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A Spectroscopic Technique for Studies of Water Transport Along the Interface and Hydrolytic Stability of Polymer/Substrate Systems

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Information on water transport along the polymer/substrate interface is valuable for understanding the mechanisms and the controlling factors affecting the water-induced adhesion loss of polymer-coated metals, adhesive-bonded joints, and polymer/fiber composites subjected to aqueous environments. This paper presents data to demonstrate the capability of a technique, which combines a vertical cell with Fourier transform infrared spectroscopy in the multiple internal reflection mode, for studying water transport along the polymer/substrate interface and interfacial hydrolytic stability of polymeric composites and systems exposed to water and high relative humidities. The technique can distinguish water transport through the film from that along the interface; the latter transport is predominant for polymer/untreated substrate systems. Spectroscopic analyses of fractured surfaces of poor and well-bonded polymer/substrate systems after water exposure indicate that the technique is capable of discerning a hydrolytically-stable interface from a water-susceptible interface.

Keywords: Water; interface; transport; internal reflection spectroscopy; hydrolytic stability; polymer/substrate

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INTRODUCTION

The combination of organic polymers with a variety of inorganic substrates has gained an important place in today's technology. Such polymer/substrate systems are used in protective coatings, adhesive bondings, and polymer/fiber composites. For these applications, hydrolytic stability of the interface is of prime importance but difficult to achieve because these materials are often subjected to hostile environments. In the presence of water, the weakest part of such systems is generally the interface between the polymer and the substrate. This is because the strength of the bonds which water forms with an inorganic oxide (40–65 kJ/mol) [1] is substantially greater than the interactions between an oxide and a polymer (< 25 kJ/mol) [2]. Consequently, the affinity of water for the oxides is greater than that between polymers and the oxides. Further, thermodynamic analysis by Gledhill and Kinloch [3] has shown that the bonds between polymers and inorganic oxides are hydrolytically unstable. The results of both bond energy and thermodynamic analyses imply that water is likely to enter the interface when polymeric systems and composites are exposed to water and high relative humidities. The presence of water at the interface is often detrimental to the durability of polymer/substrate systems. In an intensive review of water disbondment, Leidheiser and Funke [4] have concluded that a water layer of several monolayers thick at the polymer/metal (oxide) interface is responsible for adhesion loss and delamination of polymer-coated metals.

It is evident from this background that nondestructive, *in situ* analysis of buried polymer/substrate interfaces during exposure to aqueous environments is of great interest. However, spectroscopic tools suitable for such studies are scarce. One technique that can provide information of water transport along the polymer/substrate interface is Fourier transform infrared multiple internal reflection (FTIR-MIR) spectroscopy. The advantages of the FTIR-MIR technique are: (1) it is sensitive to water molecules, (2) it detects water in the interfacial region close to the substrate surface, and (3) there is no interference by water during the measurement because the infrared radiation propagates within the substrate. The applications of FTIR-MIR for studies of surface reactions, sub-monolayer, and Langmuir-Blodgett films have been

illustrated [5–8]. The uses of FTIR-MIR with a horizontal cell to measure *in situ* water at a polymer/substrate interface [9–12] and the diffusion of water through a polymer film applied to a substrate have been reported [13–15].

In a previous study, Linossier *et al.* [15] have presented relevant mathematical expressions, which were derived specifically to determine the diffusion coefficients of a penetrant in a polymer film adhered to a substrate using the FTIR-MIR technique. They also provided data of water transport in poly(methyl methacrylate)(PMMA) and polystyrene (PS) to demonstrate the use of a MIR horizontal cell for studying water diffusion in a polymer film adhered to the substrate (applied film). The results clearly showed that water transport in PMMA films followed a Fickian process while that through PS films did not. It should be mentioned that the diffusion data for applied films should be used, instead of values obtained from the free-standing films, to estimate the transport kinetics in polymer-coated materials because the former simulates actual materials in service. Nguyen *et al.* [14] have reviewed the discrepancies of water transport in free-standing films and supported films, and raised “serious doubts” about the extrapolation of free-film data to the applied films. One explanation is that, in applied films, the presence of hydrophilic materials in the polymer/substrate interfacial region, before or accumulated during exposure, may increase the rate of water transport through the film.

This study aims to demonstrate the capability of a technique, which combines a laboratory-fabricated, vertical cell with FTIR-MIR spectroscopy (FTIR-MIR/vertical cell technique) to measure *in situ* the sorption and transport behaviors of water in polymer/substrate systems. The technique provides data to discern the transport of water along the polymer/substrate interface from that through the film thickness. Well-bonded polymer/substrate systems were also investigated to demonstrate the technique’s capability for discriminating a hydrolytically-stable interface from a water-susceptible interface. Information on water transport at, and hydrolytic stability of, a polymer/substrate interface is valuable for understanding the mechanisms and controlling factors affecting water-induced adhesion loss and delamination of coatings, adhesives, asphalt pavements, and polymer/fiber composites.

MATERIALS AND EXPERIMENTAL PROCEDURES

Figure 1 schematically presents the FTIR-MIR vertical cell and specimen configuration used in this study. The geometry chosen was a double-pass internal reflection plate, as proposed by Harrick [16]. By varying the polymer film thickness and the polymer/substrate interfacial condition, this configuration would allow a simultaneous study of water transport through the film thickness and along the polymer/substrate

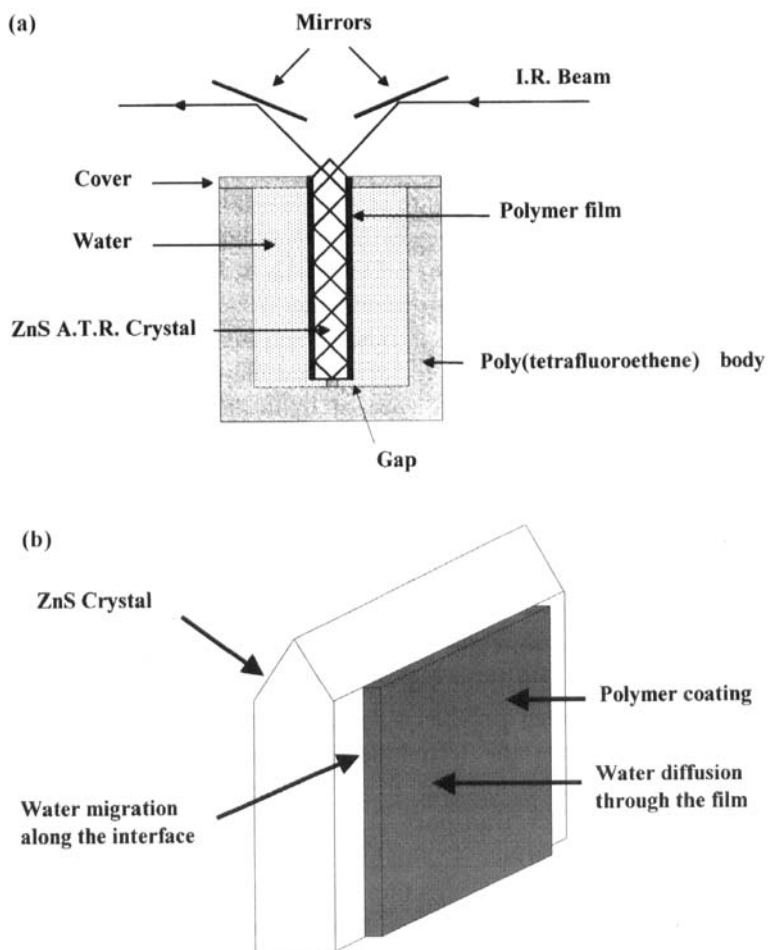


FIGURE 1 Schematic of the multiple internal reflection (MIR) vertical cell.

interface. The substrates were ZnS prisms (crystals). One end of the prism was beveled at 45° (see Fig. 1b). The cell body was made of poly(tetrafluoroethylene) and mirrors of gold-coated silicon. It is noted in Figure 1a that there is a gap between the coated prism and the bottom wall of the cell body. This allowed water to move freely to the end of the specimen and migrate vertically along the polymer/substrate interface. For the applications reported in this study, the cell was placed in a FTIR spectrometer equipped with a liquid-nitrogen-cooled, mercury cadmium telluride detector. Typically, 128 scans were collected to obtain a spectrum at a resolution of 4 cm⁻¹. The spectrum of the polymer-coated ZnS prism before exposure to water was used as a background for all subsequent spectra.

Applied films were prepared from reagent grade PMMA and PS polymers. The molecular weight (M_w and M_n) values and distribution, determined by size exclusion chromatography, of these polymers are given in Table I. Films applied to the substrates were obtained by casting solutions of PMMA or PS in carbon tetrachloride (CCl₄) directly onto the ZnS prisms. Coated specimens were allowed to dry for 8 h at room conditions (22°C and 40% relative humidity), followed by 2 h in a vacuum to remove most of the solvent from the films. A wide range of film thicknesses ranging from 100 μm to 1200 μm was selected to discern the transport behaviors of water in a polymer/substrate system.

To provide data for assessing the capability of this technique in the studies of the interfacial hydrolytic stability of a polymer/substrate system, well-bonded specimens were prepared. For this experiment, ZnS surfaces were modified by a plasma process. The treatment was performed in a reactor fed by an inductively-coupled power source operating at a radio frequency of 13.5 MHz. NH₃ gas under a pressure of 100 mtorr and a flow rate of 100 sccm (standard cubic centimeter per minute) was used for the plasma treatment. A power density of 0.27 W · cm⁻² was employed, and the duration of the treatment was 10 s.

TABLE I Properties of the polymers used

	<i>PMMA</i>	<i>PS</i>
Weight average molecular weight	43000	169000
Number average molecular weight	96000	339000
Polymolecularity index	2.2	2.0

To verify the locus of delamination of polymer/substrate specimens after water exposure, fractured surfaces were analyzed using X-ray photoelectron spectroscopy (XPS) and FTIR-MIR spectroscopy. XPS spectra were recorded on a RIBER SIA 200¹ multitechnique spectrometer, equipped with a MAC2¹ analyser. Non-monochromatic MgK α radiation, from a dual anode (Mg/Al) system, was used. FTIR-MIR analysis was similar to that described above for water transport study. Surface free energy parameters (polar and nonpolar components) of untreated and plasma-treated ZnS surfaces were determined from contact angle measurements of water and diiodomethane on the substrates using a Digidrop¹ instrument (GBX, France) and the geometric-mean approach.

RESULTS AND DISCUSSION

Water Transport Through Polymer Matrix and Along the Film/Substrate Interface

Water can enter the polymer/substrate interface by a number of pathways, by diffusing through the polymer matrix and by migrating through pinholes, pores, defects, and local inhomogeneities in the films. Once reaching the interface, water can transport along the polymer/substrate interface. Through-film transport of a polymer/substrate system is controlled by the integrity and microstructural properties of the films as well as the conditions (clean or contaminated) of the interface. On the other hand, transport along the interface is governed mostly by the film/substrate interfacial conditions and adhesion. That is, if the interface is devoid of hydrophilic species, the amount of water accumulated at the interface will be small; and if the polymer/substrate bonds are strong and capable of resisting a water displacement, the transport of water along the interface is expected to be slow. For this reason, the main parameters examined in this study are the protective properties of the polymer films and their adhesion to the substrate.

¹Certain commercial equipment is identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

In order to ascertain that a vertical MIR cell can provide information on the water transport along the interface, we investigated applied polymer films having markedly different thicknesses.

Figure 2 presents typical FTIR-MIR difference spectra (spectra of the exposed specimen minus spectrum of the same specimen before exposure) in the 2800 cm^{-1} to 4000 cm^{-1} region for several exposure times in water for a $380\text{ }\mu\text{m}$ PMMA film applied to a ZnS substrate. As seen in this figure, the intensity of the water OH-stretching band

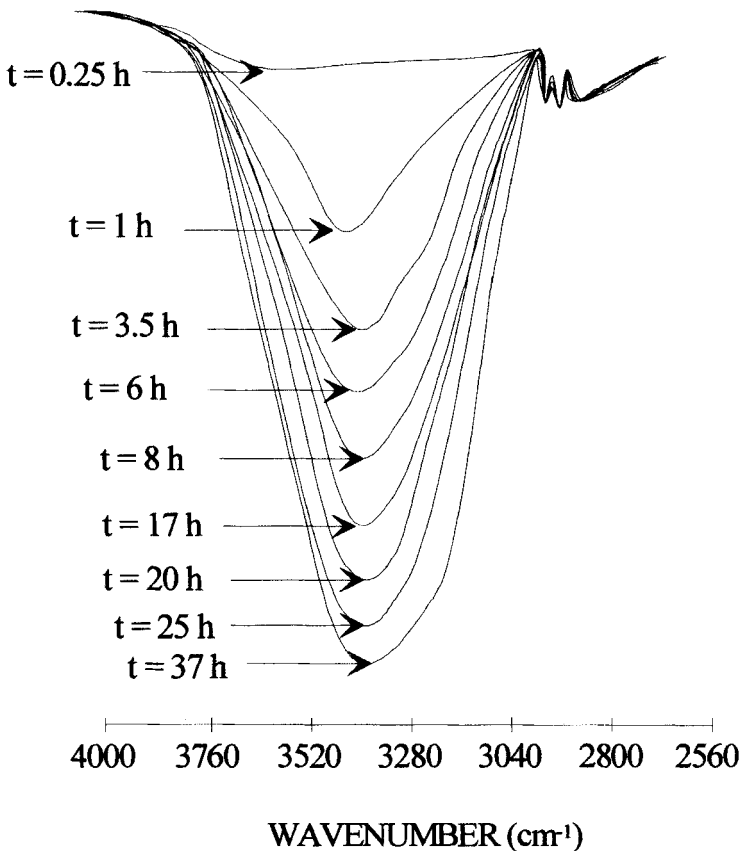


FIGURE 2 FTIR-MIR spectra of a PMMA/ZnS specimen exposed to water for different time intervals.

peaking near 3400 cm^{-1} increased with exposure time. The relative intensity of this band, which is proportional to the amount of water detected, as a function of the square root of immersion time in water for $490\text{ }\mu\text{m}$ and $1180\text{ }\mu\text{m}$ thick films applied to a ZnS substrate is displayed in Figure 3. In this figure, A_t and A_∞ represent the intensities corresponding to the amount of water at time t and at equilibrium, respectively. Symbols in Plots *a* and *b* represent the experimental results of water sorption in the $490\text{ }\mu\text{m}$ and $1180\text{ }\mu\text{m}$ PMMA-coated specimens, respectively, using the vertical cell shown in Figure 1. Plot *d* displays the experimental water sorption data for a PMMA/ZnS system using the horizontal cell described in Reference [15], and Plot *c* is the calculated curve of a PMMA film having the same thickness as that of the specimen for Plot *d*. Before discussing the results of Figure 3, it is appropriate to examine the thickness of the polymer/substrate interfacial zone in which water was detected for the systems used in this study.

The probing depth of internal reflection spectroscopy is estimated from the penetration depth of the evanescent wave in the sample, d_p , which is given by [17].

$$d_p = (\lambda/2\pi n_1)[\sin^2 \theta - (n_2/n_1)^2]^{1/2}$$

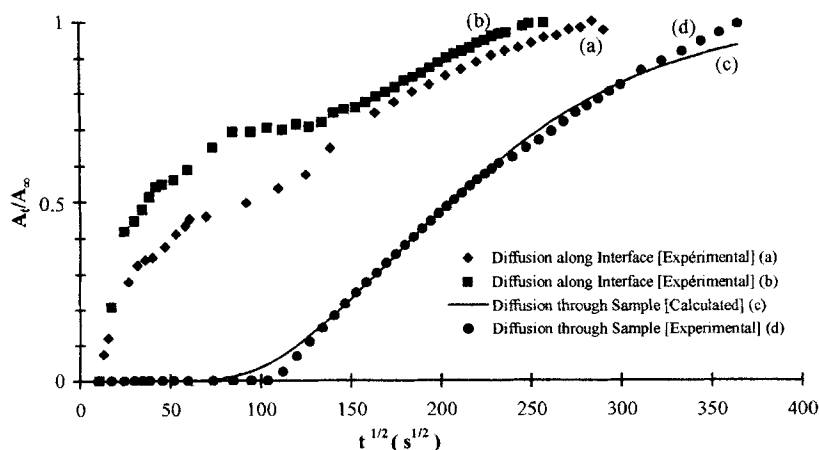


FIGURE 3 Water sorption plots obtained by the vertical MIR cell for PMMA films $490\text{ }\mu\text{m}$ thick (Plot *a*) and $1180\text{ }\mu\text{m}$ thick (Plot *b*) on ZnS substrate; Curve *c* is the calculated plot for a Fickian diffusion through the film matrix, and Plot *d* is an experimental plot obtained by the horizontal MIR cell.

where λ is the wavelength in vacuum, θ is the angle of incidence, and n_2 and n_1 are the refractive indices of the sample and the prism (substrate), respectively. d_p is defined as the distance required for the electric field amplitude to fall to e^{-1} of its value at the prism surface. It has been experimentally-demonstrated that more than 85% of the signal detected by internal reflection spectroscopy is derived from sample depth within one d_p [18], and that the total probing depth in the sample is less than three times d_p [19]. Using appropriate values of the refractive index for the polymer film ($n_2 = 1.5$), the substrate ($n_1 = 2.26$ for ZnS), and water ($n_2 = 1.32$), d_p values in polymer and water on a ZnS substrate at the water stretching frequency (3400 cm^{-1} or $2.94\text{ }\mu\text{m}$ wavelength) were calculated from the above equation to be $0.58\text{ }\mu\text{m}$ and $0.42\text{ }\mu\text{m}$, respectively. Since polymers generally take up only a small amount of water, there is little difference in d_p values between a water-saturated polymer and a dry polymer. It is clear from this calculation that water molecules detected in the interfacial region of the polymer/substrate systems used were less than $1.75\text{ }\mu\text{m}$ (three times the penetration depth of the evanescent wave in polymer, *i.e.*, $3 \times 0.58\text{ }\mu\text{m}$) from the substrate surface.

Water molecules detected by the FTIR-MIR technique consisted of two sources: water sorbed in the polymer film within the probing depth of the evanescent wave ($< 1.75\text{ }\mu\text{m}$ for the PMMA/ZnS system) and the water layer at the polymer/substrate interface. It has been shown quantitatively that, for untreated, smooth inorganic substrates where polymer/substrate adhesion is mostly governed by secondary forces, the amount of water from the former source is small compared with that from the latter [11, 13]. From the above discussion, it may be concluded that the FTIR intensities shown in Figures 2 or 3 were mostly due to water molecules present at the PMMA/ZnS interface.

Curve *c* of Figure 3 was obtained by calculation using the model proposed by Fieldson and Barbari [13], which was derived to compute the diffusion coefficient of solvents in a polymer based on data recorded by internal reflection spectroscopy combined with a horizontal cell. Plot *d* represents the experimental sorption data for a $380\text{ }\mu\text{m}$ PMMA film adhered to a ZnS substrate using the horizontal cell. It is noted that, in the horizontal cell configuration, the only pathway for water from the environment to reach the polymer/substrate interface is transport through the thickness of the polymer film. The good

agreement between Curve *c* and Plot *d* suggests that the transport of water in the PMMA film using the horizontal cell configuration was Fickian. Utilizing the model given in Reference [13] and the experimental data of Plot *d*, a diffusion coefficient of $1.27 \times 10^{-8} \text{ cm}^2/\text{s} \pm 0.13 \times 10^{-8} \text{ cm}^2/\text{s}$ was determined for the transport of water through the adhered PMMA film on a ZnS substrate used in this study. This value is in good agreement with those measured by gravimetry for free-standing PMMA films conducted in the same temperature range [20].

Figure 3 shows that the water buildup in the interfacial region of both the 490 μm and 1180 μm PMMA films applied to a ZnS substrate using the vertical cell was rapid (Plots *a* and *b*) in the first few minutes then slowed down thereafter. Further, there is essentially no difference in the time lag (time required for water from the environment to reach the polymer/substrate interface) and only a slight difference in the sorption behavior between the two plots corresponding to the two markedly different thicknesses. If the transport were through the film thickness and Fickian, as observed in Figure 3d, the times it took for water to pass through the 490 μm and 1180 μm films would be approximately 11 h and 64 h, respectively, not a few minutes as seen in Figure 3. The much shorter time lag for specimens in the vertical cell than that in the horizontal cell (compare Plots *a* and *b* with Plot *d*), despite the fact that film thicknesses of the former were greater than that of the latter, also indicates that the transport of water in the vertical cell was not through the polymer matrix. Another interesting result of Figure 3 is that the slopes of Plots *a* and *b* are greater than that of Curve *c* or *d*, indicating that the transport of water in the vertical cell specimens was much faster than that in the horizontal cell. If the PMMA/ZnS interface were hydrolytically stable, *i.e.*, it could resist water entering the interface from the end of the specimen, only through-film transport should be observed in the vertical cell experiment. In this case, the rate of water transport in the film using the vertical cell should be similar to that in the horizontal cell. An example of the sorption behavior for a hydrolytically-stable interface specimen studied by the vertical cell may be seen in Figure 6b for the PMMA/plasma-treated ZnS system; Plot *b* of Figure 6 resembles the transport through the polymer matrix, as depicted in Figure 3d.

In summary, the results of Figure 3 indicate that water migration along the polymer/substrate interface was the governing transport

process in the vertical cell specimens. The results also suggest that PMMA/ZnS specimens had a poor water-resistant interface, which was attributed to the poor adhesion between the PMMA film and the untreated ZnS surface. The results emphasize the need to take into account the interfacial transport when assessing the durability of polymer/substrate systems exposed to an aqueous environment.

Two other results of Figure 3 deserve some discussion. One feature is the small difference, in both the slope and the magnitude, between Plot *a* and Plot *b* for the two different thickness specimens in the vertical cell. This difference may be attributed to a poorer adhesion interphase/interface, which may be the result of a less complete cure, more residual solvent, or a higher compressive stress developed after immersion in water, in the thicker film specimen. Such a poorer interface is less resistant to water ingress, leading to a faster water transport along the interface. The other characteristic is the transport rate in the vertical cell specimens (Plots *a* and *b*) which approaches the Fickian behavior observed for the horizontal cell specimen after approximately 8 h exposure. No attempt was made to model this flow pattern or the rapid initial interfacial diffusion observed in Figures 3a and 3b because this transport process is complex. Not only does the interfacial water layer spread laterally on the interface surface area but also increases its thickness with exposure.

The MIR vertical cell was also used to investigate the transport characteristics of water in a polystyrene/ZnS system. Figure 4a presents the sorption plot for a 338 μm thick PS film applied to an untreated ZnS using a MIR vertical cell; Plot *b* is from experimental data obtained using the horizontal MIR cell; and Curve *c* is a plot calculated from the Fickian diffusion through the film matrix using a D value of $6.0 \times 10^{-8} \text{ cm}^2/\text{s}$ as given elsewhere [15]. Figure 4 reveals a poor protective property for the PS films, as illustrated by the fact that water went through these films rapidly. These results suggest that water transport through the PS films applied to a ZnS substrate was through pores or defects in the films. As indicated earlier, the FTIR-MIR technique only detects water in the polymer/substrate interfacial zone less than 1.75 μm from the substrate surface. Thus, if the transport were through the 338 μm thick polymer matrix, it would take a much longer time for water to reach the interface, as shown in the calculated curve (Curve *c*). This interpretation is supported by

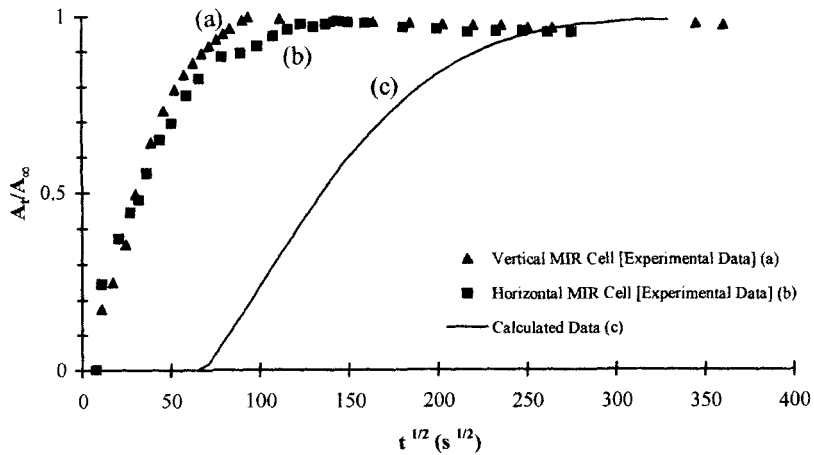


FIGURE 4 Water sorption plots for PS films on ZnS substrate obtained by the vertical MIR cell (Plot *a*) and the horizontal MIR cell (Plot *b*); Curve *c* is the calculated Fickian diffusion through the film.

transmission electron microscopy (TEM) analysis of thin slices (< 100 nm) of PS films before exposure to water. Figure 5 displays one typical TME image, which reveals the presence of numerous flaws in the films. Large cracks have also been observed in other PS specimens [15]. No TEM analysis was carried out for the film after water immersion.

Effects of Substrate Surface Treatment on Water Transport Along the Interface and Hydrolytic Stability of Polymer/Substrate Systems

Plasma treatment has been shown to increase surface polarity of substrates [21]. Further, the extent of the adhesion loss of a polymer/substrate system has been found to be largely dependent on methods of surface modification [22, 23]. Thus, any effect of substrate surface treatment on water transport along the polymer/substrate interface should be detected by the FTIR-MIR/vertical cell technique. Sorption plots of a PMMA film on untreated and plasma-treated ZnS substrates are displayed in Figure 6. The thickness of the specimen for

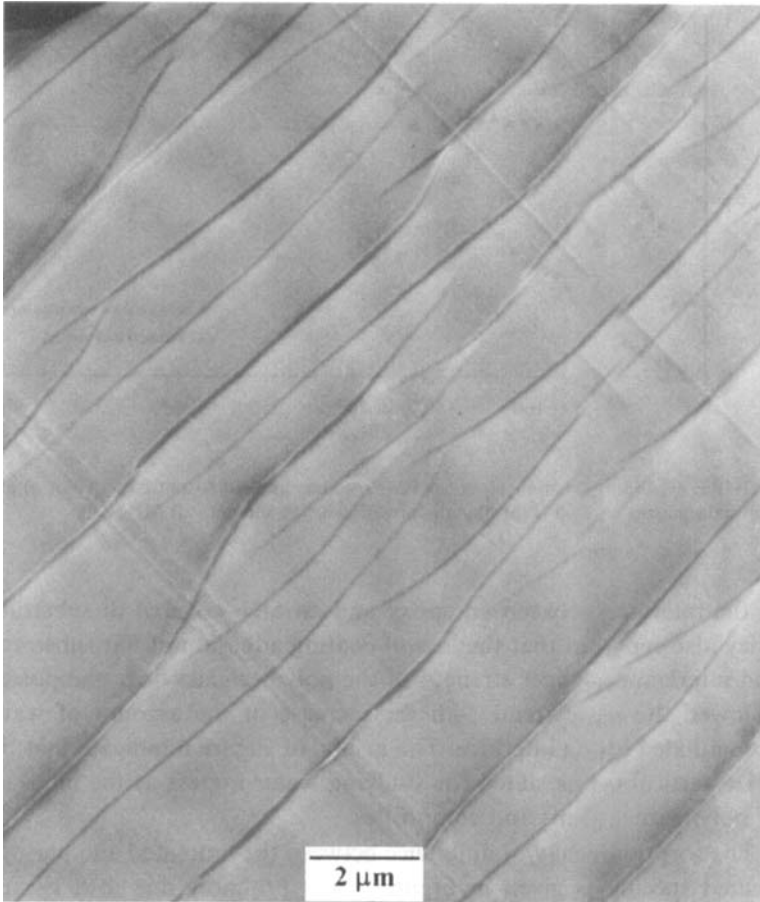


FIGURE 5 Transmission electron micrograph of a thin PS film, showing numerous defects in the film.

Plot *a* was $1180\ \mu\text{m}$ and that for Plot *b* was $317\ \mu\text{m}$. Figure 6 shows a much steeper rise of the amount of water in the interfacial zone of the untreated specimens than that of the plasma-treated ones. Evidently, plasma treatment has enhanced the hydrolytic stability of the polymer/substrate interface, resulting in a decrease of the amount of water accumulated at that location. The results are consistent with the data of Nguyen *et al.* [24], which showed that silane coupling agent treatment of the substrate surface greatly reduced the amount of water

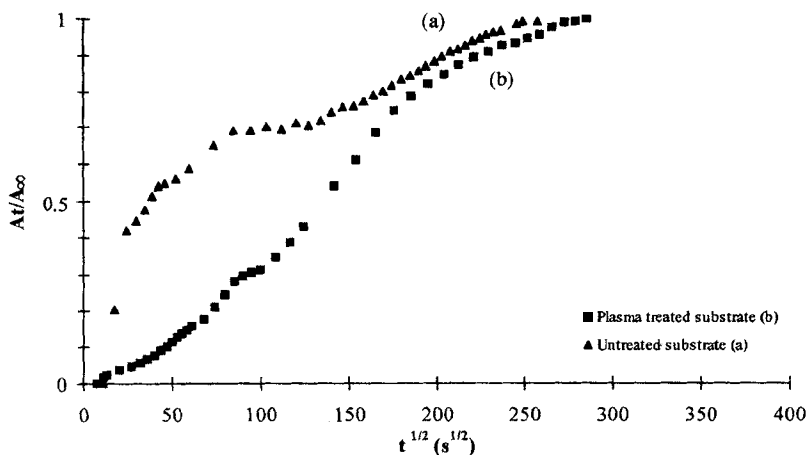


FIGURE 6 Water sorption plots for PMMA films applied to untreated (Plot *a*) and ammonia plasma-treated (Plot *b*) ZnS substrates using the vertical MIR cell.

at the interface between an epoxy and an SiO₂-covered Si substrate. They also reported that the loss of coating adhesion of flat substrates and interlaminar shear strength of the polymer/glass fiber composites followed the same trend with the increase of the amount of water accumulated at the interface. The results of Figure 6 indicate that the MIR vertical cell is suited for studying water ingress at the interface of polymeric systems and composites.

The sorption behavior difference between the untreated and plasma-treated specimens given in Figure 6 was probably due to a greater adhesion and more hydrolytically-stable interface of the treated specimens than the untreated ones. To verify this conjecture, spectroscopic and surface free energy analyses of the untreated and plasma-treated substrates and spectroscopic analysis of the specimens after water exposure were conducted. The XPS spectrum of the plasma-treated ZnS prism (Fig. 7) shows the presence of nitrogen (N1s peak) on the surface of the substrate after the plasma treatment. The FTIR-MIR spectrum (Fig. 8) confirms the formation of polar NH_x groups at the surface, as evidenced by the presence of a prominent band peaking at about 3150 cm⁻¹, probably due to stretching of the NH₃ group or its salts. The negative bands at about 2910 cm⁻¹ and 2860 cm⁻¹ (due to C—H stretching) are attributed to the removal of some organic

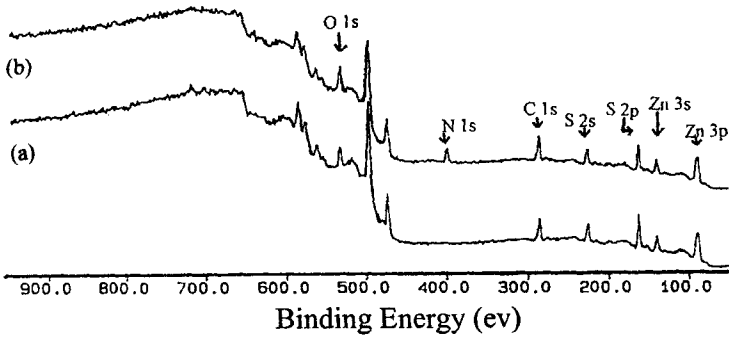


FIGURE 7 XPS spectra of the ZnS prism surface before (Curve *a*) and after (Curve *b*) ammonia plasma treatment.

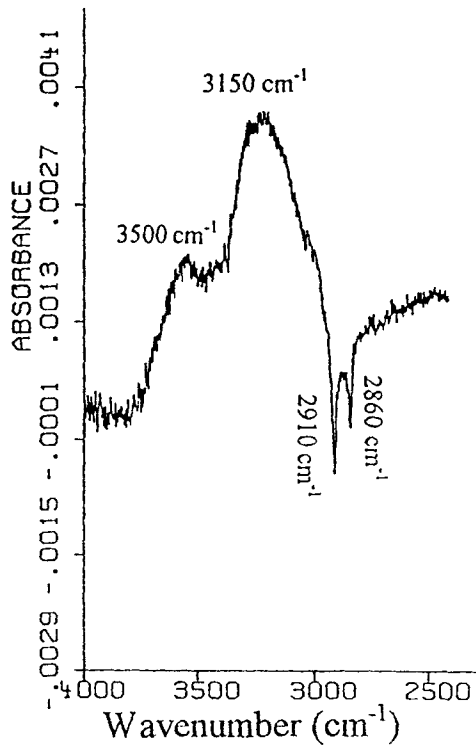


FIGURE 8 FTIR-MIR spectrum of the ZnS prism surface after ammonia plasma treatment.

contaminants by the plasma process. The results are consistent with earlier observations on stainless steel using the same treatment process [23]. Surface free energy analysis of untreated and plasma-treated substrates showed a marked increase in the nondispersive component, from 3.2 mJm^{-2} for the untreated to 18.1 mJm^{-2} for the plasma-treated surface. The increase was due to an enhancement of the polar functional groups, as revealed by FTIR and XPS results. Plasma treatment slightly increased the dispersive component, from 43.1 mJm^{-2} to 48.0 mJm^{-2} . This is attributable to the removal of organic surface contaminants by the plasma process, consistent with FTIR results of Figure 8.

The enhanced surface polarity and, hence, the interactions between PMMA film and plasma-treated surface, could affect the failure mode of a polymer/substrate system. To confirm this hypothesis, an FTIR-MIR analysis was made on the locus of failure of a PMMA film/plasma-treated ZnS specimen after it has been exposed to water. Figure 9 displays a FTIR-MIR spectrum of the treated substrate after the polymer film was removed from it. The spectrum reveals that a thin layer of the polymer was still on the treated substrate, indicating that a failure within

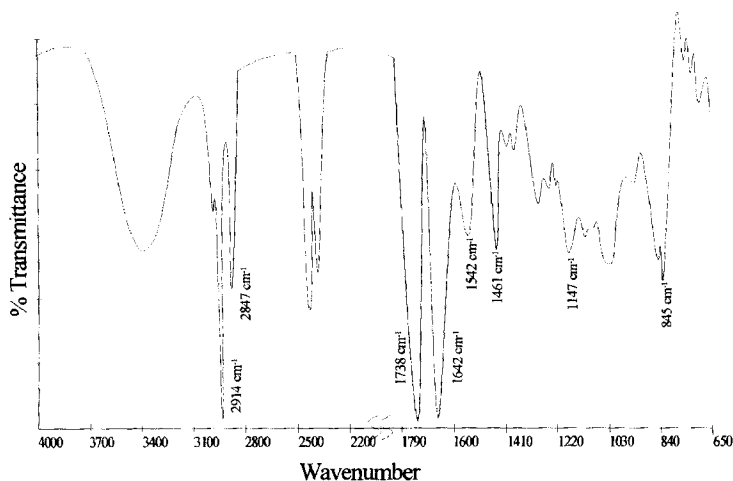


FIGURE 9 FTIR-MIR spectrum of the substrate surface after removing the polymer film from a PMMA-coated, plasma-treated ZnS specimen that has been subjected to water.

the polymer has occurred. This type of failure suggests that the interfacial adhesion between the polymer and the plasma-treated substrate was greater than the cohesive strength of the polymer after water exposure. It is noted that results of a similar experiment on an untreated ZnS prism showed an interfacial failure, *i.e.*, no evidence of the polymeric material was observed on the delaminated substrate surface.

Results in Figure 9 also illustrate the usefulness of the FTIR-MIR technique to provide molecular information of the modification of a polymer layer in the vicinity of a substrate. For instance, the absorption bands at 2914 cm^{-1} or 2847 cm^{-1} (due to C—H) and at 1738 cm^{-1} (due to C=O) are characteristic of the bulk PMMA material, but the bands near 3350 cm^{-1} and 1640 cm^{-1} are probably due to the water molecules. In addition, a band at 1542 cm^{-1} , which was not observed in the bulk PMMA specimen, is visible in Figure 9. This band, which is assigned to the carboxylate ions (COO^-), suggests that covalent interfacial bonds were formed between the polymer and the plasma-treated surface. Such a strong interaction would result in a water-resistant PMMA/treated ZnS interface, in agreement with the cohesive failure observed for these specimens. This interpretation is also consistent with the water sorption results given in Figure 6, which show a much lower rate and amount of water in the early stage of water uptake in the plasma-treated specimens as compared with that of the untreated systems.

Finally, the examples given in this paper used an infrared-transparent material as the substrate. For studies of water transport along the interface between a polymer and a metal, such as aluminum or steel, a thin film of the metal can be evaporated on the substrate prior to application of the polymer film. *In situ* measurement of water at the polymer/iron interface using a horizontal cell has been demonstrated [12]. For this arrangement, the effects of the metal film on the penetration depths of the evanescent wave in the polymer and water must be taken into account.

SUMMARY AND CONCLUSIONS

Water transport along the polymer/substrate interface is an important process in the adhesion loss and delamination of polymeric materials

and systems exposed to aqueous environments. The use of a vertical cell together with Fourier transform infrared spectroscopy in the multiple internal reflection (FTIR-MIR) mode was found suitable for studying water transport along the interface of a polymer/substrate system. Interfacial water transport was observed as the dominant process for polymer applied to untreated substrates. However, plasma treatment of the substrate surface greatly reduced the rate as well as the amount of water accumulated at the interface of a polymer/substrate system. The FTIR-MIR/vertical cell technique can also provide data to discern a hydrolytically-stable interface from a water-susceptible interface. Information on the transport and water-susceptibility of a polymer/substrate interface may provide a better understanding of the mechanisms and the controlling factors affecting the water-induced adhesion loss of polymer-coated systems exposed to water and high relative humidities.

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