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Microspectroscopic evaluations of the interfacial degradation by absorbed water in a model composite of an aramid fibre and unsaturated polyester

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Abstract

The laser Raman and the Fourier transform infra-red (*FT*i.r.) microspectroscopic analyses were conducted to monitor the interfacial degradation process in a model composite of an aramid fibre (Kevlar 49) and unsaturated polyester (UP) exposed to water at 30 and 90°C. For micro-laser Raman spectroscopy, a single long fibre was embedded in the UP resin being subjected to static tension. Removing the applied tension after curing the film specimen introduced the residual tensile stress into the fibre. The progress of degradation by water in a region of interface was monitored by measuring the peak shift of the Raman spectrum varying proportionally to the stress generated in the fibre. The micro-*FT*i.r. measurements were done to examine the quantity and the state of absorbed water in the UP resin very near the interface. The thin film specimen, in which the long fibre was not subjected to pre-tension during the cure, was analysed under transmission mode. The residual tensile stress in the fibre was monotonously decreased in hot water at 90°C, and completely released for about 150 h, although the stress reduction for early period of 24 h was mainly caused by the relaxation of elastic modulus of the UP matrix. In water at 30°C, on the contrary, the residual stress remained the initial value for a long time above 1000 h. The micro-*FT*i.r. analyses revealed that at an early stage the isolated water is mainly observed, and then larger amount of clustered water is absorbed with increasing soaking time, particularly at 90°C. At present, however, it is not clear which type of water more strongly participates in the interfacial degradation.

Keywords: Aramid fibre; Unsaturated polyester; Interface

1. Introduction

The mechanical properties of fibre reinforced polymers (FRPs) are, as well known, strongly affected by environmental water, which gradually raids into FRPs during their manufacture, storage and long-term application [1,2]. The mechanical effects of absorbed water are usually evaluated by comparing the fracture resistances and the fracture surfaces of bulk composites obtained before and after immersion in water at relatively high temperatures. It has been pointed out by many experimental results [3–9] that the deterioration in the mechanical performance is mainly caused by a decrease in the load-bearing ability of the fibre/matrix interface. However, such evaluations based on the fracture tests, for which the whole bulk specimen is an object, can offer only indirect information on the progress of interfacial degradation, because it is restricted to occuring in a microscopic region of interface. Thus, an alternative evaluating method may be desired to obtain more precise or direct information on the degradation process at the interface.

Recently laser Raman microspectroscopy has been extensively applied to the micromechanical studies of the interfacial phenomena in the composites [10–18]. It was demonstrated for several material systems that the stress–transfer characteristics between the embedded fibre and the surrounding polymer matrix are well described by this technique. The principle of this technique is based on the fact that the strong Raman scattering occurs due to the inherent atomic vibration in the fibre crystal under irradiation with a laser beam, and the peak frequency of the Raman spectrum in general shifts linearly with the applied stress or strain. Therefore, by using a calibration curve obtained preliminarily on a relationship between the shift in the Raman peaks

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and the axial stress or strain applied to the fibre, one can estimate the axial stress or strain generated in the embedded fibre in the composite from the measured Raman frequencies. Until now much work has been done by Galiotis' [10–13] and Young's [14,15] groups using this technique to monitor the fragmentation processes at different levels of applied strain for several combinations of carbon fibre and thermosetting (epoxy) and thermoplastic (poly(methyl methacrylate), polycarbonate) polymers by evaluating the distribution of interfacial shear stress along the single fibre, derived from the measurement of induced axial strain. Sato et al. [17] have revealed that a sharp stress concentration is introduced into a fibre by the breakage of adjacent fibres in the unidirectional fibre composite under external load, and also that significant stresses are generated even in the fibres off-oriented from the loading direction in the case of the randomly dispersed short-fibre composite. However, the above successful studies devotedly focus their attention to the stress–transfer characteristcs at the fibre/matrix under dry condition.

The laser Raman evaluation of the environmental interfacial degradation has been conducted by Amer et al. [16] for a composite of carbon single fibre and epoxy resin exposed to water at 100°C. They revealed that the degradation is attributed to the failure of the interfacial bonds, which is not a chemical failure such as a hydrolysis reaction [19], but primarily a mechanical one caused by the radial tensile stress generated at the interface resulting from the matrix swelling upon water absorption. Their research demonstrates the laser Raman technique to be valid for evaluating the interfacial degradation in the composite, but does not provide precise information on the advancing process of degradation during water absorption.

Fourier transform infra-red (*FT*i.r.) spectroscopy may also be useful to characterize the environmental degradation at or near the fibre/matrix interface in the composites. Hamada et al. [20] have investigated the degradation of the rondomly dispersed short-fibre composite of E-glass and unsaturated polyester (UP) immersed in water at 80 and 95°C, and analysed the variations of the i.r. spectra at the interfacial region with immersion time by using the micro-*FT*i.r. technique. They supposed that a hydrolysis reaction takes place at the interface in the composite exposed to water at 95°C for a long time (1000 h), although such chemical changes do not occur at 80°C. A recent *FT*i.r. study of Kusanagi and Yukawa [21] has provided valuable information on the structures of water absorbed in solid polymers. They concluded from the shape and the frequency range of i.r. spectra that the water molecules exist in clusters in hydrophilic polymers such as polyamide, while they are in isolated (gaseous) state in hydrophobic polymers such as poly(ethylene terephthalate). This result will be very effective for interpreting the interfacial degradation process by water in the composites.

In view of the above, in this study we conduct the spectroscopic analyses in order to evaluate the degradation behaviour in the interfacial region followed by the diffusion of environmental water for an aramid fibre (Kevler 49)/UP model composite. The time-dependent process of interfacial degradation is monitored by measuring the varations in residual stress in the single fibre by means of laser Raman microspectroscopy. In this case the tensile residual stress, which is preliminarily introduced into the fibre by releasing the applied tensile load after curing process, plays a role of a detector to sense the progress of degradation. The variations of the quantity and the structure of absorbed water with immersion time are examined by using the micro-*FT*i.r. technique for the matrix polymer in the small regions very near the interface. By combining these results obtained both from the laser Raman and from the *FT*i.r. analyses, the mechanisms of interfacial degradation followed by water absorption may be discussed.

2. Experimental

2.1. Materials and sample preparation

The fibre used is a commercially available poly(*p*-phenyleneterephthalamide), Kevlar 49 (DuPont Toray Kevlar Co. Ltd) of 195 denier (12 μm in diameter). According to the supplier's catalogue, the tensile elastic modulus and the tensile strength are 135 and 2.9 GPa, respectively. The Kevlar 49 fibre was chosen for its strong Raman scattering and weak fluorescence, leading to easy measurements, and also for the published data of the Raman spectrum which may help in confirming the accuracy of our measurements. UP, PS-2202PT (Hitachi Chemical Co. Ltd) was used as a matrix polymer, being mixed with a curing agent of methylethylketoneperoxide, Permec-N (Nihon Yushi Co. Ltd) by 1 wt%.

For the laser Raman measurements, a single long fibre was embedded in the polymer, being subjected to static tension by suspending a weight. The polymer including the fibre was sandwiched between two glass plates, the surfaces of which were previously treated with a non-shift type release agent, Chemlease/40 (Chemlease Co. Ltd), and then was cured at 100°C for 15 h in a forced-air oven. Removing the applied tension after the cure introduced the residual tensile stress into the fibre. The rectangular specimens were prepared by cutting the polymer part to give a length of 20 mm, a width of 10 mm and a thickness of 0.5 mm. The embedded fibre was adjusted to be located at the mid-width and near one side of the surfaces of the specimen. The distance from the surface of the specimen to that of the embedded fibre for each specimen was measured using an optical microscope, Axioplan (Carl Zeiss Inc), and a laser displacement transducer, model LB-1000 (Keyence Co. Ltd). The specimens were washed with soap and water, and then dried in a vacuum chamber at room temperature for 24 h.

The specimens for analysing the absorbed water by using the micro-*FT*i.r. technique were prepared in the same way as those for the laser Raman measurements, although the embedded fibre was not subjected to pre-tension during the cure. The thickness of specimen was made to about 20 μm for conducting the i.r. measurements under transmission mode.

Besides the above model composites, the rectangular bulk specimens of matrix polymer (UP) with size $80 \times 10 \times 2\ \mathrm{mm}^3$ were also prepared under the same curing condition as the above for the measurements of the dynamic viscoelastic and the stress relaxation properties, which were needed for interpreting the variations in residual stress in the embedded fibre during water absorption.

2.2. Laser Raman measurements of residual stress in the fibre

The Raman spectra were obtained by means of a laser Raman microspectrometer, model NR-1100 (Japan Spectroscopic Co. Ltd). The 514.5 nm line of an argon ion laser was focused to a 2 μm diameter spot on the fibre using a modified optical microscope with a ×50 objective lens. The power of the laser beam was kept constant as low as 2–3 mW to avoid local heating causing unnecessary Raman band shifts. The 180° backscattered beam was collected by the same microsope objective. The peak position of the Raman bands was determined from the curve-fitted spectra given by a Lorentzian function. In this study the intense band at 1618 cm^{-1} corresponding to an in-plane stretching vibration of benzene ring was adopted to monitor the deformation of the embedded fibre during the interfacial degradation.

In the experiments, first the relation of the Raman frequency shift to the applied tensile stress was obtained for a free-standing fibre subjected to different tensile stresses, by using a simple loading device of a pulley and a dead weight. In order to evaluate the effect of aborbed water, the fibres soaked previously in water at 30 and 90°C for 24 h were tested, besides the fibre kept in air. From these experiments a calibration curve for estimating the residual stress in the embedded fibre in the model composite was obtained. Next the specimens of model composite were immersed in distilled water at 30 and 90°C, and then subjected to the laser Raman measurements at appropriate time intervals. The Raman spectra were obtained by focusing the laser beam on the surface of embedded fibre. After the measurements, for which about 15 min was needed each time, the specimens were immediately returned to the former state. According to the preliminary experiments of water absorption and desorption by the model composite specimen, about 95% of equilibrium concentration was reached for about 24 h at 90°C, and only a small percentage of water was desorbed for 15 min in air at 20°C. Therefore the water desorption during the Raman measurements seems to exert only a slight influence on the variations in the residual stress. For comparison, the variations of Raman spectra with time for the specimens held in air at 90°C were also measured in the same way. Thus the residual stress in the embedded fibre was determined by comparing the peak shift of Raman spectrum with the above calibration curve.

2.3. *FT*i.r. analyses of absorbed water

In order to analyse the structure and the quantity of absorbed water participating in the interfacial degradation, the *FT*i.r. microspectra were measured by use of a *FT*i.r. microspectrometer with a MCT detector, model 8900 μm (Japan Spectroscopic Co. Ltd). Small rectangular regions 12 μm × 120 μm in the matrix polymer just adjacent to the interface and distant 100 μm from the interface were analysed under transmission mode. Sixteen scans of 4 cm^{-1} resolution were carried out for each case. As for the laser Raman measurements, the model composite specimens were immersed in distilled water at 30 and 90°C, and then periodically pulled out for measuring the i.r. spectra. The i.r. measurement was conducted just after wiping up the water on the specimen surface with tissue paper. The i.r. spectra of absorbed water were obtained by taking a difference between the spectra for the water-soaked and the as-cured specimens by using a subtraction command of a computer so as to offset each absorbance intensity at 875 cm^{-1} due to the out-of-plane bending vibration of CH in the UP matrix polymer. The concentration of absorbed water was relatively evaluated by comparing the absorbance intensity of water each other. The structure of water, i.e. gaseous or liquid state, was analysed from the shape of spectrum. After the measurements, the specimens were rapidly returned to the former state.

2.4. Evaluation of the mechanical properties of matrix polymer

The dynamic viscoelastic and the stress relaxation properties were measured using the rectangular bulk specimens of UP, for understanding the results of the above spectroscopic experiments. A dynamic viscoelastic meter, model VFA-1KNA (Orientec Co. Ltd), was used for both the purposes. The storage modulus, E', and the loss tangent, $\tan\delta$, were measured under a sinusoidal strain of the amplitude of 6.25×10^{-4} at 1 Hz at a heating rate of 2°C min^{-1} from −150°C to a certain temperature, at which the measurement was impossible by large elongation at an applied stress level of 0.98 MPa under auto-tension mechanism for preventing slack of the specimen. The dynamic viscoelastic tests were made for the as-cured specimen and the specimens pre-soaked in water at 30 and 90°C. The stress relaxation tests were conducted in air at 30 and 90°C, applying fixed strains of 1 and 4% to the as-cured specimen, respectively. The variations of the elastic moduli with time at 30 and 90°C were obtained from these experiments.

3. Results and discussion

3.1. Raman spectra against the applied tensile stress

Conducting the measurements of the Raman spectra of a free-standing single fibre of Kevlar 49 at different tensile stresses provides the result shown in Figure 1, which shows a linear relationship between the peak shift of wavenumber and the applied stress. A least-square approximation gives a straight line with a slope of 3.46 $\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$, which is the same value as that calculated from the Raman frequency gauge factor (RFGF) of 4.5 $\mathrm{cm}^{-1}\,\%^{-1}$ and the elastic modulus of 130GPa for Kevlar 49 given by Vlattas and Galiotis [10]. For examining the effects of immersion in water, the Raman band shifts for fibres pre-soaked in water at 30 and 90°C for 24 h were also measured in the same way. It may be clear in Fig. 1 that those data also lie on the same straight line for the dried fibre. Therefore this straight line may be commonly used as a calibration curve for estimating the residual stresses in the embedded fibre in the model composite exposed to both air and water environments.

It also should be preliminarily evaluated whether the matrix polymer exerts some influences on the Raman spectra of the fibre. Covering the surface of the fibre with the uncured liquid UP resin revealed that no shift of peak wavenumber occurs with no applied load, although the intensity of scattered light is somewhat weakened. In addition, any Raman scattering was not observed from the matrix polymer in the range of wavenumber examined here. Thus the Raman spectra measured for the embedded fibre in the model composite are supposed to be unaffected by the surrounding UP matrix.

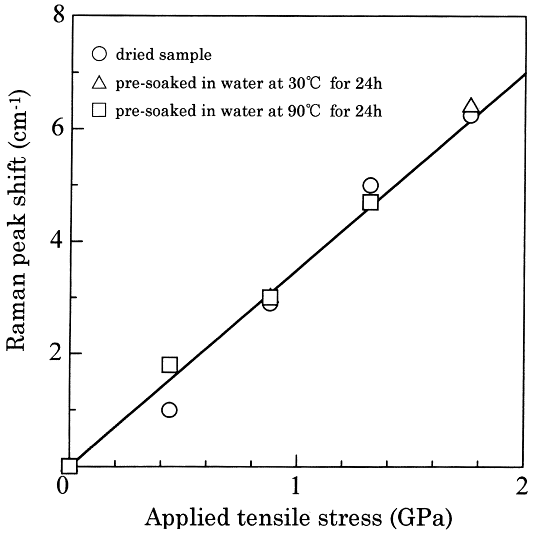

Fig. 1. Raman peak shift as a function of applied tensile stress for the Kevlar 49 fibre preserved under different conditions.

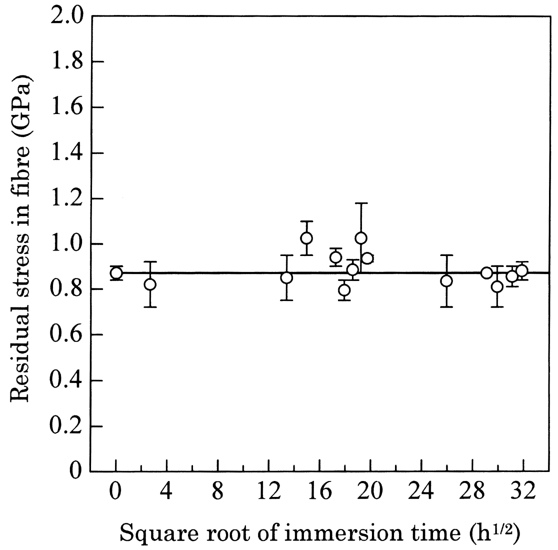

Fig. 2. Variation of the residual tensile stress in the embedded fibre with immersion time in water at 30°C.

3.2. Variations in the residual stress in the embedded fibre

Fig. 2 shows the variation of residual stress in the fibre with immersion time in water at 30°C. Although the data are somewhat scattered, the residual stress almost maintains the initial value even after immersion for 1000 h. According to the experiments of water absorption at 30°C, about 90% of the equilibrium concentration (about 0.7 wt%) was absorbed for 100 h. The dynamic viscoelastic tests revealed the storage modulus, E', of the rectangular specimen of matrix polymer immersed in water at this temperature for 100 h to have a value of 2.6 GPa at 20°C, which was about 94% of the E' of the as-cured (untreated) specimen. Fig. 3 shows the relaxation behaviour of the elastic modulus of matrix polymer measured in air at 30 and 90°C. Although at 30°C the elastic modulus is lowered to about 80% of its initial value (2.78 GPa), its relaxation is almost terminated

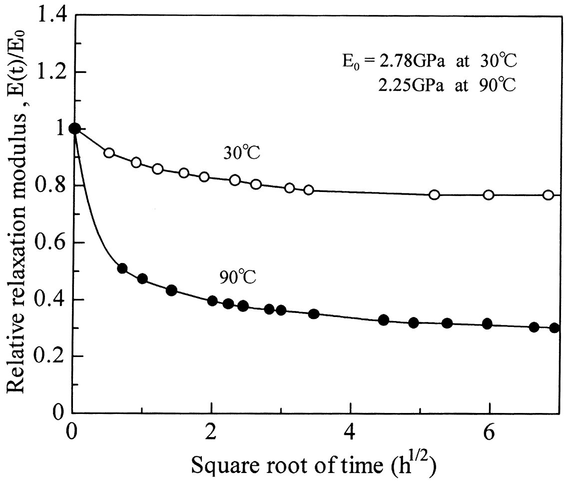

Fig. 3. Relaxation behaviour of the elastic moduli for UP matrix polymer in air at 30 and 90°C.

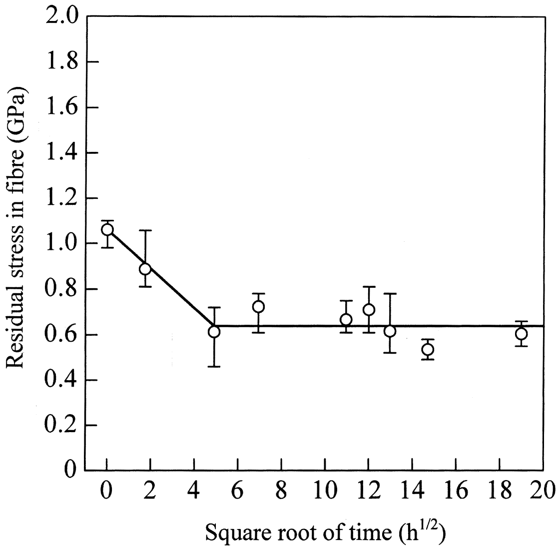

Fig. 4. Variation of residual stress in the embedded fibre with time in air at 90°C.

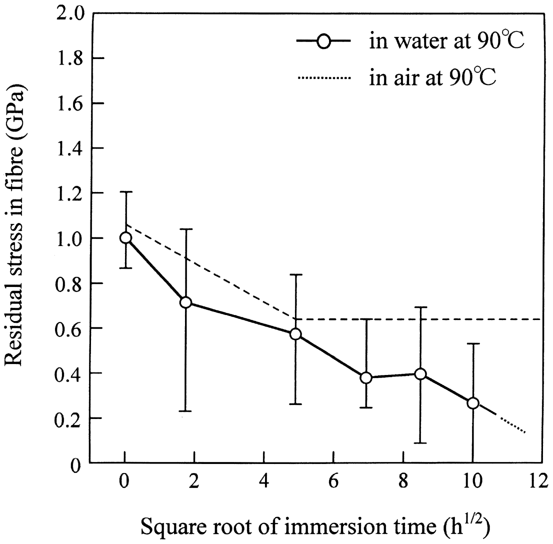

Fig. 5. Variation in the residual stress in the embedded fibre with immersion time in water at 90°C.

for a relatively short period of 16 h. The result shown in Fig. 2 may thus indicate that at 30°C the adhesion between the fibre and matrix at the interface are stable, being not apparently affected by absorbed water and ambient temperature, irrespective of slight softening and relaxation of matix polymer near the interface.

The result for the specimen placed in air at 90°C is shown in Fig. 4. Under this condition the residual stress is reduced with time for early 24 h, and then reaches a constant value of about 60% of the initial value. As shown in Fig. 3, the relative elastic modulus to its initial value (2.25 GPa) at 90°C is rapidly lowered, but its relaxation is almost finished for 24 h, as for the residual stress. In addition, according to the result of Allen and Roche [22], the stress relaxation of Kevlar 49 fibre is terminated for a very short period of about 10 s. Therefore it will not exert any influence on the variations in the residual stress in the embedded fibre. Thus it may be concluded that the trend observed in air at 90°C is mainly caused by the reduction in the elastic modulus of the matrix polymer.

The variation in the residual stress in a water environment at 90°C is represented in Fig. 5. Comparing with the result at 30°C, the experimental data are widely scattered as a whole, and the mean value is monotonously lowered with the immersing time. The previous result obtained in air at 90°C (Fig. 4) is also given by the broken line in the figure. In comparison with both the results in air and in water, at an early stage within 24 h two curves are close to each other, and hence the stress reduction in water may also be mainly attributed to the inherent reduction in the elastic modulus of the matrix polymer at 90°C, although there may be some plasticization effect of absorbed water, as noted later. At a later stage after 24 h, opposing the trend of residual stress in air which holds almost constant, the residual stress in the water environment is further reduced, and completely released for about 150 h. The measurement of weight gain in water at this temperature revealed that the weight gain of the specimen is raised up to a maximum value of 0.85% for early 10 h, and then gradually decreases, and reaches a vale of 0.6% for 900 h. This reduction in weight gain probably results from a hydrolysis reaction, as has so far been pointed out [20,23]. According to the dynamic viscoelastic tests, the value of E' of the matrix polymer at 20°C measured for the specimen pre-soaked in water at 90°C for 50 h was reduced to about 85% of that of the as-cured specimen. Therefore it may be concluded that the lowering trend of the residual stress in hot water, particularly at a later stage, is caused by the advance of interfacial degradation by absorbed water, which is probably brought about by the chemical effects such as the scisson of hydrogen bonding and the hydrolysis reaction, and also by the physical effects like softening or plasticization of the matrix polymer. With regard to the wide scattering of experimental data under this condition, it probably reflects the difference in the distance from the specimen surface to the embedded fibre, which may control the amount of water accumulated at the interface, and also the inhomogeneous states of the matrix polymer and the adhesion in the interfacial region, at every measuring site and/or for every sample.

3.3. Structure and quantity of absorbed water near the interface

In Fig. 6 the variation of the i.r. absorbance spectrum with the immersing time obtained at a position adjacent to the interface in the model composite exposed to water at 90°C. In all the spectra sharp peaks are commonly seen at the wavenumber of 3630 cm^{-1}. According to the recent *FT*i.r. study of Kusanagi and Yukawa [21] on the structure of absorbed water in solid polymers, water in hydrophobic

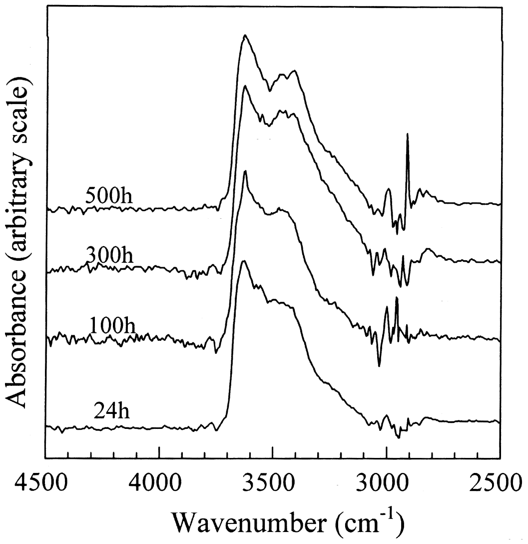

Fig. 6. *FT*i.r. spectra of absorbed water in the matrix at a position adjacent to the interface in the model composite immersed in water at 90°C for various times.

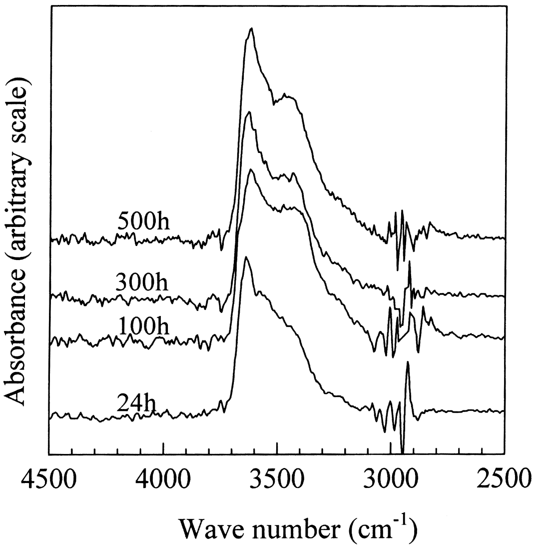

Fig. 7. *FT*i.r. spectra of absorbed water in the matrix at a position adjacent to the interface in the model composite immersed in water at 30°C for various times.

polymers is generally in isolated (gaseous) state, indicating two clearly distiguished peaks corresponding to the antisymmetric and the symmetric vibrations of hydroxyl (OH) at relatively high wavenumbers (Completely gaseous water shows an absorption at 3756 cm^{-1} for the former). On the other hand, in hydrophilic polymers water exists in clusters showing blunt peaks at lower wavenumbers (Completely liquid water indicates only one broad peak at 3430 cm^{-1}). By refering to the above, it may be interpreted that the sharp absorption at 3630 cm^{-1} is due to the antisymmetric vibration of OH in water exsisting in a state near the gaseous state, probably being adsorbed to the ester group of the matrix UP resin. We can also see a broader peak at a lower wavenumber of 3440 cm^{-1}, which becomes clearer with an increase in the immersion time. This broad peak may indicate the existence of clustered water near liquid state. An absorption due to the symmetric vibration of OH expected to appear at a medium wavenumber is perhaps contradicted by this broad peak. In Table 1 the relative values of i.r. absorbance at 3630 and 3440 cm^{-1} for different immersion times in water at 90 and 30°C are summarized by adopting the peak height at 3630 cm^{-1} for a soaking time of 24 h at 90°C as a standard of comparison. It is noted from the table that at 90°C the concentration of water, especially that of clustered water represented by the broader peak at 3440 cm^{-1}, increases with increasing time of immersion except for the case of the longest time of 500 h. In addition, compared with the data obtained at an another site distant from the interface, a larger amount of water was always observed in the region very near the interface.

Fig. 7 shows the i.r. absorbance spectra of absorbed water at 30°C also at the position in close vicinity to the interface. Compared with the above results at 90°C, similar trends are observed, but the intensity of absorbance indicating the water concentration is weak, as a whole, excluding the case for 500 h. Particularly the broad peak at lower wavenumber of 3440 cm^{-1} corresponding to the clustered water is weak at an early stage of immersion, as also shown in Table 1. As for the case at 90°C, a higher concentration of water was measured at the position adjacent to the interface.

For the above results of the Raman and the i.r. measurements one may suggest that the clustered water assembling at the interface for long time immersion at higher temperature actively contribute to the interfacial degradation, probably both by physical failure like plasticization of matrix polymer and by chemical failures such as the scission of

Table 1
Relative absorbance intensity obtained from *FT*i.r. spectra of absorbed water shown in Figs 6 and 7

	Temperature 90°C				Temperature 30°C			
	Immersion time 24 h	Immersion time 100 h	Immersion time 300 h	Immersion time 500 h	Immersion time 24 h	Immersion time 100 h	Immersion time 300 h	Immersion time 500 h
Wavenumber 3630 cm^{-1}	1.00	1.02	1.07	0.91	0.87	0.89	1.02	1.13
Wavenumber 3440 cm^{-1}	0.71	0.78	0.91	0.78	0.49	0.76	0.71	0.80

hydrogen bonding and the hydrolysis reaction. However, an another explanation may also be possible. Since the isolated water may be more reactive due to the free OH unit, it will greatly promote the hydrolysis reaction at the interface and in the matrix polymer. From this viewpoint the clustered water detected by the i.r. measurement may be formed by the accumulation of isolated water at some defective sites at the interface, which are introduced by the chemical failures mentioned above. In this explanation the clustered water is not a cause, but a result of interfacial degradation. At present, which interpretation is adequate may not be decided, because of lack of precise information on the mechanisms of defect formation at the interface in relation to the reactivity of water molecules.

By the way both the above interpretations for the interfacial degradation may be quite different from that of Amer and coworkers [16,24] derived from the experimental results for a model composite of carbon single fibre and epoxy resin immersed in hot water at 100°C. They indicated that the failure of interfacial bonds is not caused by the hydrolysis reaction [19] in the matrix polymer, but primarily by a mechanical failure due to the radial tensile stress generated at the interface by the swelling of matrix polymer during water absorption. This result may be an effect of the fact that the epoxy resin can absorb higher content of water, and is relatively stable in hot water for long time, in comparison with the UP resin. Amer et al. [16] reported a maximum weight gain of 3.28% after 141.5 h. Our preliminary experiments also revealed that for the epoxy specimen the weight gain of about 6.5% is achieved at saturation and maintained for about 400 h immersed in water at 90°C. These results may suggest that the degradation by the hydrolysis reaction with water leading to the weight loss of the specimen does not take place in epoxy. On the other hand, as previously mentioned, in the UP resin only 0.85 wt% of water was absorbed at a saturation at 90°C, and subsequent reduction in the weight gain took place, probably due to the hydrolysis reaction with water. In addition, the volume expansion of UP resin was hardly observed after long time immersion in water. Therefore, as discussed above, alternative degradation mechanisms independent of the matrix swelling may act in the interfacial region of our model composite.

Finally it should be noted that Kevlar 49 fibre inherently tends to attract water molecules due to amide group in its structure [25]. Consequently larger amount of water observed in the interfacial region may possibly result from this tendency of the fibre. Comparing the present result with that for a carbon fibre will be useful for confirming this hypothesis.

4. Conclusions

The microspectroscopic analyses using laser Raman and *FT*i.r. techniques were conducted for evaluating the intefacial degradation caused by absorbed water in a model composite of an aramid fibre and UP. The time-dependent process of environmental degradation in an interfacial region was monitored by measuring periodically the peak shift of Raman spectrum corresponding to the residual tensile stress introduced preliminarily to the embedded fibre. The residual tensile stress in the fibre remained the initial value for a long time above 1000 h in water at 30°C. In hot water at 90°C, by contrast, the residual stress was monotonously decreased, and completely released for about 150 h, although the stress reduction for early 24 h was mainly caused by the relaxation of elastic modulus of the matrix polymer. The micro-*FT*i.r. analyses indicated that water absorbed in the matrix polymer very near the interface exists in isolated or clustered state, and its concentration increases with an increase in the soaking time. Which type of water more strongly contributes to the interfacial degradation remains to be elucidated. It may be concluded that the present method of microspectroscopic evaluation is significant to investigate the environmental degradation at the fibre/matrix interface.

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