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A Fourier transform Raman study of water sorption by Kevlar-49

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Summary

The Fourier transform (FT) Raman spectrum of poly (*p*-phenylene terephthalamide) (Kevlar-49) is reported. Additional bands, not observed in the conventional Raman spectrum, have been assigned. The changes to the FT-Raman spectrum of Kevlar due to the presence of water have also been examined. As a consequence of the intensity changes to certain Raman modes in this preliminary study, it is postulated that water molecules form liquid-like clusters between the crystallite regions of Kevlar fibres.

Introduction

An understanding of the nature of the interactions between water molecules and polymers is of importance as the presence of water can have profound effects on the mechanical properties of polymers. One such polymer is poly (*p*-phenylene terephthalamide) (PPT), which is commonly known as Kevlar-49 and is used in composites and reinforced resins. Kevlar fibres are capable of absorbing up to 3% moisture, which can weaken the interfacial adhesion of Kevlar composites [1].

Kevlar is an aromatic polyamide fibre and the structure of the polymer is shown in Figure 1. Crystallographic studies [2] showed that the *para*-substituents of the phenyl groups are in a *trans* configuration. In addition, the substituents are not quite coplanar with the phenyl groups. Kevlar-49 is highly crystalline and does not appear to possess regularly occurring amorphous segments. Kevlar fibres consist of rod-like crystallites of approximately 500Å in diameter and 2100Å in length [3].

A limited number of Raman studies of Kevlar-49 have been reported [4-6]. The conventional Raman spectrum of Kevlar-49 was reported by Penn and Milanovich [4]. Fibre samples exposed to heat, stress and a radiation showed no significant changes to the Raman spectrum. However, the spectrum of Kevlar-49 fibre under stress did indicate a change in the alignment of the crystallinity along the fibre axis. The difficulty in obtaining an adequate Raman spectrum of Kevlar has been due in large part to the problem of sample fluorescence in the fibre. However, with advances in Fourier transform (FT) Raman spectroscopy, the problem of fluorescence has been eliminated.

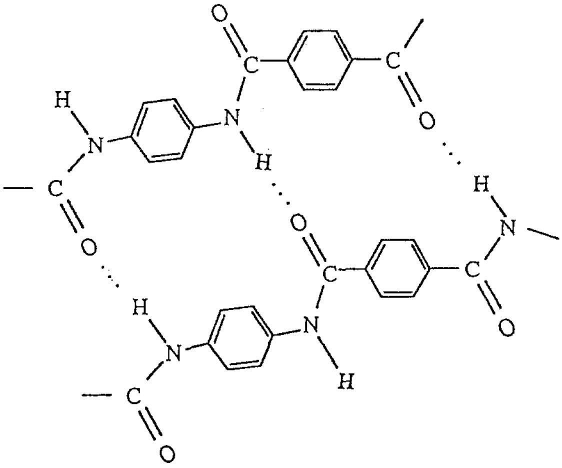
In addition, the development of FT-Raman microscopy has allowed single fibres to be investigated [5,6].

Infrared spectroscopy has been applied to the problem of water absorbed by Kevlar-49 [1,7]. Chatzi *et al.* [1] carried out a diffuse reflectance Fourier transform infrared (FTIR) spectroscopy study of the sorption of water by 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.

Raman spectroscopy is an ideal technique for examining the effects of water on polymers. Unlike infrared spectroscopy, which suffers from the disadvantage that the infrared spectrum of water is strong and masks the polymer spectrum, the Raman spectrum of water is very weak and causes no intereference. FT-Raman spectroscopy has already been successfully applied to the study of the sorption of water into another polyamide, Nylon 6 [8]. The study demonstrated that water molecules disrupt the inter-chain hydrogen bonding which exists in the polyamide, producing augmented hydrogen bonding in Nylon 6.

In this preliminary study FT-Raman spectroscopy is used to examine the effect of water on the structural properties of Kevlar-49.

Figure 1. The structure of poly (*p*-phenylene terephthalamide) (Kevlar-49).



Experimental

Poly (*p*-phenylene terephthalamide) (Kevlar-49) fibres were supplied by DuPont de Nemours, U.S.A. For the investigation into the effect of water, Kevlar was exposed to water at room temperature for 24h prior to spectral examination.

All the FT-Raman spectra were recorded using a Bomem Ramspec 152 Fourier transform Raman spectrometer equipped with an indium gallium arsenide (InGaAs) photodiode detector and using approximately 1.0W of 1064nm 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}.

The relative intensities of the major Raman modes were calculated by fixing the intensity of the 1277 cm^{-1} band, a ring vibration, at 1.00. This band was selected by Penn and Milanovich [4] as a reference when determining the changes in intensity of the amide II band at 1570 cm^{-1} as a function of stress applied to the Kevlar-49 fibre.

Results and Discussion

The FT-Raman spectrum of Kevlar as received at 25°C was recorded and is shown in Figure 2. Table 1 summarises the assignment of the FT-Raman modes for Kevlar. A number of bands appear in the present FT-Raman study which were not observed in the conventional Raman spectrum reported by Penn and Milanovich [4]. Two weak bands at 1809 and 1714 cm^{-1} are assigned to C-H out-of-plane bending overtones and combinations bands. The weak bands at 3082 and 3058 cm^{-1} may be attributed to C-H stretching.

Table 1. The assignment of the FT-Raman modes of Kevlar-49.

frequency / cm^{-1}	assignment
630, 732, 786	ring vibrations
845	C-H out-of-plane bending
863	ring vibration
1103	C-H in-plane bending
1181, 1277, 1327, 1514	C-C ring stretching
1318	C-H in-plane bending
1569	amide II (60% N-H bending; 40% C-N stretching)
1610	C-C ring stretching
1648	amide I (80% C=O stretching; 10% C-N stretching; 10% N-H bending)
1714, 1809	C-H out-of-plane bending overtones and combination bands
3058, 3082	C-H stretching

Figure 2. The FT-Raman spectrum of Kevlar as received.

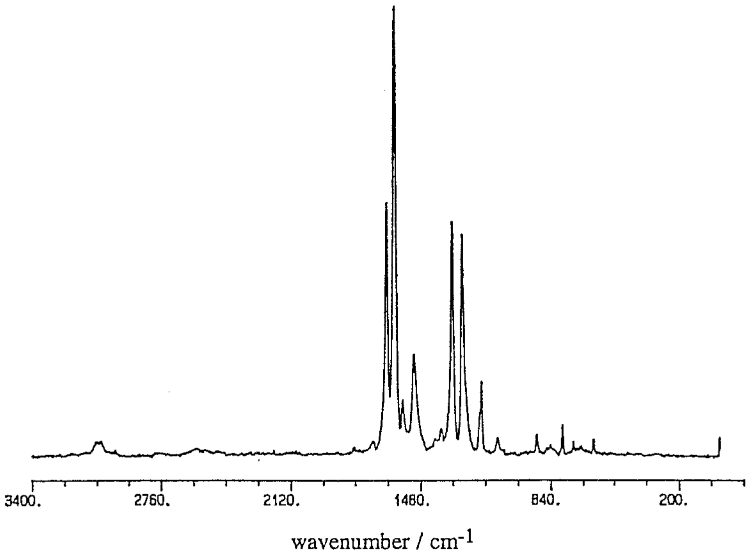
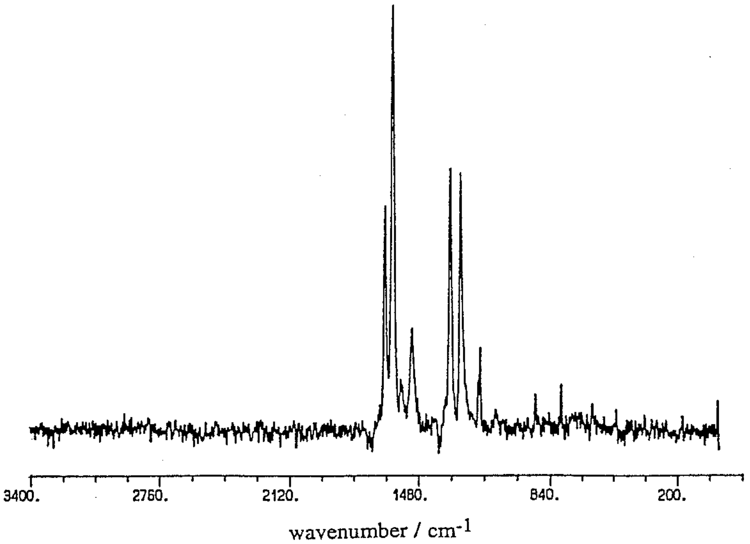


Figure 3. The FT-Raman spectrum of Kevlar after exposure to water for 24h.



The Raman spectrum of Kevlar after immersion in water for 24h at 25°C was recorded and is shown in Figure 3. The relative intensities of the major Raman modes of Kevlar affected by water are listed in Table 2. There are some notable changes to the relative intensities of certain modes: decreases in the intensities of certain modes were noted when spectral subtraction was applied. The most significant changes occur to the C-C ring stretching mode at 1610 cm^{-1} and the amide I band at 1648 cm^{-1}. It should be noted that very weak bands observed in the as received spectrum are difficult to observe in the spectrum after water treatment, probably due to the increased baseline noise in the latter spectrum. The frequencies of all Raman modes are not significantly altered by the presence of water.

The presence of such liquid-like water in Kevlar is thought to result in a decrease in the Raman amide I mode because the formation of water clusters disrupt the weak hydrogen bonding between the crystallites. A decrease in intensity of the amide I band of Nylon 6 was observed with increasing temperature [8]. This study showed that disrupting hydrogen bonding by increasing the temperature lead to a decrease in the relative intensity of the amide I band. The intensity of the C-C ring stretching mode of Kevlar at 1610 cm^{-1} also decreases in the presence of water, and this is attributed to the change in environment of those phenyl groups influenced by the presence of water molecules.

Table 2. The effect of water on the relative intensities of Raman modes of Kevlar-49.

frequency / cm^{-1}	assignment	relative intensities	
		as received	water treated
1181	C-C ring stretching	0.33	0.32
1277	C-C ring stretching	1.00	1.00
1327	C-C ring stretching	1.06	1.02
1514	C-C ring stretching	0.45	0.40
1569	amide II	0.25	0.21
1610	ring vibration	2.04	1.65
1648	amide I	1.13	0.88

standard deviation: ±0.05

Intensity changes to the Raman spectra of other polymers have been observed due to the presence of a variety of solvents [8-11]. Another polyamide, Nylon 6, has been investigated by FT-Raman spectroscopy before and after exposure to water [8]. It is interesting to compare the observations made in the current study for Kevlar with those made for Nylon 6. Stuart [8] showed that the presence of water causes the intensity of the amide I band of Nylon 6 to increase in intensity. The change was attributed to the water molecules disrupting the inter-chain hydrogen bonding in the polyamide and producing hydrogen bonded "water bridges" between the polymer chains. Hydrogen bonding between polyamide chains is fundamental to the morphology of both Kevlar and Nylon 6, but clearly the presence of water has entirely different spectroscopic consequences in each case. The same water bridging model is not demonstrated for Kevlar as result of the studies carried out here. The FTIR study by Chatzi *et al.* [1] produced evidence for the presence of liquid-like water clustered in microvoids inside the fibres. Rather than the water molecules disrupting the interchain hydrogen bonding between the Kevlar molecules, it is proposed that the water is actually accumulating between the crystallites formed by Kevlar.

Additionally, despite Nylon 6 and Kevlar being polyamides, these polymers have quite different morphology due to the presence of the phenyl groups in the Kevlar backbone. The crystallites of Kevlar are regularly packed and held together in the radial direction of the fibre by weak intermolecular forces [12]. The diameters of the interstices between the crystallites in Kevlar has been estimated to be of the order of a hundred Angstroms [1], providing enough space for clusters of water to develop. A polymer which has a similar morphology to Kevlar is collagen, and so provides a better model for comparison with Kevlar. Collagen rods are packed parallel to the fibre axis and in an ordered lattice. The collagen lattice has been shown to expand after the addition of water without destroying the crystalline regularity [13].

Conclusions

The results of a preliminary study of the FT-Raman spectra of Kevlar-49 fibres treated with water were presented here. It is proposed, that water molecules form liquid-like clusters between the crystallite regions of Kevlar fibres. This results in a decrease in the intensity of several Raman modes. Further studies investigating the effect of purging Kevlar fibres of water may provide further information about the intermolecular interactions and interactions between the crystallites. Likewise, studies of water absorption as a function of time may also provide some insight into the progress of water molecules into Kevlar fibres. The study reported here also serves to demonstrate that FT-Raman spectroscopy provides a useful technique for examining the effect of liquids on polymer morphology.

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