes the characteristic absorption of N–H or C=O functional groups to be shifted to lower frequencies. In aliphatic polyurethanes all NH groups are essentially hydrogen bonded at room temperature. It has been suggested that the three most likely hydrogen bonding proton acceptors in polyurethanes are urethane carbonyl in the hard segments and ester carbonyl or ether oxygen in the soft segments. The electron donating ability, relative concentrations, and spatial arrangements of these groups are considered to be critical factors in determining the actual hydrogen bonding sites. Hydrogen bonding in polyester-urethanes is predicted to depend on the competition between ester carbonyl and urethane carbonyl groups for the NH protons [15].

NH bands were also observed in the finger-print region at (1530, and 1310 $\mathrm{cm}^{-1}$). These bands were due to amide (CNstretch + NHbend) absorption and assigned by using the available literature [6–14].

Hydrogen bonding in the carbonyl stretching region is less complex than that in the NH stretching region due to the fact that carbonyl groups remain in a hard segment chain and bond to an NH group in the hard block. In the carbonyl region 1750 to 1690 $\mathrm{cm}^{-1}$, the peaks due to hydrogen bonded C=O stretching centred at 1712 $\mathrm{cm}^{-1}$ were more prominent than the peak due to free C=O stretching that appeared as a shoulder in the 1741–1733 $\mathrm{cm}^{-1}$ region.

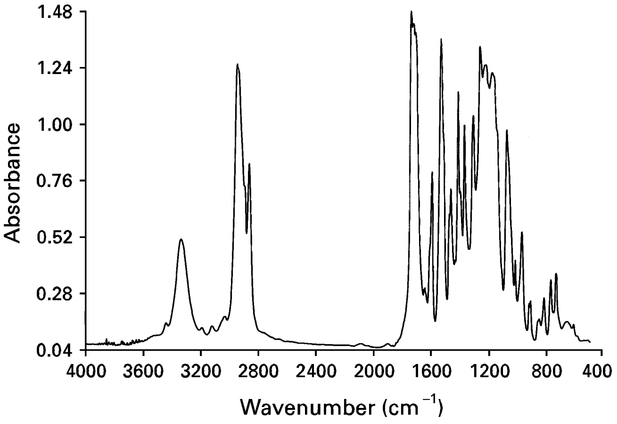

*Figure 2* FTIR spectrum of polyurethane before cooling the sample.

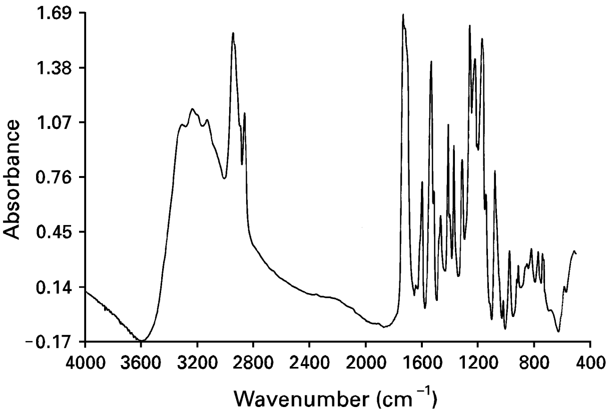

*Figure 3* FTIR spectrum of polyurethane after cooling the sample at − 165 °C.

The typical behaviour for highly phase separated polyurethanes is that interurethane bonded hard segments generally reside in the interior of the hard block. The bonded C=O peaks are generally broader for the low hard segment content polyurethanes than those for the higher hard segment content materials and this broadening was observed in nearly all the spectra obtained [6–15].

The ester link region basically showed two features, the C–O–C antisymmetric stretching vibration of the polyester and the COC stretching of the (C=O) OC group, centred at 1065 and 1085 $\mathrm{cm}^{-1}$ respectively.

The aromatic, C–H stretch, ring of the diisocyanate (MDI) gave rise to peaks centred at three positions 1598, 1413 and 514 $\mathrm{cm}^{-1}$ [6–15].

The CH band of the ($-CH_2-$) group appeared at several positions and was due to the presence of different ($-CH_2-$) groups in the polymer chain which arise from chain extender, butane diol, and polyols. The C–H bond in the ($-CH_2-$) group was centred at 2952, 2872, 1464, 960 and 770 $\mathrm{cm}^{-1}$. The peaks at 2952, 2872 and 1464 $\mathrm{cm}^{-1}$ appeared to belong to the polyester whilst the peaks at 960 and 770 $\mathrm{cm}^{-1}$ could arise from the ($-CH_2-$) group of butane diol [9–14].

## 3.2. The effect of temperature on the hydrogen bonding

Polyurethanes are extensively hydrogen bonded which is a result of the presence of the –NH group which is a proton donor, and the carbonyl or ether/ester linkage that are hydrogen bond acceptors. At room temperature about 90% of the –NH groups in the hard segment are hydrogen bonded [16]. The extent of hydrogen bonding is disrupted with an increase in temperature, at 200 °C the amount of hydrogen bonding is reduced to 35–40% [4, 16–18].

The rigidity of the hard segments below their $T_g$, restricts hydrogen bonding disruption and this effect is clearly observed in the spectra in the N–H and C=O region (Figs 4 and 5). At low temperatures (below

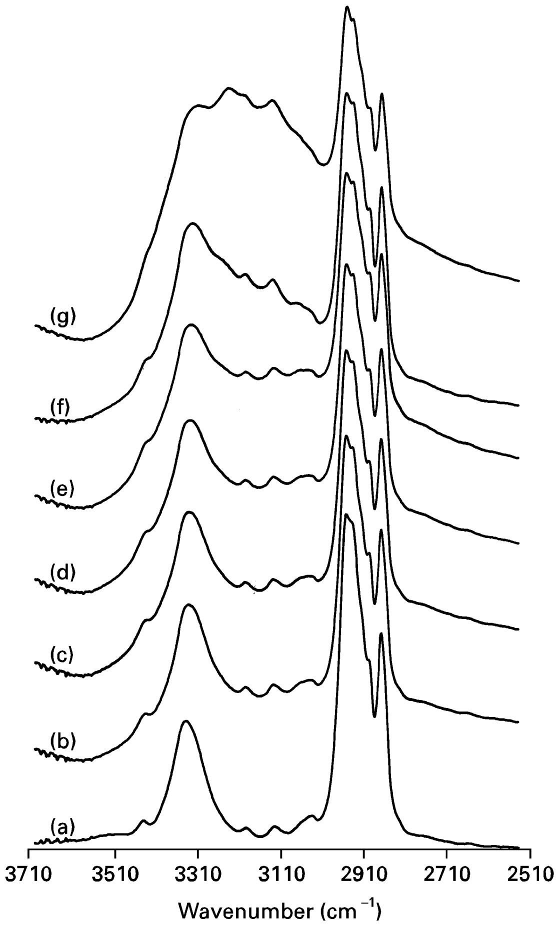

*Figure 4* Effect of temperature on the spectra of the cooled sample (in the N–H region) at (a) room temperature, (b) $-50\,°C$, (c) $-75\,°C$, (d) $-100\,°C$, (e) $-125\,°C$, (f) $-150\,°C$ and (g) $-165\,°C$.

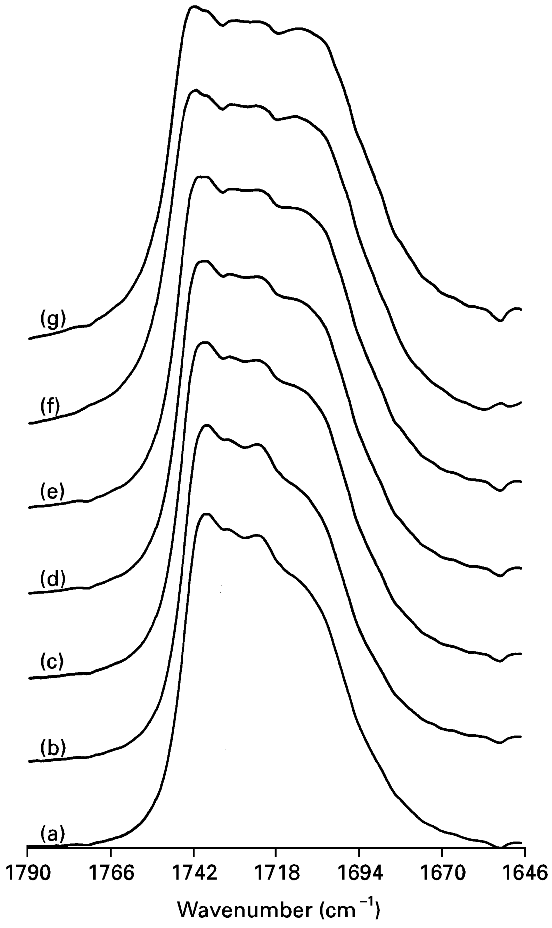

*Figure 5* Effect of temperature on the spectra of the cooled sample (in the C=O region) at (a) $-165\,°C$, (b) $-150\,°C$, (c) $-125\,°C$, (d) $-100\,°C$, (e) $-75\,°C$, (f) $-50\,°C$ and (g) $+25\,°C$.

$T_g$ the mobility of molecules is restricted which results in disturbance of the hydrogen bonding with the NH region in the spectra showing the maximum change with respect to temperature. Hydrogen bonding causes the characteristic absorption of N–H or C=O functional groups to be shifted to lower frequencies. Shifting of the peak at 3338 cm$^{-1}$ indicates the change in the hydrogen bonding of the hard segment. The peak is also shifted towards lower wavenumbers, from 3338 to 3317 cm$^{-1}$ which also suggests a change in the hydrogen bonding of the hard segment. The greater the decrease in temperature the greater is the observed shift. As previously described the hydrogen bonding involves the NH, C=O and ester\ether linkage, therefore a maximum change in the frequencies of these groups is expected. The carbonyl group (which is a proton acceptor) also showed a significant change. The peaks in the region of 1780–1710 cm$^{-1}$, that are associated with hydrogen bonded and non-bonded carbonyl, are shifted to lower values and shrink in width with a lowering of the temperature which indicates a disruption in the hydrogen bonding. Other carbonyl peaks centred at 1741 and 1733 cm$^{-1}$ related to the soft segment of polyurethane (non-hydrogen bonded) remained unchanged (see Fig. 5).

Ester linkage of the polyurethanes (another site for hydrogen bonding) also showed changes in the region of 1335–1120 cm$^{-1}$ which also suggests that the hydrogen bonding changed as the temperature was lowered (Fig. 3). The assignment of bonded and non-bonded absorption bands to specific functional groups is made on the basis of established group frequencies [7–16].

## 4. Conclusions

FTIR spectroscopy has been shown to be a valuable technique to study the hydrogen bonding in polyurethanes. The versatility of this technique combined with the use of a cooling stage allows the monitoring of intermolecular forces and segmented behaviour in specific domain locations in polyurethanes and the analysis of low temperature hydrogen bonding characteristics. The cooling stage allows us to perform an *in-situ* infrared study in transmittance mode at controlled low temperatures.

## Acknowledgement

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