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Characterization of absorbed water in aramid fibre by nuclear magnetic resonance

C. CONNOR, M. M. CHADWICK
Defence Research Establishment Pacific, FMO Victoria, British Columbia, Canada V0S 1B0

While many studies have focused on the mechanical degradation of aramid/epoxy composites by water absorption, little work has been done to gain a deeper understanding of the interaction between absorbed water and aramid fibres. In this study, ^{13}C, ^{1}H, and ^{23}Na nuclear magnetic resonance was used to show that the absorbed water in Twaron fibre is located in small pores in the skin region of the fibres, and in larger core defects. The absorbed water partially dissolves sodium salts, consisting mainly of sodium carbonate, which are present in the pores. No evidence of chemical breakdown of the aramid polymer, or of water ingress within the polymer lattice, was observed.

1. Introduction

The absorption of water has been reported to affect the mechanical properties of aramid/epoxy composites. Results include a 14% increase in tensile strength [1], a negligible difference in tensile strength [2, 3], a 15–40% decrease in flexural strength [4, 5] and a 35% decrease in transverse strength [6]. Increases in tensile strength are attributed to plasticization of the resin, enabling fibre reorientation [1]. Decreases in flexural strength are due to a degraded fibre–matrix interface promoting delamination [4] and matrix plasticization allowing filament buckling to occur [5]. In transverse tension, moisture reduces the skin/core bonding strength of the fibres, allowing the skins to be pulled away. It also facilitates internal filament cracking through the pre-existing defect structure which exists in the fibres [6]. In addition, in fatigue the fibre/matrix interface is degraded and more fibre splitting occurs in the moisturized samples [2, 7]. Thus the results are generally attributed to increased plasticization of the resin and a change in fracture mechanism of the aramid fibres.

The effect of moisture on individual Kevlar fibres has also been investigated. There is a negligible effect on tensile strength [8] and modulus [9] at room temperature. A decrease in the fibre split length has been reported for fibres loaded in tension [10] and a mechanism of hydrolytically-induced chain scission of the amide linkage in the fibre was proposed [11].

Although it is well known that aramid fibres absorb water, the question remains: where does the water reside and how does it affect the molecular structure of the fibre. X-ray data have shown that the water does not enter the unit cell of the crystal lattice [12]. Moisture absorption has been related to the ash content of the fibre, with the ash being high in sodium sulphate [13]. Based on Morgan *et al.*'s [11] report of sodium sulphate in Kevlar, Ashbee and Ashbee [14] proposed that fibre fracture is caused by the volume expansion due to hydrating the salt to the decahydrate species. Voids in aramid fibres have been documented extensively by Dobb and co-workers and Young *et al.* [15–18]. The interaction of the water molecules with the polyamide fibres investigated by infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) give contradictory results. NMR results suggest that the water molecules do not interact with the amide groups [19], whereas Kim *et al.* attribute the decrease in intensity of the N–H stretching vibration in IR spectra to deuterated water interacting with the amide band [20].

The purpose of the present work was to determine the physical and chemical state of the absorbed water, primarily through the use of NMR spectroscopy. The mechanism of salt hydration proposed by Ashbee and Ashbee [14] will be addressed.

2. Experimental procedure

Two samples of Twaron 1055 yarn (Akzo Fibers, Conyers, GA) were packed in zirconia NMR rotors, then dried at 120 °C for 24 h, under a partial vacuum of 44 kPa. The weight loss of the two samples during this process was 2.48% and 2.60%. One sample was then exposed to 100% relative humidity at room temperature for 95 h, and at the end of this time the weight increase of the yarn had stabilized at 5.7%, compared to the weight of the dry yarn. The rotors were sealed with tight-fitting plastic caps to maintain the moisture content of the yarn during the NMR studies.

To determine the rate of uptake of moisture by the dried fibres, a 0.5 g sample of Twaron, dried under the conditions described above, was packed tightly into a glass vial and exposed to 100% relative humidity at room temperature. The vial was removed periodically for weighing over a period of 28 days.

Reagent grade Na_2SO_4 (Matheson, Coleman and Bell, Norwood, OH) was dried at 140 °C for 2 h before packing into a zirconia rotor. No significant weight change was observed after the first 30 min. $Na_2SO_4 \cdot 10H_2O$ was prepared from reagent grade Na_2SO_4 by slow evaporation of a saturated solution. The resulting transparent crystal mass was ground and packed in an NMR rotor. To prevent loss of water, the material was kept in contact with the supernatent liquid during this procedure. Both samples were tightly sealed inside the rotors using plastic caps.

NMR spectra were recorded with a Bruker MSL NMR spectrometer, operating at a magnetic field strength of 7.05 T. Magic angle spinning (MAS) was used for some of the spectra, with spinning rates of 3–5 kHz [21]. ^1H and ^{23}Na spectra were recorded using a single 1 μs pulse for excitation, while ^{13}C spectra were recorded using the cross polarization technique [22–24]. The cross polarization time, and the ^1H spin lattice relaxation time in the rotating frame, were determined by varying the contact time during cross polarization, with ^{13}C observation. ^1H chemical shifts are referenced to TMS, and ^{23}Na chemical shifts are referenced to aqueous Na^+.

X-ray diffraction patterns were obtained with a Scintag XDS-2000 diffractometer, with CuK_α radiation.

3. Results and discussion

3.1. Water absorption measurements

Fig. 1 shows the weight increase of a sample of dry Twaron exposed to 100% relative humidity. Although most of the weight gain occurs during the first 24 h, further increase in the weight occurs for at least 28 days. The final weight increase measured for this sample, about 5.7%, was also observed for several other Twaron samples hydrated in a similar manner.

Using an optical microscope, we determined the average fibre diameter was approx 12 μm. Assuming the fibre surface is smooth and impermeable to water, a weight increase of 5.7% corresponds to about 600 monolayers of water on the surface. Molecular dynamics data, extracted from the ^{13}C NMR measurements as described in the following section, support the assertion that the water does not penetrate the polymer network. However, it does not seem physically reasonable for a film of water 600 monolayers thick to build on the fibre surface, because the outer layers would not be influenced to any appreciable extent by the fibre surface.

A more satisfying explanation for the relatively large water uptake by the Twaron fibres is suggested by work carried out by Dobb and co-workers [15–17]. They have reported that several aramid fibres, including Twaron, have an outer skin containing a large number of elongated pores, with typical dimensions of 5 nm × 5 nm × 25 nm long. Because the dimensions of these microvoids were determined by impregnation with silver sulphide, many of them must be accessible to water and other small molecules. Core defects, which are voids approximately two orders of magnitude larger than the pores in the surface region, have also been reported for Twaron fibre [16]. It appears quite likely that a large fraction of the water absorbed by the Twaron fibre may have penetrated into the pores in the outer skin, and into the larger core defects.

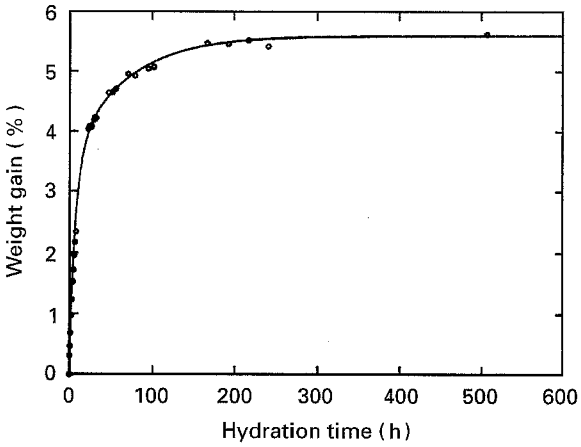

Figure 1 Weight increase versus time for dry Twaron yarn exposed to 100% relative humidity, at room temperature. (—) Fit to the experimental data using a biexponential function.

3.2. ^{13}C NMR spectroscopy

Aside from a significant improvement in spectral resolution, our ^{13}C NMR spectra of Twaron (Fig. 2) do not differ greatly from those previously reported for Kevlar 49 [19]. Like Fukuda *et al.* [19], we do not observe appreciable differences between the spectra of the wet and dry fibres. This shows that there is very little, if any, change in the chemical structure of the polymer due to hydration.

While the chemical shift spectra, as shown in Fig. 2, are sensitive to the chemical makeup of the polymer, many changes in polymeric materials are more evident in studies of the molecular dynamics [25–27]. To determine if any changes in the rates of molecular motion occur during hydration, we measured T_{CH}, the cross relaxation time between ^1H and ^{13}C, and $T_{1\rho}$, the ^1H spin lattice relaxation rate in the rotating frame [24]. The relaxation time, T_{CH}, is sensitive to motions occurring at frequencies below a few kilohertz, while $T_{1\rho}$ depends on motions occurring at tens of kilohertz. These low-frequency motions are generally twisting or bending of the polymer backbone. Both relaxation times are also sensitive to the proximity of protons in the polymer, the cross relaxation time, T_{CH}, especially so. Because the NMR spectra in Fig. 2 do not show any evidence of changes in the chemical structure of the polymer after hydration, we can assume that changes in the relaxation times are due to differences in the motional rates of the polymer, rather than to changes in the arrangement of protons around the carbon nuclei. The relaxation times measured for each of the six resonance peaks in the ^{13}C NMR spectra are listed in Table I. The assignment of the six peaks, as shown in Fig. 2, is based on the work by Fukuda *et al.* [19].

The peaks can be clearly grouped into protonated carbons, which have T_{CH} values of tens of microseconds, and non-protonated carbons, which have T_{CH} values of a few hundred microseconds. However,

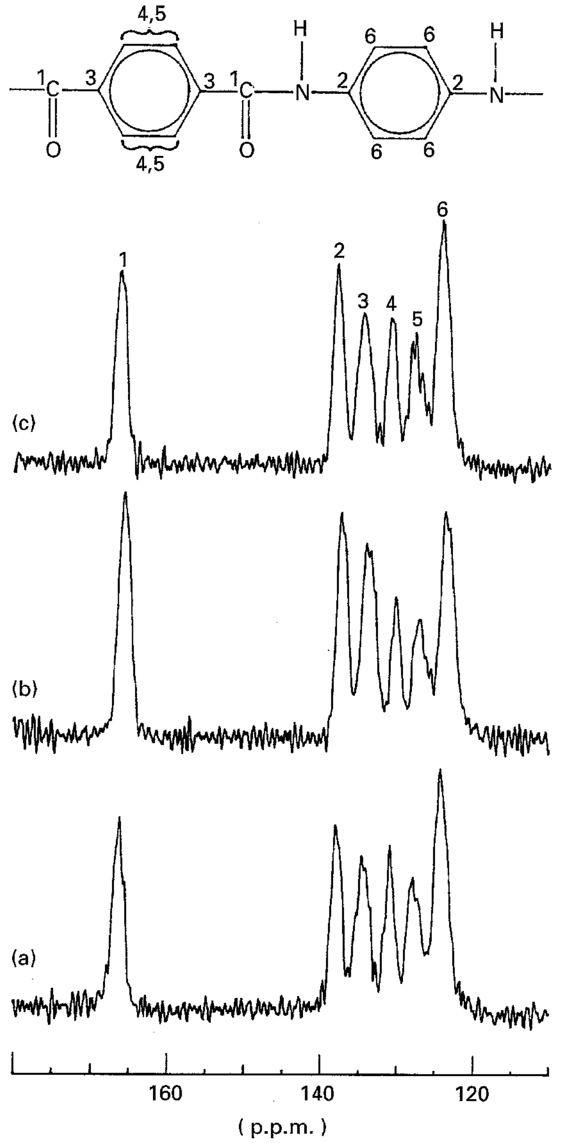

Figure 2 ^{13}C cross polarization magic angle spinning NMR spectra of (a) dry Twaron (b) with 2.7% absorbed water, and (c) with 5.7% absorbed water. The similarity of the spectra shows that there are no major chemical changes in the yarn during hydration.

TABLE I Relaxation times for dry and wet Twaron

Relaxation time (μs)[a]		Peak number					
		1	2	3	4	5	6
T_{CH}	Dry	400	270	190	50	48	50
	Wet	440	270	250	45	32	38
$T_{1\rho}$	Dry	6400	6500	6100	4900	5500	4700
	Wet	3800	4300	3800	3800	3900	4000

[a] The typical error in the relaxation times is about 10%.

the T_{CH} values do not differ significantly between the dry and wet material, so the presence of water has little effect on the very slow motions of the polymer. In contrast, the $T_{1\rho}$ values are distinctly shorter for the hydrated Twaron, showing that the amount of motion in the 10–100 kHz frequency range has increased. An increase in the amount of motion in this frequency range is generally correlated to an increase in the plasticity of the polymer [25]. However, the observed reduction in $T_{1\rho}$ of 15–40% probably corresponds to only a modest change in the mechanical properties of the Twaron after hydration, since $T_{1\rho}$ may decrease by several orders of magnitude when a material changes from being very rigid to very soft.

3.3. ^{1}H NMR spectroscopy

The key to interpreting the results obtained from ^{1}H NMR is based on the effect of motion on the NMR spectra of protons [28]. In rigid solids, the interaction between the magnetic dipole moment of any one proton and the magnetic dipole moments of the surrounding protons broadens the resonance line. This dipolar interaction produces a ^{1}H linewidth of several kilohertz in rigid solids. In low-viscosity liquids, rapid molecular motion averages the dipolar interaction to zero, yielding linewidths of 1 Hz or less. In the intermediate motional regime the dipolar interaction is partially averaged, and the observed linewidth is correspondingly scaled.

^{1}H spectra of dry Twaron and Twaron with 5.7 wt % absorbed water are compared in Fig. 3. The spectra consist of the superposition of a very broad resonance line, with a linewidth of about 35 kHz, and a narrower line with a linewidth of about 2 kHz. The broader line can be attributed to a relatively rigid phase, consisting of the aromatic and amide protons chemically bound to the backbone of the polymer, and the narrower line to a more mobile phase composed mainly of adsorbed water. This assignment is based on the phenomenon discussed in the preceeding paragraph, and is confirmed by the fact that the intensity of the broader line is relatively insensitive to the degree of hydration of the Twaron, while the narrower line increases dramatically during hydration.

A measurement of the integrated intensities of the spectra shown in Fig. 3 can help to illuminate the interaction between Twaron and water, because these intensities are proportional to the number of protons present in the corresponding phase. Based on the known number of protons per gram of the Twaron

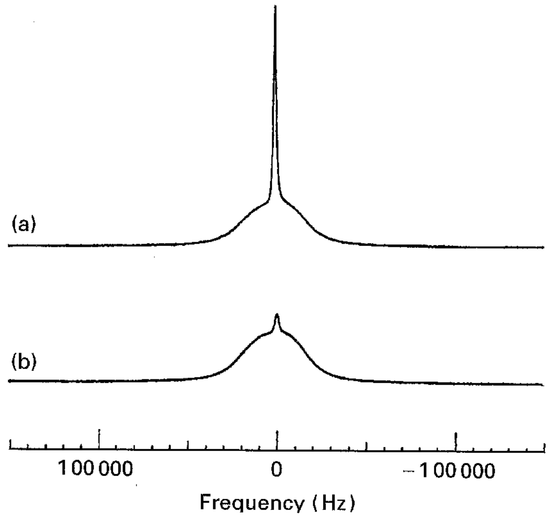

Figure 3 ^{1}H NMR spectra of the static samples of (a) dry Twaron and (b) Twaron with 5.7 wt % absorbed water. The broad peak is from relatively slow moving protons on the aramid polymer backbone, while the narrow peak is mainly due to the more rapidly moving absorbed water.

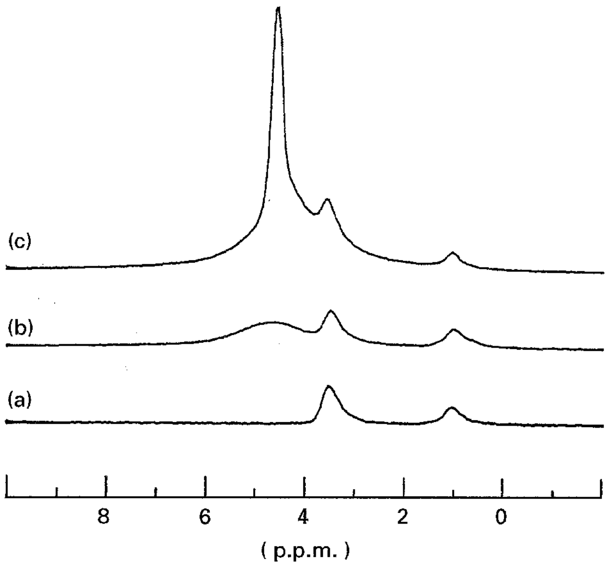

Figure 4 Magic angle spinning (MAS) spectra of ^1H in (a) dry Twaron, (b) Twaron with 2.7% absorbed moisture, and (c) with 5.7% absorbed moisture. The peaks at 1.0 and 3.6 p.p.m. are attributed to a coating or sizing on the fibres, while the narrow peak at 4.6 p.p.m. is due to very mobile absorbed water. The broader peak at about 4.5 p.p.m. arises from less mobile absorbed water molecules, probably located in smaller voids within the fibre than those which contribute to the 4.6 p.p.m. peak. For comparison with Fig. 3, 1 p.p.m. = 300 Hz.

polymer, the total intensity of the ^1H spectrum, during uptake of 5.7% water, should increase by 15%. The measured increase in the total intensity is 16%, after correction for the proton background in the NMR probe and for the effect of the probe recovery time, in good agreement with the predicted value. In addition, all of the intensity increase occurs in the narrow line, indicating that all of the absorbed water is weakly bound, with motional rates similar to those of bulk water, rather than as the more rigid phase observed for waters of hydration in inorganic salts [28].

The narrow peaks in the ^1H spectra presented in Fig. 3 can be resolved into individual components when magic angle spinning (MAS) is used. The MAS spectra of wet and dry Twaron are shown in Fig. 4, as well as a MAS spectrum of the yarn with 2.7% absorbed moisture. Note that the spectral width of the plots shown in Fig. 4 is much less than the width of those in Fig. 3, so that the very broad line due to the stationary protons is not observed. Clearly there is a large increase in the intensity of the peak at 4.6 p.p.m. when the material is hydrated, and the chemical shift of this peak agrees well with that of water.

Also present in the upper spectrum in Fig. 4 is a broader peak at about 4.5 p.p.m., which is probably due to absorbed water molecules which are in a different environment than those which resonate at 4.6 p.p.m. This line at 4.5 p.p.m. can also be seen in the spectrum of Twaron with 2.7% absorbed moisture (middle spectrum, Fig. 4). The larger linewidth of this peak, as compared with that at 4.6 p.p.m., indicates that these water molecules are more motionally constrained than those which appear at 4.6 p.p.m. These two peaks can be tentatively assigned to water in two different types of voids. As Dobb and Robson [16] have reported, Twaron contains core defects which are approximately two orders of magnitude larger than the pores in the surface region. Water in these larger voids is relatively unaffected by the pore walls, and would probably experience motions similar to bulk water. We assign the narrow resonance line at 4.6 p.p.m. to this very mobile water phase. In contrast, the motion of water molecules in the smaller surface pores will be constrained by the walls of the pores, producing the broader line at 4.5 p.p.m.

The fact that the narrow peak at 4.6 p.p.m. is absent in the partially hydrated material would suggest that initially the water molecules are absorbed in the small surface pores. After continued exposure to moisture, these molecules migrate into the core defects, and are replaced with newly added water molecules. The relative intensity of the broad 4.5 p.p.m. line, as compared to the 4.6 p.p.m. line, indicates that about 25–50% of the water is present in the surface pores.

Besides the two resonance lines assigned to absorbed water, there are also relatively sharp peaks at 3.6 p.p.m. and 1.0 p.p.m. in the ^1H MAS spectrum. These narrower peaks, which comprise about 2% of the total number of protons in the dry material, are responsible for the small narrow peak in the static spectrum of dry Twaron shown in Fig. 3. The most likely source of these sharp lines is a sizing or coating on the exterior of the fibre, because they are not observed in a sample of yarn that had been thoroughly washed in petroleum ether. Dioctylphthalate has been previously reported as a major component of the coating found on Kevlar 29 fibres [29]. However, the IR spectrum of the residue from an alcohol wash of the Twaron fibres clearly shows that the coating does not contain carbonyl groups, and most closely matches those obtained from fatty acids. The observed ^1H NMR spectra are consistent with the spectra expected from either dioctylphthalate or a fatty acid.

3.4. ^{23}Na NMR spectroscopy

Results from ^{23}Na NMR spectroscopy may determine the validity of the model proposed by Ashbee and Ashbee, regarding the hydration of residual Na_2SO_4 in aramid fibres [14]. NMR spectra of ^{23}Na nuclei ($I = 3/2$) in solids are dominated by the quadrupolar interaction, as is the case for most isotopes with nuclear spin quantum number $I \geqslant 1$ [30]. The quadrupole interaction is determined by the distribution of electrons around the ^{23}Na nuclei, which is different for each chemical compound. Two parameters, e^2qQ and η, are commonly used to characterize the quadrupolar interaction. The first, e^2qQ, roughly represents the strength of the interaction, while η is a measure of the deviation of the electric field gradient from cylindrical symmetry. The range of η is from zero to one, with zero corresponding to cylindrical symmetry. The lineshape in the ^{23}Na MAS NMR spectrum is partially dictated by the quadrupolar interaction in second order. By simulating this lineshape, one can determine the quadrupolar parameters, and hence obtain information on the chemical environment of the ^{23}Na nuclei [30–32].

Our goal in using ^{23}Na NMR was to determine if anhydrous Na_2SO_4 is present in dry Twaron, and if so, whether it is converted to the decahydrate during hydration of the fibre, as Ashbee and Ashbee have suggested. To help in interpreting the ^{23}Na spectra of wet and dry Twaron, the ^{23}Na NMR spectra of anhydrous Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ were recorded. Although Ashbee and Ashbee refer to the monohydrate of Na_2SO_4, this is not generally recognized as one of the stable forms of hydrated sodium sulphate [33, 34]. Spectra of the sodium carbonates were also recorded because the sulphuric acid used in aramid fibre production is neutralized by sodium carbonate [13]. When an excess of sodium carbonate is used during neutralization, the sodium salt present in the fibres will be a mixture of carbonates and sulphates. The phase composition of the model compounds studied by NMR was confirmed by X-ray diffraction.

The ^{23}Na MAS NMR spectra of anhydrous Na_2SO_4, $Na_2SO_4 \cdot 10H_2O$, aqueous Na^+, Na_2CO_3, and $NaHCO_3$ are shown in Fig. 5. The anhydrous Na_2SO_4 yields a typical powder pattern produced by the second-order quadrupolar interaction, as well as several spinning sidebands at multiples of the rotor rotational frequency. The spectrum can be well modelled assuming a single type of sodium site in the lattice, with $e^2qQ = 2.64$ MHz, $\eta = 0.62$, and a chemical shift $\delta = 0$ p.p.m. (see Fig. 6). No attempt was made to simulate the spinning sidebands, as these yield little additional information for nuclei with $I = 3/2$. The $Na_2SO_4 \cdot 10H_2O$ spectrum exhibits a very narrow line, with a chemical shift of 0.0 p.p.m., overlapping a broader line. The sharp line is due to Na^+ ions in solution, as can be seen by comparing it to the spectrum of aqueous Na^+. The broader portion of the spectrum can be fit to a single sodium site with $e^2qQ = 0.0$, a chemical shift of 2 p.p.m., and a Lorentzian broadening of 500 Hz. The spectrum of Na_2CO_3 can be well modelled using two sites. The parameters which describe the sites are $e^2qQ = 1.20$ MHz, $\eta = 0.0$, $\delta = 8.0$ p.p.m. and $e^2qQ = 2.52$ MHz, $\eta = 0.4$, $\delta = 3.0$ p.p.m., with approximately equal populations. The spectrum of $NaHCO_3$ appears to be a simple Lorentzian line centred at $\delta = -6.25$ p.p.m.

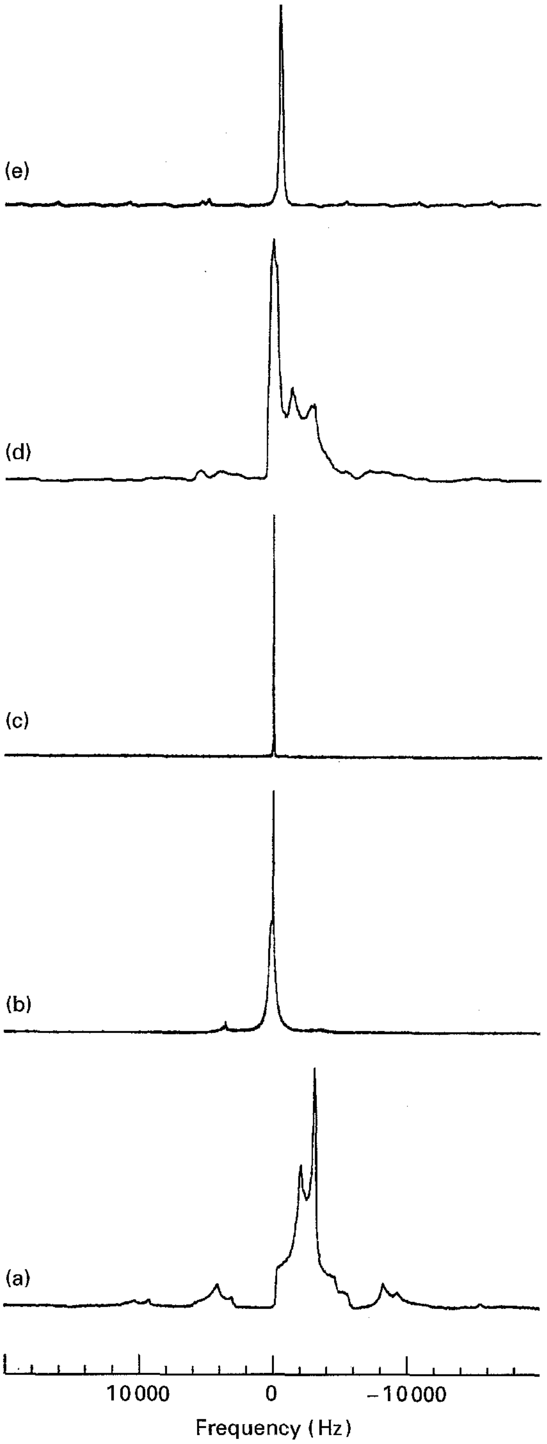

Figure 5 ^{23}Na MAS NMR spectra of (a) Na_2SO_4, (b) $Na_2SO_4 \cdot 10H_2O$, (c) Na^+ in aqueous solution, (d) Na_2CO_3, and (e) $NaHCO_3$. The spectra of these model compounds were recorded to help in determining the chemical composition of the sodium salt present in Twaron fibres.

Shown in Fig. 7 are the spectra of ^{23}Na in wet and dry Twaron. Because of the lack of sharp features in the spectra, the degree of confidence in the stimulated spectra is somewhat reduced. However, reasonable results were still obtained, as can be seen in Fig. 8. The spectrum of dry Twaron agrees fairly well with simulations using three sites. Two of the three sodium lattice sites have the same parameters as were used to simulate the Na_2CO_3 spectrum, with an additional Gaussian broadening of 1000 Hz. The third site has $e^2qQ = 1.68$ MHz, $\eta = 0.9$, $\delta = 1.0$ p.p.m., with a Gaussian broadening of 400 Hz. There are about three times as many nuclei in the third site as in each of the other two. The spectrum of wet Twaron more closely resembles that of Na^+ in water than the spectra of any of the forms of sodium sulphate. In particular, the nearly symmetrical shape of the peak of ^{23}Na in wet Twaron suggest that the sodium atoms occupy a site with tetrahedral or higher symmetry (i.e. a site with no quadrupolar coupling). The simulation of this spectrum was based on a Lorentzian line at $\delta = 0$ p.p.m., as was used for Na^+ in water, combined with a much weaker component using the same parameters as those for $NaHCO_3$.

The reduction in linewidth of the Twaron ^{23}Na resonance line due to hydration clearly indicates that the absorbed water directly affects the motion of the sodium ions. This will occur if the sodium is present as a salt in the voids of the Twaron fibres, and during water uptake by the fibres the salt becomes partially or fully dissolved. This interaction between the salt

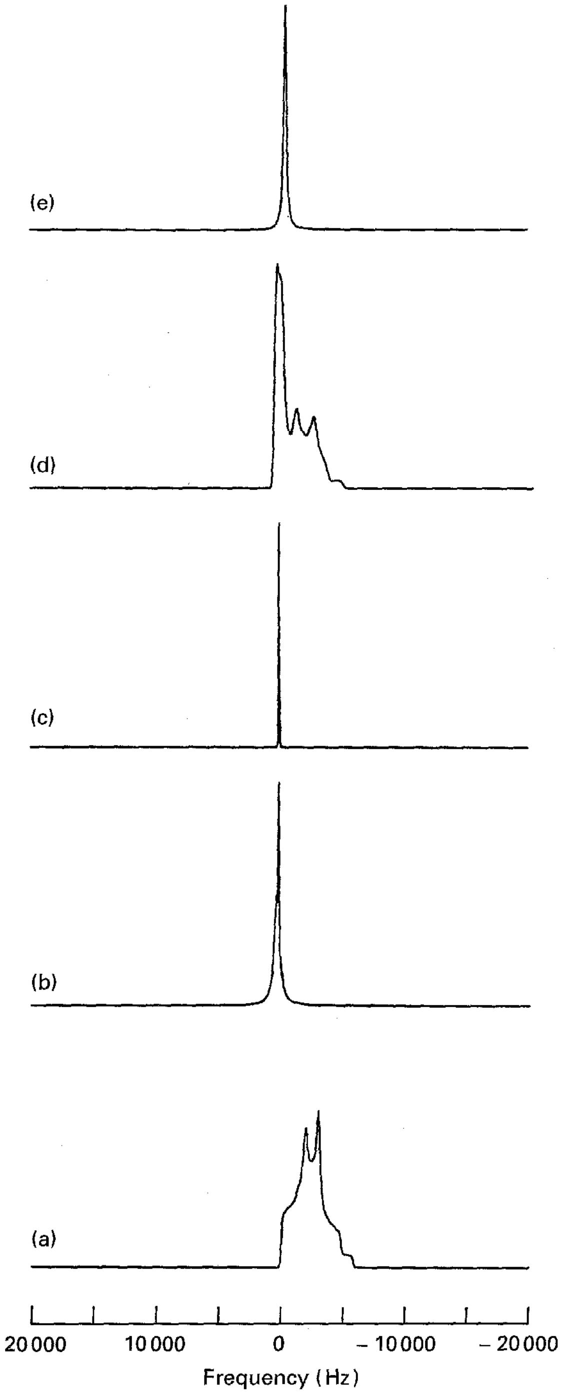

Figure 6 Simulations of the experimental spectra shown in Fig. 5, using second-order perturbation theory. See text for the quadrupolar parameters used in the simulations.

and the absorbed water also accounts for the narrow lines observed in the ^1H spectrum of wet Twaron.

In summary, the following conclusions can be drawn from the simulations of the ^{23}Na spectra. The spectrum of dry Twaron suggests the presence of Na_2CO_3, as well as sodium in one other site, while the spectrum of wet Twaron is consistent with a mixture of aqueous Na^+ and $NaHCO_3$ in the yarn. While these results are reasonable, they cannot be stated unequivocally because of the lack of sharp features in the experimental spectra. From this rather detailed study of the ^{23}Na spectra, we obtain no evidence for the presence of either Na_2SO_4 or $Na_2SO_4{\cdot}10H_2O$ in Twaron. Thus the mechanism proposed by Ashbee and Ashbee [14] to explain the degradation in strength of wet Kevlar does not appear applicable to Twaron fibre.

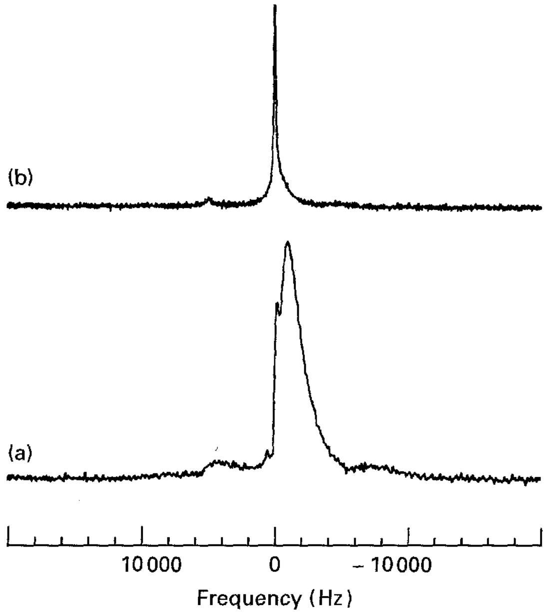

Figure 7 ^{23}Na spectra of (a) dry Twaron and (b) Twaron with 5.7% absorbed moisture.

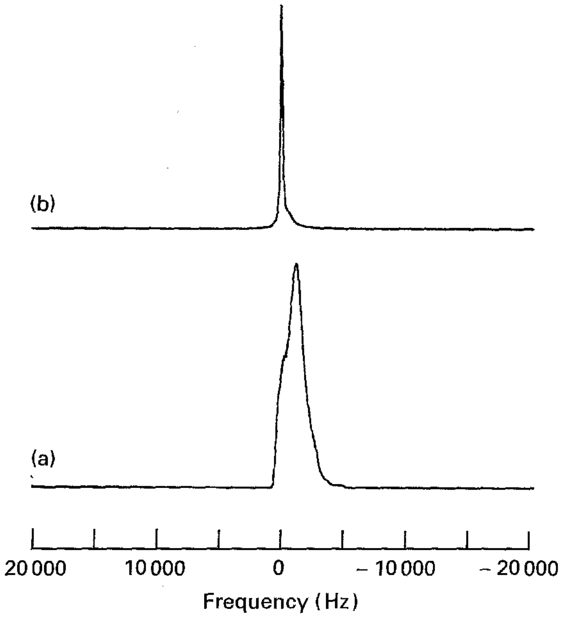

Figure 8 Simulations of the Twaron ^{23}Na spectra shown in Fig. 7. The spectrum of dry Twaron can be simulated using the parameters for Na_2CO_3, with additional Gaussian broadening, and including one additional site. The simulated spectrum of Twaron with 5.7% absorbed moisture is a sum of the spectra for aqueous Na^+, with extra broadening, plus a small amount of the spectra of $NaHCO_3$.

4. Conclusion

Measurements of the quantity of water absorbed by dry Twaron yarn suggest that the water is absorbed into the voids in the fibres.

Our ^{13}C NMR results show that there are no major changes in the chemical structure of the Twaron fibre during hydration, in agreement with previous work on Kevlar 49 fibres [19]. Measurements of the ^1H to ^{13}C cross relaxation rate, and the rotating frame spin lattice relaxation rate of ^{1}H nuclei bound to ^{13}C nuclei, indicate there is very little change in the amount of motion at low frequencies, and only a modest increase in the amount of motion in the 10–100 kHz frequency range. The latter increase is indicative of a slightly increased plasticity of the fibre after hydration. If all the absorbed water actually penetrated into the molecular lattice of the polymer, one would expect a larger change in the molecular dynamics of the polymer.

The relatively narrow lines in the ^{1}H NMR spectra of the water absorbed on Twaron show that essentially all the absorbed water is loosely bound, because there is still sufficient molecular motion to eliminate almost completely the dipolar coupling between protons in the water molecules. The ^{1}H magic angle spinning NMR spectra show that the absorbed water can be further distinguished on the basis of the NMR linewidth. It appears that the water is located at two sites, which differ in the amount of constraint placed on the motion of the water molecules. Based on work by Dobb and Robson [16], who have observed both small surface pores and larger core defects in Twaron fibre, the two sites can be assigned to the two different sizes of voids. In the smaller voids, the water molecules are more rigidly constrained, and hence produce a broader resonance line.

^{23}Na spectra of both wet and dry Twaron can be readily observed, demonstrating that sodium is present at levels of about 1% or more, in agreement with previous reports [13, 14]. However, a comparison with spectra of sodium sulphates shows major differences between the spectra of ^{23}Na in Twaron and in sodium sulphate. This leads us to conclude that the sodium in Twaron is not present as sodium sulphate, and therefore the proposed mechanism for strength degradation in wet Kevlar, due to heaving of the sodium sulphate upon hydration, is not applicable to Twaron. The ^{23}Na spectrum of dry Twaron can be simulated using the parameters used for Na_2CO_3, with one additional sodium site, while the spectrum of wet Twaron can be simulated using the parameters for Na^+ in water, with a small amount of $NaHCO_3$ included.

All of our results may be drawn together to support a model in which the voids in the dry fibres contain a sodium salt, largely made up of sodium carbonate. During hydration, these voids become filled with water. Depending on the fraction of the pore initially filled by the salt, the absorbed water may either partially or fully dissolve the salt.

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References

1. M. ROYLANCE, in "11th National SAMPE Technical Conference", November 1979.
2. K. KOMAI, K. MINOSHIMA and S. SHIROSHITA, *Mater. Sci. Eng.* **A143** (1991) 155.
3. M. ROYLANCE, *Polym. Sci. Eng.* **22** (1982) 988.
4. R. E. ALLRED, *J. Compos. Mater.* **15** (1981) 117.
5. *Idem, ibid.* **15** (1981) 101.
6. R. E. ALLRED and D. K. ROYLANCE, *J. Mater. Sci.* **18** (1983) 652.
7. K. KOMAI, S. SHIROSHITA, and M. BRUSCHKE, in "Proceedings of the 31st Japan Conference on Materials Research" (1988) p. 159.
8. C. C. CHIAO and T. T. CHIAO, Lawrence Livermore Laboratory Report UCRL-80400 (1977).
9. N. J. ABBOTT, J. G. DONOVAN, M. M. SCHOPPEE and J. SKELTON, Fabric Research Laboratory Report AFML-TR-74-65, Part III, Dedham, MA, March 1975.
10. C. O. PRUNEDA, R. J. MORGAN, F.-M. KONG, J. A. HODSON, R. P. KERSHAW and A. W. CASEY, in "Proceedings of the 29th SAMPE Symposium", April 1984.
11. R. J. MORGAN, C. O. PRUNEDA, N. BUTLER, F.-M. KONG, L. CALEY and R. L. MOORE, *ibid.*
12. M. SHUBHA, H. V. PARIMALA and K. VIJAYAN, *J. Mater. Sci. Lett.* **12** (1993) 60.
13. L. PENN and F. LARSEN, *J. Appl. Polym. Sci.* **23** (1979) 59.
14. E. ASHBEE and K. H. G. ASHBEE, *J. Mater. Sci. Lett.* **4** (1985) 249.
15. M. G. DOBB, D. J. JOHNSON, A. MAJEED and B. P. SAVILLE, *Polymer* **20** (1979) 1284.
16. M. G. DOBB and R. M. ROBSON, *J. Mater. Sci.* **25** (1990) 459.
17. M. G. DOBB, C. R. PARK and R. M. ROBSON, *ibid.* **27** (1992) 3876.
18. R. J. YOUNG, D. LU, R. J. DAY, W. F. KNOFF and H. A. DAVIS, *ibid.* **27** (1992) 5431.
19. M. FUKUDA, H. KAWAI, F. HORII and R. KITAMARU, *Polym. Commun.* **29** (1988) 97.
20. P. K. KIM, C. CHANG and S. L. HSU, *Polymer* **27** (1986) 34.
21. M. MEHRING, "High Resolution NMR in Solids" (Springer, Berlin, 1983).
22. A. PINES, M. G. GIBBY and J. S. WAUGH, *J. Chem. Phys.* **59** (1973) 569.
23. C. P. SLICHTER, "Principles of Magnetic Resonance", 2nd Edn, Springer Series in Solid-State Sciences, Vol. 1, edited by P. Fulde (Springer, Berlin, 1980).
24. C. S. YANNONI, *Acc. Chem. Res.* **15** (1982) 201.
25. J. SCHAEFER, E. O. STEJSKAL and R. BUCHDAHL, *Macromolecules* **10** (1977) 384.
26. V. D. FEDOTOV and H. SCHNEIDER, "Structure and Dynamics of Bulk Polymers by NMR-Methods", "NMR–Basic Principles and Progress", Vol. 21, edited by P. Diehl, E. Fluck, H. Günther, R. Kosfeld and J. Seelig (Springer, Berlin, 1989).
27. N. J. CLAYDEN, *Polymer* **33** (1992) 3145.
28. A. ABRAGAM, "Principles of Nuclear magnetism" (Clarendon Press, Oxford, 1983).
29. M. S. TOY and R. S. STRINGHAM, *Polym. Mater. Sci. Eng.* **51** (1984) 146.
30. M. H. COHEN and F. REIF, *Solid State Phys.* **5** (1957) 322.
31. G. H. STAUSS, *J. Chem. Phys.* **40** (1963) 1988.
32. F. LEFEBVRE, J.-P. AMOUREUX, C. FERNANDEZ and E. G. DEROUANE, *ibid.* **86** (1987) 6070.
33. M. WINDHOLZ (ed.), "The Merck Index" (Merck and Co., Rahway, NJ, 1983) p. 1242.
34. R. C. WEAST (ed.), "CRC Handbook of Chemistry and Physics" (CRC Press, Boca Raton, FL, 1982) p. B-150.

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