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A Fourier transform Raman study of water sorption by Nylon 6

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Summary

The changes to Fourier transform Raman spectra of Nylon 6 due to the presence of water have been examined. It is postulated that water molecules disrupt the inter-chain hydrogen-bonding which exists in the polyamide; water molecules have a greater propensity to interact at the basic carbonyl sites of Nylon than adjacent Nylon chains. The Raman spectra of thermally softened Nylon are also reported. Increased temperature is shown to destroy hydrogen-bonding. Comparison of thermally and solvent plasticised Nylon 6 indicate differing spectral changes.

Introduction

The strength and toughness of the thermoplastic Nylons has led to their acceptance as important engineering materials. However, Nylons are known to be particularly affected by water, with moisture causing plasticisation and having a profound effect on the mechanical properties of the polymer [1]. Clearly, this phenomenon raises problems in the manufacture of engineering components from Nylon. Thus, an understanding of the absorption mechanism and the ability to predict solvent behaviour is of obvious importance.

The infrared spectra of Nylons are well charaterised and this technique is useful for the examination of interchain hydrogen-bonding in these polyamides. However, water produces a very intense infrared spectrum, making interpretation of a water affected Nylon sample difficult. By comparison, the use of water as a solvent in Raman spectroscopy provides no difficulties as the Raman modes of water are weak.

Raman spectroscopy has been used to characterise Nylons [2-4]. Also, Fourier transform (FT) Raman spectroscopy has already been successfully applied to the investigation of the thermal and solvent induced plasticisation of the thermoplastic poly (ether ether ketone) [5-7]. The use of FT-Raman spectroscopy is extended in the current study to the examination of the effect of water on the properties of Nylon 6. The Raman spectra of thermally softened Nylon 6 is also reported here to compare the effects of these two plasticisation mechanisms.

Experimental

Nylon 6 pellets were supplied by Scientific Polymer Products (glass transition temperature T_g = 63 °C; melting temperature T_m = 229 °C). Nylon 6 films of approximately 500 µm in thickness and dimensions 10 x 10 mm were cast from formic acid solution onto glass plates.

All the FT-Raman spectra were recorded using a Bomem Ramspec 152 equipped with an indium gallium arsenide (InGaAs) photodiode detector and using approximately 1.0 W of 1064 nm radiation from a Quantronix Series 100 Nd:YAG laser. For each spectrum. 200 scans were co-added, apodised with a cosine function and Fourier transformed with a resolution of 4 cm^{-1}.

For the temperature studies, the samples were mounted into the hot stage of a Linkam THMS 600 temperature cell. The sample was allowed to thermally equilibrate at the appropriate temperature for 5 min before scanning 10 min at each temperature. At high temperatures some distortion of the baselines of the spectra was observed. As this distortion occurred mainly in the higher frequency range (>3000 cm^{-1}) and only for temperatures exceeding 200° C, quantitative analysis of the spectra recorded at lower temperatures was feasible. For the water studies, Nylon was exposed to water in sealed containers at room temperature for 24 h prior to spectral examination.

The relative intensities of the major Raman modes were calculated by fixing the intensity of the 2902 cm^{-1} band, due to C-H stretching, at 1.00. This band was selected because it remains the most unaffected by the presence of solvent and the increasing temperature.

Results and Discussion

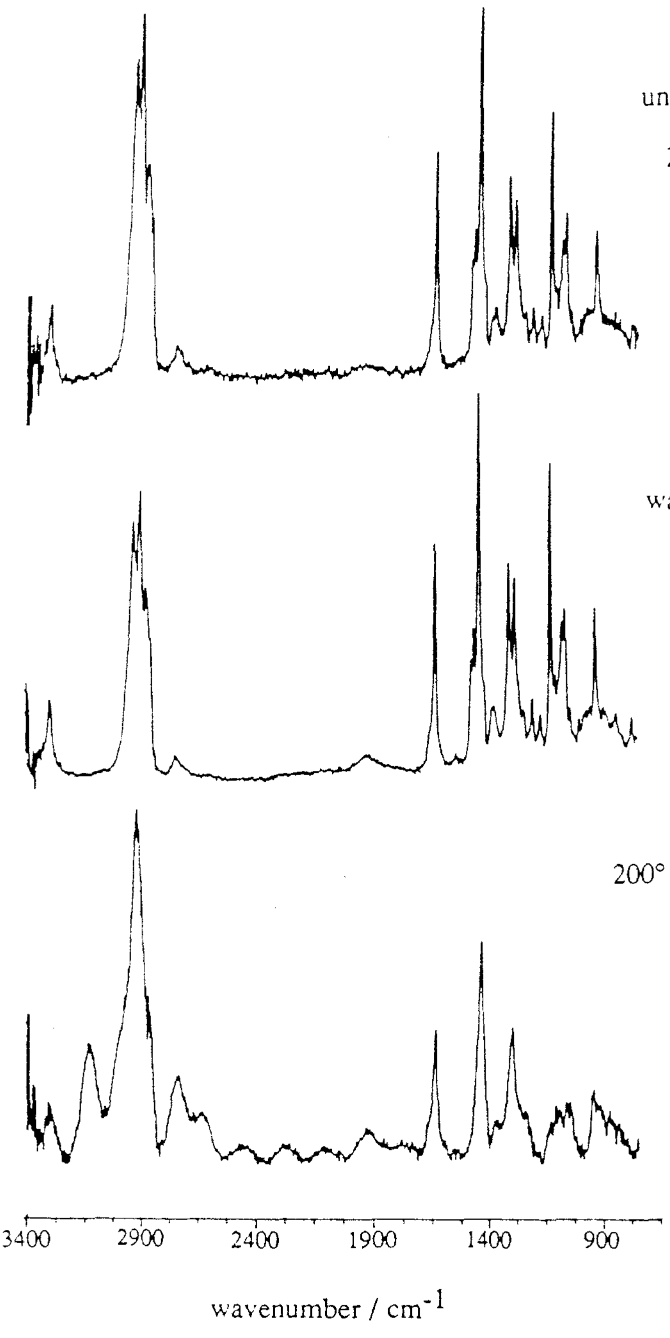
The FT-Raman spectrum of untreated Nylon 6 at 25 °C was recorded and is shown in Figure 1. The FT-Raman spectra of a series of Nylons were reported in two recent studies [3,4] and the current study reports a similar spectrum for untreated Nylon 6 to that observed by Hendra *et al.* [3], with only relatively minor differences in the designated frequency values. Table 1 summarises the assignment of the Raman modes for Nylon 6. The only significant difference appears to be to the intensity of the C-C stretching mode observed at 1126 cm^{-1} in Figure 1. This discrepancy is possibly due to the different synthetic origins of the Nylon 6 samples used in each study.

Table 1. The assignment of the FT-Raman modes of Nylon 6.

frequency / cm^{-1}	assignment
931	C-CO stretching
1062, 1074, 1126	C-C stretching
1280	amide III
1308	CH_2 twisting
1376	CH_2 wagging
1420, 1444, 1447, 1479	CH_2 bending
1636	amide I
2738	overtone or combination band
2877, 2902, 2928	CH_2 stretching
3301	N-H stretching

The Raman spectra of Nylon 6 were recorded over a range of temperature from 25 to 200° C. The spectra recorded at 25° C and 200° C are shown in Figure 1. There are several changes observed to the intensities of certain spectral modes due to increasing temperature. Table 2 shows the relative intensities of the major Raman modes of Nylon 6 at both 25° C and 200° C. Examination of spectra at intermediate temperatures shows that there is a gradual decrease in the intensities of the C-C stretching (1126 cm^{-1}), amide III

Figure 1. The FT-Raman spectra of Nylon at 25° C, 200° C and after exposure to water; 200 scans.



(1280 cm^{-1}), CH_2 bending (1444 cm^{-1}), amide I (1636 cm^{-1}) and N-H stretching modes (3301 cm^{-1}) with increasing temperature, particularly as T_m is approached. Despite the fact that the reference used to calculate relative intensities, the C-H stretching mode at 2902 cm^{-1}, is also itself decreasing in intensity with the increasing temperature, the changes to the other bands appear to be much more dramatic. Notably, the frequencies of most of the Raman bands of Nylon 6 are not significantly affected by such an increase in temperature. However, the frequency of the amide I stretching mode of Nylon 6 is somwhat affected by increasing temperature, although the overall shift to a higher value when the temperature is increased from 25 to 200° C is only of the order of 4 cm^{-1}.

Table 2. The effect of water on the relative intensities of Raman modes of Nylon 6.

frequency / cm^{-1}	assignment	untreated 25°C	water treated	200°C
1126	C-C stretching	0.67	1.12	0.12
1280	amide III	0.40	0.67	0.15
1444	CH_2 bending	0.93	1.52	0.62
1636	amide I	0.56	0.88	0.37
2902	symmetric C-H stretching	1.00	1.00	1.00
3301	N-H stretching	0.21	0.27	0.17

standard deviation: ±0.04

The changes observed to the Raman spectra of Nylon 6 due to increasing temperature may be interpreted in terms of a thermal breakdown of the intermolecular hydrogen-bonding within the Nylon. This effect has been extensively studied using infrared spectroscopy [8-11]. An increase in thermal energy causes hydrogen-bonding to be destroyed. In the Raman spectra this destruction manifests itself as a decrease in intensity, particularly for groups associated with the amide group. The decrease in intensity for the CH_2 bending mode also indicates that such a mode associated with the methylene chain of Nylon 6 is also affected by an increase in thermal energy. That is, the longer range interactions which occur between the adjacent hydrogen-bonded Nylon hydrocarbon chains are also disturbed by an increase in the temperature.

The Raman spectrum of Nylon 6 after immersion in water for 24 hours at 25 °C was recorded and is also shown in Figure 1. There are some notable changes to the relative intensities of certain modes. The relative intensities of the major Raman modes of Nylon 6 affected by water are listed in Table 2 and increases in the intensities of the CH_2 bending, amide III, C-C stretching, N-H stretching and amide I modes are noted. The frequencies of all modes are not significantly altered by the presence of water.

Although an increase in temperature and exposure to water produce a similar rheological change to Nylon 6, that is, plasticisation, these two factors have very different consequences on the structural properties of the polymer observed have on the Raman spectra. The changes observed to the water-treated Nylon sample are notably opposite to those changes observed as a consequence of raising the sample temperature. It follows that the changes caused by exposure to water may be caused by the formation of stronger hydrogen-bonds by water molecules with the Nylon molecules. In the untreated Nylon the intermolecular hydrogen-bonding occurs between the amide groups of adjacent chains. It is proposed that water molecules disrupt the existing hydrogen-bonds. There is competition between the N-H hydrogens of Nylon and the O-H hydrogens of water for the basic carbonyl oxygen sites. As the O-H hydrogen is a stronger electron acceptor than the N-H hydrogen, the carbonyl oxygen atoms favour coordination to the O-H hydrogens. The plasticisation of Nylon occurs because the interaction of water with the polymer results in solution of some of the solvent in the polymer phase and solution of some of the polymer in the solvent phase.

A water-bridging model for polyamides is supported by several other studies [12-15]. For instance, Roberts and Jenekhe [12] were able to use changes to the infrared spectra of Nylon to demonstrate that the strong Lewis acid, gallium chloride ($GaCl_3$), causes the complete scission of the polyamide hydrogen-bonds by site-specific Lewis acid complexation at the basic carbonyl oxygen sites of the amide group. Puffr and Sebenda [16] developed a model of the mechanism of water sorption into Nylon 6 and proposed that in an accessible region three molecules of water are sorbed onto two neighbouring amide groups. The first molecule forms a double hydrogen-bond between the C=O groups by means of free electron pairs on the oxygen atoms, and is regarded as being firmly bound water whose activity is low. The other two water molecules will join the already existing hydrogen-bonds between the carbonyl groups and the hydrogen atoms of amide groups and may be classified as loosely bound water. Further evidence in support of this model is supplied by a spectroscopic study of a different type of polyamide. Chatzi *et al.* [14] carried out a diffuse reflectance Fourier transform infrared spectroscopy study of the sorption of water onto poly(*p*-phenylene terephthalamide) (Kevlar-49) fibres. They were able to assign three different stretching vibrations of water sorbed onto the fibres. A band at 3560 cm^{-1} was assigned to the water which is most strongly bonded to the polymer, that is, water hydrogen-bonded to two carbonyl groups. The band observed at 3640 cm^{-1} was attributed to water hydrogen-bonding between the carbonyl of one amide group and the N-H group of another. The existence of a third type of absorbed water was also postulated as a result of the appearance of band at around 3450 cm^{-1}. This is believed to be due to liquid-like water clustered in the small openings between the crystallites inside the fibres.

In summary, changes to the Raman spectra of Nylon 6 with increasing temperature can be interpreted in terms of the thermal breakdown of the intermolecular hydrogen-bonding of Nylon. By comparison, the Raman spectra of water-treated Nylon demonstrated that water produces augmented hydrogen-bonding in Nylon 6. The water molecules have a greater propensity to interact at the carbonyl sites of Nylon than the adjacent polyamide chains. Despite the apparently similar effect that these two factors have on the rheological properties of this polymer, they have very different consequences at a molecular level.

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