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Effects of absorbed water on the interfacial fracture between two layers of unsaturated polyester and glass

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The effects of absorbed water on the interfacial fracture resistance between two layers of unsaturated polyester (UP) and glass of the bilayer specimen were evaluated by measuring a load for producing the fracture by inserting a razor blade into the interface. The specimens were subjected to the cyclic absorption-desorption and the continuous absorption processes of water. The load to initiate the interfacial fracture was markedly lowered by the early absorption process for short period, and then gradually reduced with increasing cycle or period of water absorption, although it slightly recovered after the first great reduction when the specimens were subjected to the soaking process at lower temperatures. The micro-FTIR (ATR) analyses of the detached surface of the UP resin from the glass plate revealed that the water is accumulated in the resin at the interface in the cluster, showing the concentration to increase with increases both in the temperature of environmental water and in the water-soaking period. The IR analyses also demonstrated the hydrolysis reaction to take place on the detached resin surface of specimen exposed to water at high temperature. Thus the accumulated water at the interface may remain and promote the interfacial degradation even under the drying process by various mechanisms like the hydrolysis reaction in hot water environment.

1. Introduction

The preservation of adhesive bond strength between polymer and glass is one of the significant subjects for the glass fibre reinforced polymers (GFRPs), because it directly participates in their durability for long-term applications. The mechanical resistance of the matrix polymer-glass interface to the fracture (debonding) is of particular importance in several problems relating to the above subject, and therefore is required to adequately evaluate.

The adhesive bond strength is generally evaluated by using various types of adhesive joint [1, 2]. In these methods, however, the adhesive failure does not always take place only in a manner of interfacial fracture. The cohesive and/or the mixed modes of fracture are sometimes observed in the adhesive and the substrate depending on the test conditions. Therefore the current testing methods using the adhesive joints are usually difficult to establish the conditions for controlling the fracture to occur only at the interface. Other types of testing method, on the other hand, which in common evaluate the adhesive strength of coatings by inserting a sharp knife blade along the interface between the coating and the substrate have so far been proposed by Asbeck [3] and Nishiyama and Takahashi [4]. According to their analyses, the stratified structure of coating and the interfacial strength may be assessed from the variations in the mechanical resistance during inserting the knife blade into the coating from its surface. Smith *et al.* [5] have recently evaluated the interfacial adhesive strength in terms of the toughness for crack propagation when a razor blade was transferred along the interface between the glass substrate and the adhering polymer layer. Their testing method is a sort of double cantilever beam test, and has a merit that the interfacial fracture may steadily take place in wide area, which may ease to analyse the interfacial crack surface.

Incidentally GFRPs are frequently applied to the structural components exposed to water environments (e.g. craft, bathtub, water tank, etc.). Under such environments, in general, water gradually penetrates into GFRPs, and deteriorates their mechanical performance relating to the durability for long-term applications. Many past experimental studies [6–11] have supposed that such environmental degradation of GFRPs is mainly caused by a reduction in load-bearing ability of the interfacial region between the fibre and the matrix polymer, by the action of water through physical and/or chemical mechanisms like plasticization, swelling and hydrolysis reaction in the matrix polymer. This supposition is mainly derived from the variations of the fracture resistance and the fracture surface of bulk GFRP specimen with exposure to water environments. In these testing methods, however, it may be difficult to decide upon the true interfacial fracture to take place between the matrix polymer and the glass fibre, and furthermore to analyze the materials degeneration being occurred in a very small region of interface. It thus may be required to adopt different ways to realize only the interfacial fracture in wide area, for evaluating the progress of interfacial degradation by penetrating water which may be accumulated at the polymer-glass interface.

In view of the above, making main reference to the study of Smith *et al.* [5], we evaluated the effects of penetrating water on the mechanical resistance of the polymer-glass interface to the fracture (debonding) by measuring the load for inserting the sharp razor blade into the interface between two layers of unsaturated polyester (UP) and glass subjected to continuous or intermittent exposure to water at different temperatures. In addition, the quantity and the structure of water being accumulated at the interface and also the hydrolysis reaction in the UP resin promoted by the accumulated water were examined by means of the micro-Fourier transform infra-red (FTIR) analyses of the new surface of UP resin formed by detachment from the glass plate. By combining these results obtained from the debonding test and the micro-FTIR measurements, the mechanisms of interfacial degradation followed by water absorption may be discussed.

2. Experimental

2.1. Materials and specimen preparation

The polymer used is commercially available unsaturated polyester (PS-2202PT, Hitachi Chemical Co. Ltd.). It was mixed with a curing agent of methylethylketoneperoxide (Permec-N, Nihon Yushi Co. Ltd.) by 1wt%, and then applied onto a glass plate ($13 \times 38 \times 1.3$ mm^3) cut from the standard laboratory microscope slide, the surface of which was preliminarily treated γ-methacryloxypropyltrimethoxysilane (A-174, Nippon Unicar Co. Ltd.). The silane coupling agent dissolved in methanol (1:4 in vol.) was coated on the glass surface, and dried in air at 100°C for 1 h. The UP resin on the glass was flattened by being covered with another glass plate treated by non-shift type release agent (Chemlease/40, Chemlease Co. Ltd.). The thickness of UP resin was adjusted to 1.0 mm by inserting a spacer of steel plate. The specimen was left at 60°C for 15 h in a forced-air oven for curing the resin, and offered to the tests mentioned below about 200 h later after mixing the resin with the curing agent. The curing at temperatures above 60°C frequently brought about the accidental detachment of resin layer from the glass substrate during or after the curing treatment, probably due to greater residual stress caused by greater shrinkage of UP resin, as indicated later. All the specimens were stored in a desiccator (20 ± 1°C, RH14%) until the experiments. In this paper, hereafter, the specimen prepared in the above way is called a bilayer specimen. The geometry of bilayer specimen is shown in Fig. 1.

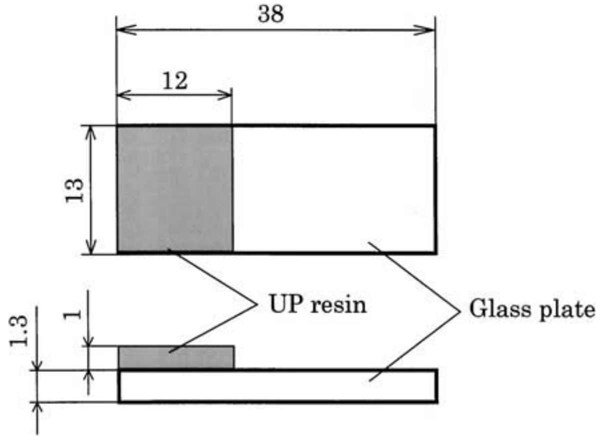

Figure 1 Geometry of bilayer specimen (dimensions in mm).

2.2. FEM analysis of residual stress

The residual stress was supposed to generate in the bilayer specimen both by the shrinkage of UP resin during the curing process and by the thermal shrinkage under cooling. For qualitatively evaluating its effects on the start of interfacial fracture, the residual stress was broadly estimated by means of the finite element method (FEM). According to the preliminary measurements, the shrinkage of UP resin was mostly observed after the beginning of solidification. Thus in the calculation, for simplicity, the UP resin was assumed to behave as an elastic solid as well as glass plate during the curing process. Three-dimensional analysis was performed by use of a commercially available program for the thermal stress analysis (ANSYS 5.0A, Swanson Analysis Systems Inc.). For the calculation of residual stress due to the shrinkage of UP resin, the thermal expansion coefficient of resin was replaced by the volume shrinkage of resin during the curing process, approximating that the shrinking process does not proceed one by one, but is completed at a time. Considering the symmetrical geometry of specimen, the stress calculation was performed for its half part, which was divided into 6000 small elements of a rectangular prism. The basic properties of resin required for the calculation, i.e. the elastic modulus, Poisson's ratio, the shrinkage under curing and the thermal expansion coefficient, were preliminarily measured. The elastic modulus given by the storage modulus E' was measured by using a dynamic viscoelastic analyser, VFA-1KNA (Orientec Co. Ltd.), under a sinusoidal strain at 0.1 Hz. Poisson's ratio was obtained from the deformation of small rectangular specimen under compression by use of a hydraulic servo-controlled testing machine, EHF-FBKN-10LA (Shimadzu Co. Ltd.). The shrinkage at 60°C was measured by means of a laser displacement transducer, LB-1000 (Keyence Co. Ltd.). The thermal expansion coefficients of UP resin and glass plate were measured by a thermal dilatometer, TD5030 (MAC Science Co. Ltd.). The elastic modulus and Poisson's ratio of glass plate were given by the general values of soda glass quoted from a literature [12]. The detailed procedure of FEM analyses will be described elsewhere [13].

2.3. Procedure of interfacial fracture tests

The bilayer specimens were subjected to the cyclic absorption-desorption treatments, the elemental process of which was done by soaking the specimen in distilled water at 20, 30, 40 and 50°C for 24 h and subsequently drying it in air at 20 ± 1°C. It was noted in the soaking process that only the upper surface of UP resin opposite to the interface is always in contact with water, and that the side surfaces are coated with a silicone adhesive to prevent water from penetrating. For comparison, the bilayer specimens which were continuously in contact with water at each temperature and then dried in air at 20±°C were also prepared. Some bilayer specimens subjected to the continuous absorption treatment of water were periodically weighed with an electronic balance for evaluating the behaviour of water absorption. After weighing, these specimens were immediately returned to the former state without excessive drying process.

The mechanical resistance of the polymer-glass interface to the fracture was evaluated by a blade-insert-testing (BIT) method, which was designed by making reference to the method of Smith and coworkers [5]. The razor blade was mounted on a holder of our own making, and inserted into the interface between two layers of UP resin and glass substrate of bilayer specimen at an angle of 55° to the glass surface at a moving speed of 5 mm/min by means of the hydraulic servo-controlled testing machine, as shown schematically in Fig. 2. The load and the displacement for advancing the blade were recorded on a X-Y recorder. According to the preliminary experiments, the following deformation processes were observed. When the razor blade encroaches upon the edge of UP resin layer, a small crack (detachment) is formed at the interface in front of blade tip. Under this situation the layer of UP resin is begun to bend by the blade. As the razor blade advances, the bending deformation (deflection) of resin and the load acting on the blade are increased, although the small crack in front of blade tip almost holds the size. Presently the crack rapidly grows, and the load is drastically decreased, because the crack growth rate is much greater than the advancing speed of blade. Thus the recorded curve of load and displacement may be interpreted to describe the bending deformation behaviour of UP resin until the crack begins to unstably grow along the resin-glass interface. This further suggests that the peak load is available to evaluate the mechanical resistance of the interface to the start of rapid crack growth. In addition, the measurements by micro-FTIR spectroscopy also revealed that no vestige of applied UP resin exists on the glass surface which is newly formed during inserting the razor blade. This result may mean that the present BIT method using the bilayer specimen actualizes a real interfacial fracture. Therefore it will be possible to adequately evaluate the variations of the interfacial fracture resistance with the cyclic process of water absorption-desorption by comparing each peak load corresponding to the start of rapid crack propagation.

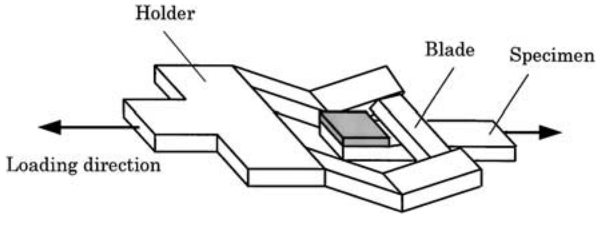

Figure 2 Schematic drawing of blade insert test (BIT).

2.4. Micro-FTIR analyses of interface

In order to examine the quantity and the structure of water which may be accumulated at the interface and to confirm the hydrolysis reaction in the UP resin also taking place at the interface, the micro-FTIR spectroscopic analyses were conducted by use of a FTIR microspectrometer with a MCT detector (model 8900μ, Japan Spectroscopic Co. Ltd.). The bilayer specimens, only the UP resin surfaces of which were kept in contact with water at 20, 30, 40 and 50°C for some periods, were subjected to the BIT experiments, and then the detached resin surfaces were immediately offered to the IR measurements under a mode of attenuated total reflection (ATR) using a ZnSe prism. Fifty scans of 4 cm^{-1} resolution were carried out for the square regions of 120 μm × 120 μm of detached surface. The IR spectra due to the stretching vibration of hydroxyl (OH) of absorbed water at wavenumbers ranging from 3200 to 3650 cm^{-1} were obtained by taking a difference between the spectra for the water-soaked and the as-cured specimens by using a subtraction command so as to offset each absorbance intensity at 875 cm^{-1} due to the out-of plane bending vibration of CH in the UP resin, which is not affected by water. By this operation both the effects of water which was originally absorbed in the UP resin during the storage and of hydroxyl groups in the resin are cancelled. A Lorentzian curve-fitting was used to determine the peak wavenumber of absorbance spectrum. The concentration of accumulated water was relatively evaluated by comparing the absorbance intensities (peak heights) due to water to each other. The structure of water, i.e. isolated or clustered structure, was analysed from the shape and wavenumber range of IR spectrum, obeying the study of Kusanagi and Yukawa [14].

In addition the micro-FTIR examinations for the hydrolysis reaction in the UP resin which may be promoted by the accumulated water at the interface were also conducted in the same way as for the structural analyses of water. The variation in the content of carboxylate was relatively evaluated by an area ratio of absorbance spectrum by the carboxylate at 1580 to 1600 cm^{-1} to that by the ester group of UP resin at 1720 cm^{-1}.

3. Results and discussion

3.1. Behaviour of UP-glass interfacial fracture affected by water

Fig. 3 represents the typical examples of load-displacement relation for advancing the razor blade along the interface of bilayer specimens subjected to

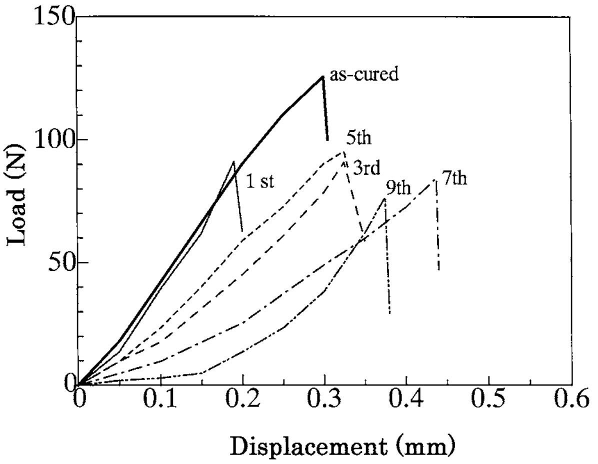

Figure 3 Load-displacement relation for advancing the razor blade along the resin-glass interface of bilayer specimen.

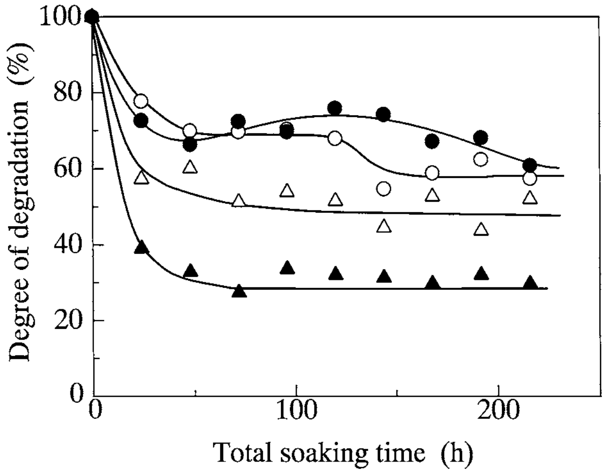

Figure 4 Variation in the peak load for the bilayer specimen under cyclic absorption-desorption process of water at different temperatures. (○) 20°C, (●) 30°C, (△) 40°C, (▲) 50°C.

several cycles of soaking in water at 30°C and drying in air at 20°C. As mentioned in the previous section, these curves express the bending deformation of UP resin until the start of rapid crack growth along the resin-glass interface. The ordinal numbers in the figure denote the number of repeating cycles. For the as-cured specimen the load is almost linearly increased with increasing displacement, and abruptly reduced showing a sharp peak, which corresponds to the start of unstable crack propagation along the interface. Since such peaks in the load are commonly seen for all the specimens subjected to the cyclic treatment, the interfacial fracture is supposed to always take place for all the cases. Only by one cycle of treatment both the load and the displacement at the peak are much lowered, although the linear relation between them is almost maintained. It is noted that the peak load and the displacement are somewhat increased by three to five cycles of treatment, indicating lower inclination probably due to a plasticization effect of absorbed water on the UP resin layer which is bent by the inserted razor blade. For the specimen subjected to seven cycles of treatment the peak load is again lowered, and finally both the load and the displacement at the peak are greatly reduced by nine cycles of treatment.

The peak loads were measured in the same way for the bilayer specimens subjected to the cyclic processes with water-soaking treatment at different temperatures. In Fig. 4 their mean values for five different samples normalized by the peak load of as-cured specimen are plotted against the sum total of each soaking time in water. When the temperature of water-soaking process is raised, the load for initiating the interfacial fracture is more greatly lowered by the first cycle of treatment. After the second treatment the fracture resistance at 40 and 50°C holds almost constant depending on the soaking temperature, although the results at 20 and 30°C show a two-step reduction and an exceptional recovery trend in the fracture loads, respectively, at the medium stage of cyclic treatment.

For comparison the results obtained under continuous soaking in water at different temperatures are shown in Fig. 5, where the mean values for five different samples are given, and the abscissa simply denotes the soaking time. The results are very similar to those in Fig. 4 for the cyclic treatments. The two-step decrease and the temporary increasing behaviour in the fracture resistance are also shown at 20 and 30°C, respectively. It is thus indicated that the reduction in the interfacial fracture resistance followed by water absorption is not suppressed even by conducting the drying process in air at 20°C for a relatively short period of 24 h. Such behaviour of interfacial degradation may be caused by the water which is supposed to be continued to exist at the interface even under drying process.

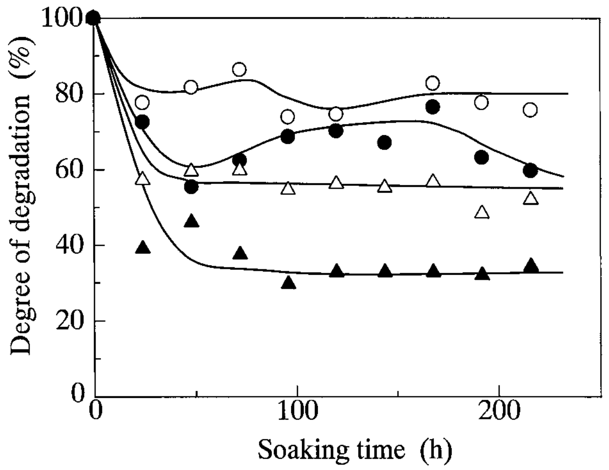

Figure 5 Variation in the peak load for the bilayer specimen under continuous absorption process of water at different temperatures. (○) 20°C, (●) 30°C, (△) 40°C, (▲) 50°C.

Fig. 6 shows the behaviour of water absorption by the bilayer specimen, the UP resin surface of which was continuously in contact with water at different temperatures. Since the weight gain proportionally varies with the square root of soaking time at the initial stage, the water penetration into the bilayer specimen is apparently regarded to obey the Fick's law of diffusion. Both the initial slope corresponding to the diffusion coefficient and the saturated value of weight gain generally increase with increasing temperature of environmental water, although the weight gain in water at 50°C shows slight decrease after indicating the maximum for about 100 h, probably due to the dissolution of UP resin by a chemical degradation mechanism like

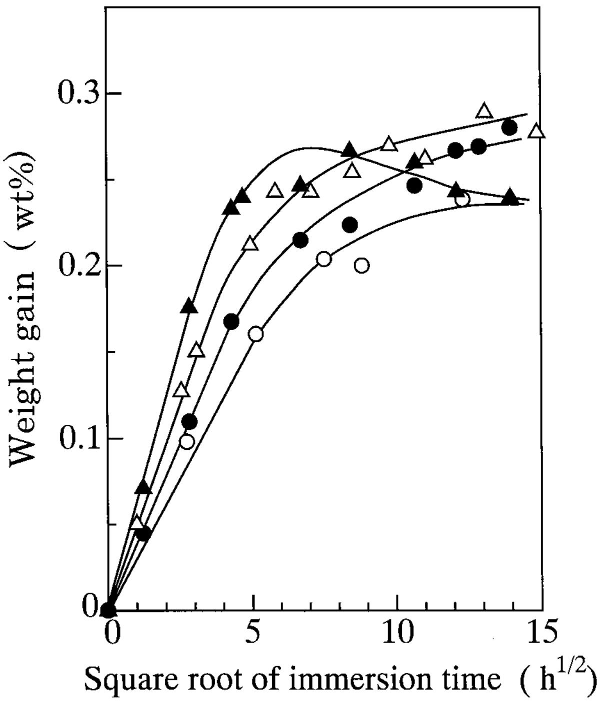

Figure 6 Behaviour of water absorption by bilayer specimen at different temperatures. (○) 20°C, (●) 30°C, (△) 40°C, (▲) 50°C.

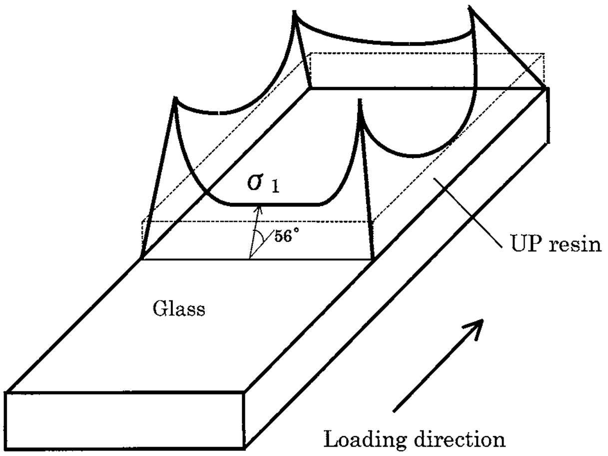

Figure 7 Schematic illustration of maximum principal stress remaining in the resin at the interface.

hydrolysis reaction of ester group in the resin [15]. The water penetrating into the bilayer specimen in this manner may lead to the reduction not only in the mechanical performance of UP resin but also in the interfacial fracture resistance, as mentioned for Figs 3–5.

Fig. 7 schematically shows the distributions of magnitude and direction of maximum principal stress σ_1 remaining in the resin at the interface. This result was calculated by the FEM for the as-cured specimen. The figure represents σ_1 to be always tensile and take larger value at each edge. The mean value of σ_1 along the line A-A in the figure is calculated to take 84.2 MPa. Since the stress due to thermal shrinkage under cooling is only 2.3 MPa (2.7%), the residual stress may be mostly generated by the shrinkage of resin during the curing process at 60°C. According to the preliminary measurements, the volume shrinkage of UP resin at 60°C was about 12%. In addition, σ_1 is oriented at an angle of 56° to the glass surface at the centre of line A-A, and therefore may assist the interfacial fracture when the razor blade is inserted into the interface at the angle of 55°. The calculation also showed the residual stress to be lowered with decreasing the elastic modulus of resin. Consequently, with regard to the effect of residual tensile stress, water absorption may rather contribute to suppress the reduction in the the interfacial fracture resistance through the plasticization of UP resin at the interface by accumulated water, contrary to the above effects on degradation. The temporary trend of recovering the fracture resistance for the specimen exposed to water at 30°C may result from such a relaxation effect. By the way since the swelling of UP resin followed by water absorption, which also will relieve the residual tensile stress in it at the interface, was hardly observed, it was not considered in the present calculation.

3.2. Structure and action of water at UP-glass interface

The IR (ATR) absorbance spectra of water observed on the detached resin surfaces of bilayer specimen placed in water at different temperatures for 500 h are shown in Fig. 8. A relatively broad peak is clearly seen at a wavenumber of about 3450 cm^{-1} at every temperature of water. The peak height and/or area of spectrum corresponding to the quantity of water increases with increasing temperature of environmental water. Much broader and lower peaks were observed at the same wavenumber for shorter period (e.g. 150 h) of water-soaking. Such trends may be correlated with the behaviour of water absorption represented in Fig. 6.

Kusanagi and Yukawa [14] have performed the IR analyses of the absorbed water in solid polymers, and revealed that the structures of water, i.e. the isolated (gaseous) and the clustered (liquid-like) states, are clearly distinguished from each other by the shape and the absorption bands of spectrum. According to them, the isolated water indicates two marked peaks corresponding to the anti-symmetric and the symmetric vibrations of hydroxyl (OH) at higher wavenumbers (Completely gaseous water shows a sharp peak at 3756 cm^{-1} for the former). On the other hand, water existing in cluster shows blunt peaks at lower wavenumbers (Completely liquid water indicates only one broad

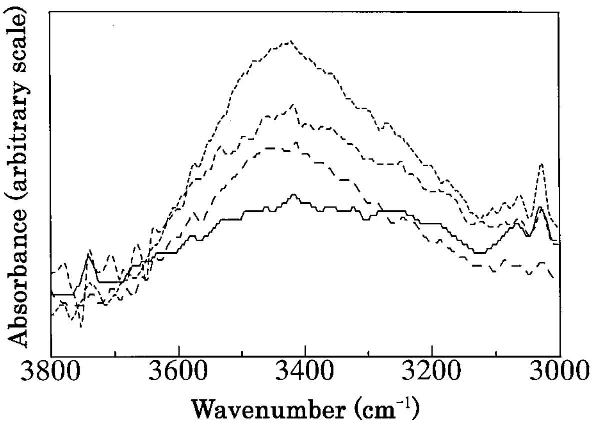

Figure 8 IR absorbance spectra of water on the detached resin surface of bilayer specimen placed in water at different temperatures for 500 h. (——) 20°C, (– – –) 30°C, (- - - -) 40°C, (· · · ·) 50°C.

peak at 3430 cm^{-1}). In general the isolated water is observed in hydrophobic polymers, while the clustered water in hydrophilic ones.

Making reference to their results, it may be interpreted that the IR spectra with a broader peak at 3450 cm^{-1} in Fig. 8 shows the existence of clustered water. It is of interest that the clustered water can exist in UP which is fundamentally hydrophobic, and becomes much clearer with an increase in the water temperature. In the previous IR studies of one of the authors [16] on the structure of absorbed water in a UP film the isolated water also was clearly observed, especially at an early stage of water absorption. In addition it was speculated from the cyclic absorption-desorption behaviour [17, 18] that the clustered water unstably exists in some structural heterogeneties or defects like micro-voids, which may be originally introduced during the cure process and/or be subsequently formed by the progress of degradation by absorbed water. Consequently, the water being accumulated in the resin being in contact with the glass surface may be liable to form the cluster, which may result from or in the interfacial degradation leading to the reduction in fracture resistance. One of the mechanisms of such interfacial degradation caused by the accumulated water may be the hydrolysis reaction in the UP resin [15], as shown below.

Fig. 9 represents the variations in area ratio of IR (ATR) absorbance spectrum by the carboxylate at 1580 to 1600 cm^{-1} to that by the ester group of UP resin at 1720 cm^{-1} for the detached surfaces from the bilayer specimens which were kept in contact with water at different temperatures. This ratio may indicate the change of ester group to the carboxylate, and thus an index of advancement of hydrolysis reaction in the resin at the interface. The ratio at a water temperature of 50°C markedly and proportionally increases with the square root of soaking time, while the ratios at 20 to 40°C hold almost constant for long time, taking values near that for the as-cured specimen. This result may demonstrate the hydrolysis reaction to take place at the interface in the UP resin of bilayer specimen exposed to water at 50°C, leading to the greatest reduction in the interfacial fracture resistance observed at this temperature.

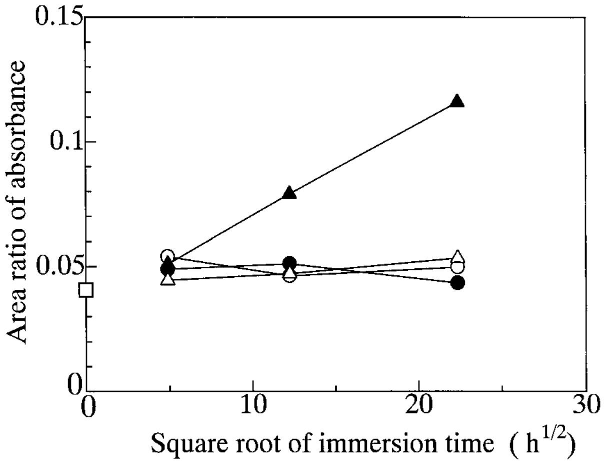

Figure 9 Advancement of hydrolysis reaction in the resin at the interface expressed by the area ratio of IR absorbance spectrum by the carboxylate to that by the ester group of resin. (□) as-cured, (○) in water 20°C, (●) 30°C, (△) 40°C, (▲) 50°C.

The accumulated water is further supposed to affect the interfacial degradation by mechanisms such as the scission of hydrogen bonding between UP resin and glass, and also the rupture of Si—O—Si bond of siloxane produced by the silane coupling agent to a pair of silanol (Si—OH) groups under the action of residual tensile stress [19]. These effects, however, were not confirmed by the present study.

Eventually the result and discussion on our experiments are briefly summarized as follows. The mechanical resistance of the interface between two layers of UP resin and glass to the fracture is strongly affected by water, which gradually penetrates into the resin and is accumulated at the resin-glass interface in the clustered structure. The plasticization effect of absorbed water leads to the reduction in the resistance of resin layer to bending under inserting the razor blade, and on the contrary to the relaxation of residual tensile stress in the resin at the interface, which contributes to recovering the resistance to the interfacial fracture initiation. The accumulated water causes the hydrolysis reaction in the resin at the interface, and as a result promotes the reduction in the interfacial fracture resistance, particularly in case of soaking in water at higher temperature. Such effects of absorbed water are commonly confirmed both for the cyclic absorption-desorption of water and for the continuous water absorption. Therefore the drying the specimen in air for a period as short as 24 h after the immersion in water hardly contributes to the suppression of interfacial degradation by water.

4. Conclusions

The effects of absorbed water on the interfacial fracture resistance were evaluated by the blade-insert-testing (BIT) method, which measures the load for initiating the interfacial fracture by inserting a razor blade into the interface between two layers of UP resin and glass of bilayer specimen. The BIT method was demonstrated to actualize the real interfacial fracture and well evaluate the mechanical resistance to it. The load to initiate the interfacial fracture was greatly lowered by the early process of water absorption for short period, particularly at higher temperature of environmental water. The subsequent desorption process of water at room temperature for 24 h scarcely affected the load for interfacial fracture initiation. Therefore the interfacial degradation is supposed to result from the water which is accumulated in the resin at the interface during the absorption process and is not completely desorbed even by the drying treatment. The micro-FTIR analyses revealed that the accumulated water exists in cluster at the interface with larger amount at higher temperature of environmental water. The IR analyses also demonstrated the hydrolysis reaction to take place in the resin at the interface in an environment of hot water, leading to the great reduction in the load for initiating the interfacial fracture.

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