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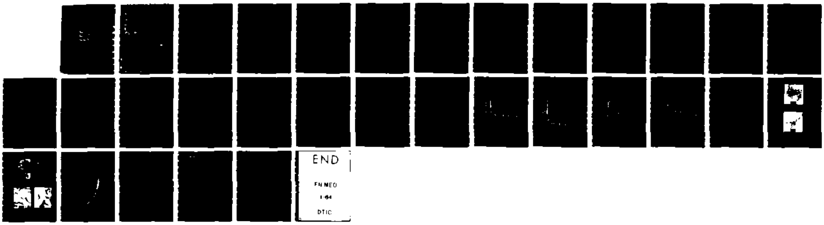

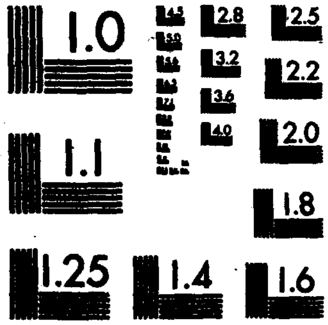

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Durability and Failure Analyses of A Silane Treated α-Al_2O_3/Polyethylene Joint In Wet Environment

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I. INTRODUCTION

Adhesion promoters of the organo silane type have been used to modify the surface of adherends prior to bonding with polymers in order to enhance joint strength. In order to understand the mechanism of adhesion promotion by an organofunctional silane in joints where its chemical reaction with a polymer matrix may be negligible, ~~we studi~~ed the role of γ-aminopropyltriethoxy silane (γ-APS) in α-Al_2O_3/polyethylene joints. ~~As~~ reported in our recent paper (1), dry joint strength of such a joint can be markedly improved by the application of γ-APS on α-Al_2O_3, which forms a multimolecular polysiloxane film. There was a strong experimental evidence for the limited interdiffusion between γ-APS silane film and polyethylene at the silane/polyethylene interface and we proposed this interdiffusion to be an important mechanism for adhesion promotion of the joint at least in <u>dry</u> environment. Drying the silane at an elevated temperature prior to joint formation reduces joint strength and also changes the failure mode from cohesive failure through polyethylene to a mixed mode near the silane/polyethylene interface. It was found that this trend was due to the reduced interdiffusion since dried silane is more fully cured glassy matrix.

In general, when the joints are exposed to wet environment, absorption of water plays an important role in the degradation on the joints. Huneke and Dorey (2) studied the electrical performance of fiber glass/epoxy laminates. Laminates with silane treatment were susceptible to water absorption as determined by the electrochemical potential for a conductive growth along the glass/resin interface, but the laminate without any silane treatment was most susceptible. Gettings (3) has used Auger and ESCA to study the locus of failure of iron oxide/epoxy joints glycidoxypropyltrimethoxysilane after soaking in water at 60°C. The results suggest that the silane primer is the weakest link in the joint and fracture occurs by cohesive failure of this layer. Schrader and Block (4) studied the life-time of pyrex/epoxy/pyrex block adhesive joints under static load in hot water. Examination of the debonded joints for radioactivity indicated that failure resulted from hydrolysis of siloxane bonds. Ishida and Koenig (5) show that extensive polysiloxane networks must be hydrolyzed by moisture to low molecular weight oligomers which lead to the observation of threshold periods before any desorption is detected. Reformation of the Si-O-Si bond during redrying and the loss of silane layers during hydrolysis are suggested by Ishida and Koenig (6) through FT-IR studies of vinyltrimethoxysilane on E-glass fibers. Williams and Boerio (7) subjected iron-epoxy lap joints primed with γ-APS to water and found that the bonded area near the center of the joint gradually decreased with time due to continuing water diffusion into the joint.

In this study we subjected α-Al_2O_3/γ-APS/polyethylene joints to wet environment to see if such variables as the drying of the silane or the thickness of the silane layer would also affect the joint strength as in dry environment. Redrying will also be studied to confirm the reversibility of the joint durability and its effect on failure mode. Peel test was used to evaluate the joint strength and the failure surfaces were analyzed by ESCA and SEM to more fully elucidate the degradation mechanism in wet environment. The trends observed in wet environment will be compared with those for the dry environment.

II. EXPERIMENTAL

II-A. Materials

The polyethylene is GULF 1117, provided by the Kendall Co., Lexington, MA. γ-aminopropyltriethoxysilane (γ-APS) is supplied by Union Carbide Corp. The sapphire plates are purchased from Tyco-Saphikon Co., Milford, NH. The plates used in water immersion experiments have a dimension of 2" X 1" X 0.02" and the surface plane was determined to be $(11\bar{2}0)$. The 100% relative humidity (RH) experiments were made with 2" X 0.5" X 0.018" plates having a surface orientation of $(11\bar{2}0)$. Water used in all experiments is doubly distilled.

II-B. Peel Specimen Preparation

Peel specimens are prepared according to procedures outlined in references (1,8). Briefly, the polished α-Al_2O_3 plates are heat-treated at 110°C for 1 hour followed by baking in a muffle furnace at 350°C for 1 hour. γ-APS is hydrolyzed in water at its natural pH. The silane film is spray-deposited at ambient conditions and the films are either standard dried (STD) at 25°C under vacuum for 1 hour or dehydrated (DEH) at 110°C under vacuum for varying periods of time. Film thickness is varied by changing the solution concentration. Both primed and unprimed plates are laminated with PE at 149°C in a hot-press. The joints are then exposed to water by immersion or to a 100% RH environment for various durations and the strengths are measured as a function of exposure time, γ-APS film thickness, and film dehydration. The temperature is held constant at 25°C. In order to study strength recovery after exposure by redrying, the peel specimens are first dried in room air for 5 hours and then further dried in a vacuum oven for 5 days at 25°C before testing.

II-C. Mechanical Testing

A 180° peel test is used to measure the strength of the joint. Testing is performed on an Instron machine. The peel rate employed is 25 mm/min. and the chart speed is maintained at 20 mm/min.

II-D. ESCA Analysis

Failure surfaces generated by peel tests are analyzed by electron spectroscopy for chemical analysis (ESCA) using a PHI Model 548 Electron Spectrometer, with MgK_α radiation as the exciting photons and with the sample chamber pressure of about $10^{-8} \sim 10^{-9}$ torr.

II-E. SEM Analysis

The scanning electron micrographs are obtained on an AMR Model 1000A with gold coated failure surface specimens.

III. RESULTS and DISCUSSIONS

III-A. Joint Durability Studies

1. Effect of γ-APS film thickness.

The effect of the coupling agent film thickness is found to be considerable in dry joint strength, reaching a maximum when adsorbed from a 2% γ-APS solution and leveling off beyond that thickness. (see Fig. 4 in Ref. 1). The effect of the γ-APS film thickness in wet environment is found to be quite different. An example is shown in Fig. 1, where a 0.3% solution treatment is compared with a 2% solution treatment. For both specimens, the initial drop in strength is rapid but 2% specimen seems to degrade a little faster than 0.3% specimen. In the sample from a 2% solution which was dried under standard drying condition, the peel strength rapidly drops to about 40% in 6 hours and to about 10% in one day. The strength drops to below 1% of the dry joint strength after about 5 days. At this strength, it is comparable to the unprimed joint in dry environment which quickly (within a few hours) loses all of its already low strength when immersed in water. For a specimen primed from 0.3% solution, the absolute strength after 6 days of immersion in water is also comparable to the unprimed, dry joint strength.

Degradation of the strength is qualitatively same when exposed to 100% RH environment as shown for a specimen primed from 2% solution in the second lower (from bottom) curve in Fig. 2, but a little slower than when immersed in water (compare two lower curves in Fig. 2). It was also noted that the peel width in water exposed samples is less than the original width of the dry specimen. In both Fig. 1 and 2, the strength retention was calculated based on the initial dry peel width rather than the actual peel width.

A more extended dependence of the γ-APS film thickness on wet strength retention is shown in Fig. 3, when the joints were exposed to 100% RH for one or five days, respectively. For both duration of exposure, the peel strength retention increases with γ-APS concentration reaching a maximum somewhere between 0.3 and 1% solution, but drops sharply beyond that concentration. In other words, the joints primed with thicker than 1% treatment very quickly loses its strength, while their dry strengths were quite high.

2. Effect of Dehydration of γ-APS Film

Dehydration of silane film prior to joint formation leads to lower dry strength. For example, dehydration of a 0.3% γ-APS film at 110°C under vacuum for 40 hours lowers the dry strength by about 55%

(see Fig. 6 in Ref. 1). This was due to the increased curing of γ-APS film, which reduced the interdiffusion of γ-APS into polyethylene. In wet environment, however, the effect of dehydration of γ-APS film is found to increase the durability of the joint to some extent. A representative case is shown in Fig. 4 for 0.3% solution primed joints. The joint with a dehydrated film degrades at a significantly slower rate as compared with the joint with a standard dried film. When immersed in water, the joints with dehydrated γ-APS films up to 3 days of drying exhibited better peel strength retention as shown by the lower curve of Fig. 5. The peel strength retention at zero day of dehydration corresponds to the standard drying condition. Similar trend was observed when the joints were exposed to 100% RH as shown by the upper curve of Fig. 5.

3. Effect of Redrying The Joint After Exposure To Wet Treatment

When the joint exposed to water is redried, part of the peel strength is recovered as shown in the curve B of Fig. 2. After 6 hours of exposure, only 55% of the dry strength is recovered under the redrying conditions. After 10 days of exposure, redrying recovers about 20% of the strength. Similar trend is observed for joints exposed to 100% RH, as shown by the curve A of Fig. 2. Here the recovery is greater than the water immersion case.

III-B. Failure Surface Analysis

We will first describe the failure surface analysis obtained with the joints primed with a 2% γ-APS solution after standard drying condition. As long as the joint has low yet measurable peel strength, the SEM micrographs of the failure surfaces look like those shown in Fig. 6. Fig. 6(A) is the α-Al_2O_3 side and Fig. 6(B) is the PE side of the joint peeled after 5 days of immersion in water. The area shown is the center portion of the joint. On both surfaces (A and B), we observe some clean areas as well as deformed polyethylene. It appears that the load bearing is carried out only by the area where deformed polyethylene is shown. Even in this area, the extent of fibrillation of polyethylene is much less than the case of the dry joint strength (see Fig. 7 of Ref. 1). In clean areas, the joint has little strength. The overall effect of these two areas is the low peel strength retention. Failure surfaces after exposure to 100% RH are very similar to those shown in Fig. 6. It appears that the clean areas are where water penetrated and the deformed PE area is where water has not completely degraded the adhesion.

The nature of the clean area can be better elucidated by ESCA analysis. Table 1 shows the ESCA results averaged on an area much bigger than shown in SEM. In addition to O_{1s} and C_{1s} peaks detected on both sides of the failure surfaces, N_{1s} and Si_{2p} peaks are also detected. Since N_{1s} and Si_{2p} come from γ-APS film, these elements must be present on clean areas of both surfaces. Since a small Al_{2p} peak at 77.7eV is detected on the sapphire(α-Al_2O_3)side, it suggests that the γ-APS film on sapphire side is less than 20 Å (approximate escape depth for Al photoelectrons) thick in some regions. The area of deformed polyethylene contributes to the overall C_{1s} intensity. Therefore, when N/C and Si/C of the failed surfaces are compared with that of standard dried γ-APS film, we should observe smaller values of N/C and Si/C in failed surfaces. This is confirmed since N/C and Si/C ratio in Table 1 are smaller than those expected(>0.25 and >0.21,respectively). The ESCA analysis for the failure surfaces after exposure to 100% RH is very similar in nature and in N/C and Si/C values.

With the joints primed with a 0.3% γ-APS solution, the SEM micrographs of the failure surfaces also showed two regions (i.e., clean area and polyethylene covered area) but polyethylene was not deformed as much as for the 2% solution. The ESCA analyses of such a failure surface are consistent with the view suggested by the SEM micrographs. As shown in Table 1, we observed N_{1s} from γ-APS on both surfaces but Si_{2p} was too weak to be detected. Atomic ratios of N/C and Si/C are even smaller than 2% case and Al/C ratio is greater than 2% case. These results are due to the thin and originally non-uniformly covered γ-APS film at this low concentration. The exposure to 100% RH produces very similar results on the failure surfaces as characterized by SEM and ESCA.

To summarize the failure surface analyses with standard dried γ-APS film (either 0.3% or 2%) when the joint is exposed to water or 100% RH, in some regions of the joint (i.e., clean area in the SEM micrographs), the failure occurred through the silane layer close to sapphire side probably due to hydrolytic degradation and in other regions where water has not severely degraded, the failure is through polyethylene. Therefore, the failure is of a mixed mode.

Dehydration of γ-APS film prior to the joint formation was found to improve the durability of the joint in wet environment as discussed in the previous section. However, the failure mode as examined by SEM and ESCA is also of mixed nature with both polyethylene region and clean region as in standard dried case. The only difference is that in dehydrated γ-APS film, the polyethylene is much less deformed and thus shows smooth profiles - as was the case in dry joint strength test (see Fig. 8 in Ref. 1).

In the previous section, we have demonstrated that redrying the joint even under mild conditions after exposure to water enabled the joint to recover part of the dry strength. Therefore, it was of interest to examine the failure mode of such redryed joints. Upon redrying, the severely damaged region near the edges due to the initial water takeup became delaminated before peeling. Thus when peeled, there are two clearly separate failure regions, as shown in Fig. 7 (A) and (B). Fig. 7 (A) shows both sides of the failure surface in the delaminated area, while Fig. 7 (B) is for the central region. In Fig. 7 (A), there is little evidence of deformed polyethylene while in Fig. 7 (B), extensive deformation and fibrillation of PE is shown. This type of extensive deformation and fibrillation was characterstic of dry joint failure with the standard dried γ-APS (see Fig. 7 of Ref. 1). ESCA analyses on these two clearly separated failure regions are summarized in Table 2, and confirm the observation based on SEM. On the delaminated region, we observe the presence of silane on both sides, even though the failure is closer to the sapphire side as indicated by a high concentration of aluminum. On the peeled central region, no silane is detected on either side with mostly PE present on both surfaces. Therefore, we may summarize that in the redried joint, the peeled region fails mostly via cohesive failure of polyethylene with extensive deformation and fibrillation, while in delaminated region, the failure is through silane but closer to the sapphire side.

III-C. Mechanism of Strength Degradation in Wet Environment

Since the peel specimen in this study is a joint consisting of α-Al_2O_3, γ-APS polysiloxane film and polyethylene, water will primarily diffuse into the γ-APS layer and at the interface between α-Al_2O_3 and γ-APS layer. At the interface between α-Al_2O_3 and γ-APS layer, some covalent bonds of the Al-O-Si type can be formed when primed with γ-APS. With a model compound, γ-aminopropyldimethylethoxysilane, Naviroj et al. (9) were able to detect Al-O-Si antisymmetric frequencies at 963 cm^{-1} by FT-IR. This frequency which agrees favorably with the calculated value was found to disappear when immersed in water, indicating a poor hydrolytic stability of Al-O-Si bond.

Due to the poor hydrolytic stability of Al-O-Si bond as well as of γ-APS polysiloxane itself, it is expected that the joint will fail in γ-APS layer close to α-Al_2O_3 side. This is what we observe in the clean areas of the failure surface by ESCA as discussed in the previous sections. In the central areas where water has caused little damage, polyethylene fails when peeled,as shown by SEM and ESCA results. Therefore, the diffusion of water and the subsequent hydrolyses of interfacial bond and γ-APS itself are the critical parameters for the durability of the joints consisting of α-Al_2O_3/γ-APS/polyethylene.

In view of these considerations, the effects of γ-APS film thickness,dehydration and redrying on the rate of the joint strength degradation can be at least qualitatively explained, as follows:

a) In wet environment, the joints primed with 0.3 ∿ 1% aqueous γ-APS solution (thin film) are more durable than the joints with higher concentration γ-APS treatment (thicker film). When γ-APS film is thin as in 0.3 ∿ 1% treatment, γ-APS layer may be a mixture of polyethylene due to interdiffusion. while in thicker films, the interdiffused layer is limited at the interface between PE and the top part of γ-APS, leaving some γ-APS layer unmixed (1). In the former case, the water diffusion and hydrolyses will be slower than in the latter case where water can more quickly attack unmixed γ-APS layer. This may explain the trend observed in Fig. 3 where very thick film treatment (> 2% γ-APS concentration) leads to a very fast rate of the joint strength degradation.

b) When γ-APS film is dehydrated prior to the joint formation, the rate of joint strength degradation in wet environment is slower than the standard dried case. This result can be explained based on the fact that dehydration leads to more extensive curing in γ-APS film as evidenced by the higher T_g (1) thus making diffusion of water and the hydrolyses slower than in standard dried silane. Furthermore, the standard dried silane is more susceptible to diffusion and hydrolyses because there are significant number of Si-OH groups present, as evidenced by IR spectra. (see Fig. 1(e) in Ref. 1).

c) When the joints after exposure to water are redryed before peeling, it recovers some of its strength based on the original width. The failure mechanism clearly shows two regions in such cases where the edges are delaminated after redrying and the load is borne only by the central portion where extensive deformation and fibrillation is indicated. The redrying is not effective in the edge areas where there may be too much water and severe hydrolyses taken place, but in the central regions of joint reversible bonds of Si-O-Si type may be formed due to less water-penetration and damages incurred. When based on the reduced actual peel width, the peel strength recovers most of its value after redrying.

As described earlier. the peel width gets smaller and smaller as the exposure time to water increases because of the water diffusion. Water boundary is moving with a front toward the central portion of the joint. Such a movement can be experimentally estimated by measuring peel width from redrying experiments, since the area where water moved in has been delaminated. It is of interest to see if the experimentally measured peel width can be reasonably predicted from a model based on the diffusion of water.

We used the following transient diffusion equation to determine the rate of water diffusion into the laminated area:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \qquad (1)$$

with boundary conditions for a rectangular area given by: $-a< x< a$ and $-b< y< b$, where a, b correspond to one half of the dimensions on x and y axes as shown in Fig. 8(A). The solution to this equation is given by (10);

$$\frac{c(x,y)}{c(\infty,\infty)} = 1 - \phi(a,x)\ \phi(b,y) \qquad (2)$$

where $c(\infty,\infty)$ is the maximum water absorption by γ-APS layer, and

$$\phi(a,x) = \frac{4}{\pi} \sum_{0}^{\infty} \{(-1)^n/(2n+1)\ \exp(-(2n+1)^2\pi^2 Dt/4a^2) \cdot$$
$$\cos((2n+1)\pi x/2a))\} \qquad (3)$$

The term $\phi(b,y)$ has a similar expression. When monitoring the diffusion along the center line (x-axis), Eq. (2) becomes simpler to calculate as follows:

$$\frac{c(x,0)}{c(a,0)} = 1 - \phi(a,x)\ \phi(b,0) \qquad (4)$$

and can be computed as a function of x when $a = 0.95$ and $b = 1.905$, provided that the diffusion coefficient D in Eq. (3) is known. For soluble polymers such as polyethylene oxide, D is about 3×10^{-8} cm^2/ sec at 25°C (11). Since the standard dried γ-APS is a low molecular weight, amorphous polymer which is soluble in water, we may use a somewhat higher value than for polyethylene oxide. Using a value of 8×10^{-8} cm^2/sec as a diffusion coefficient for γ-APS, Fig. 8(B) shows the plot of the water concentration ratio as a function of the distance in the x axis from the center of the joint. From this figure, it can be seen that buildup of water concentration occurs from the edge inwards with increasing exposure time. The debonding occurs when a critical concentration is reached (12), reducing the peel width from original one. From the swelling and solubility data of γ-APS and assuming arbitrarily 1/3 hydrolyses of Si-O-Si bond to be the critical stage, we estimate that the critical concentration ratio $c(x,o)/c(a,o)$ to be approximately 0.09 (8). By drawing a line at 0.09 across the distance in Fig. 8 (B) and reading the values as it crosses with the curves, we can estimate the predicted peel width which should correspond to twice the number read off Fig. 8 (B). Fig. 9 compares experimentally obtained peel width with the predicted values, as a function of exposure time with the joint primed with 2% standard dried γ-APS film. The agreement is reasonable between the two, supporting that the delamination is a diffusion controlled phenomenon.

IV. CONCLUSION

In this study, we investigated the durability of the joints (α-Al_2O_3/γ-APS/PE) in wet environment as a function of the γ-APS thickness, dehydration prior to joint formation and redrying the joint after a certain exposure. The joint strength was estimated by peel strength, and the failure mode and mechanism were studied by scanning electron microscope and ESCA analyses. The joint strengths are found to decrease with exposure time in wet environment more rapidly in water than in 100% RH. With exposure time. the debonded area increases from the edge toward the central area of the joint. Relatively thin γ-APS primer treatment of α-Al_2O_3 appears to provide more durable joint (slower rate of strength loss) than the thicker γ-APS primer treatment. Optimum thickness level is observed in the range of 0.3 ∿ 1% γ-APS concentration level while for dry strength, the γ-APS film obtained from 2% was optimal. Dehydration of γ-APS before joint is made resulted in more durable joint than the standard dried film at a given concentration. There appears to be an optimal dehydration condition such that maximum strength retention occurs between 1 ∿ 2 days of dehydration at 110°C in a vacuum oven. At prolonged dehydration time, some degradation can occur which makes γ-APS less durable to water attack. Regardless of the γ-APS thickness and dehydration history, the failure in the debonded area in wet environment seems to occur by the hydrolyses of γ-APS near α-Al_2O_3 side and in the peeled area by the deformation of polyethylene (cohesive failure), as characterized by SEM and ESCA.

When the joints are redried after exposure to wet environment, debonded area at the edges does not recover much strength but in the bonded central areas, the strength is recovered, characterized by the extensive deformation of polyethylene. This supports the reformation of Si-O-Si after hydrolyses upon redrying in the central region.

Diffusion of water in γ-APS near α-Al_2O_3 side rather than PE side can explain at least qualitatively most of the observed trends in durability as a function of γ-APS thickness, dehydration of γ-APS prior to joint formation and redrying.

A model based on water diffusion with the hypothesis of the critical water concentration as a necessary step to debond has been used to predict the actual peel width reduction. The predicted peel width reduction as a function of immersion time has the same trend as the experimentally measured values.

Acknowledgements

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REFERENCES

(1) N.H. Sung, A.Kaul, I.Chin, and C.S.P. Sung, Polym. Eng. and Sci., 22, 637 (1982)

(2) J.T. Huneke and J.K. Dorey, II, Proceedings of 37th Annual Technical Conference, RP/C Institute, SPI. Session 2-B (1982)

(3) M.Gettings, J. Appl. Polym. Sci., 21, 2375 (1977)

(4) M.E. Schrader and A. Block, J. Polym. Sci., Part C, No. 34, 281 (1971)

(5) H. Ishida and J.L. Koenig, J. Polym. Sci., Polym. Phys. 18, 1931 (1980)

(6) H. Ishida and J.L. Koenig, J. Polym. Sci., Polym. Phys. 18, 233 (1980)

(7) J.W. Williams and F.J. Boerio, Proceedings of 37th Annual Technical Conference, RP/C Institute, SPI. Session 2-D (1982)

(8) A. Kaul, Ph.D. Thesis, Dept. of Chemical Engineering, Tufts University, May (1983)

(9) S. Naviroj, J.L. Koenig and H. Ishida, ONR Technical Report No. 6 Contract No. 0014-80C-0533, Dept. of Macromolecular Science, Case Western Reserve University, Dec. 1, (1982)

(10) H.S.Carlson and J.C. Jaeger, "Conduction of Heat in Solids", 2nd Ed. Oxford Univ., p. 173 (1959)

(11) J.L. Williams and V. Stannett, J. Appl. Polym. Sci., 14, 1949 (1970)

(12) R.A. Gledhill, A.J. Kinloch, and S.J. Shaw. J. Adhesion 11, 3 (1980)

Table 1.

ESCA Analyses on Failure Surfaces of α-Al_2O_3/γ-APS/ PE Joints After Water Immersion (5 days at 25°C)

	2% γ-APS Standard Dried		0.3% γ-APS Standard Dried	
	α-Al_2O_3 Side	PE Side	α-Al_2O_3 Side	PE Side
	Binding Energy (eV)			
O_{1s}	535.9	535.1	535.0	534.4
N_{1s}	402.9	402.5	403.0	402.2
C_{1s}	288.5	288.3	288.2	287.0
Si_{2p}	105.9	105.6	NP	104.4
Al_{2p}	77.7	NP*	77.6	NP
	Atomic Ratios			
N/C	0.16	0.09	0.04	0.02
Si/C	0.12	0.07	0.00	0.01
Al/C	0.02	0.00	0.11	0.00

*NP; Not present

Table 2.

ESCA Analyses on Failure Surfaces of Redried α-Al_2O_3/γ-APS/PE Joint After Water Immersion (5 days at 25°C)*

	DELAMINATED REGION		PEELED REGION (Central)	
	α-Al_2O_3 Side	PE Side	α-Al_2O_3 Side	PE Side
		Binding Energy (ev)		
O_{1S}	535.2	534.0	533.8	533.7
N_{1s}	403.1	401.6	NP**	NP
C_{1S}	288.6	286.8	287.2	286.6
Si_{2P}	105.8	104.2	NP	NP
Al_{2P}	78.2	NP	77.0	NP
		Atomic Ratio		
N/C	0.10	0.06	0.00	0.00
Si/C	0.07	0.05	0.00	0.00
Al/C	0.27	0.00	0.05	0.00

* Redrying at 25°C in vacuum for 5 days.

**NP; not present

FIGURE CAPTIONS

Fig. 1 Effect of water immersion on peel strength retention expressed in the percentage of dry peel strength, based on initial peel width. Comparison with 2% γ-APS concentration is shown for 0.3% γ-APS concentration.

Fig. 2 Effects of exposure to water or 100% RH (two lower curves) and of redrying on peel strength retention (curves A & B), based on initial peel width. (2% γ-APS, standard dried).

Fig. 3 Effect of γ-APS concentration (film thickness) on peel strength retention after exposure to 100% RH based on initial peel width.

Fig. 4 Effect of dehydration of γ-APS film prior to joint formation in comparison with standard dried γ-APS film on peel strength retention after exposure to water (0.3% γ-APS)

Fig. 5 Effect of the extent of dehydration (100°C, vac) on peel strength retention after exposure to 100% RH (upper curve) and water (lower curve) for 5 days at 25°C.

Fig. 6 SEM micrographs of failure surfaces of α-Al_2O_3/γ-APS (2%, standard dried)/PE joint after exposure to water for 5 days at 25°C.

Fig. 7 SEM micrographs of failure surfaces of redried α-Al_2O_3/γ-APS 2%, standard dried)/PE joint after exposure to water for 5 days at 25°C.

Fig. 8 (A) Definition of the axes in peel joints at $t = o$ of water immersion and the qualitative contours showing critical concentration of water at $t>o$.

(B) Profiles of computed water concentration expressed in the ratio of actual concentration to maximum concentration due to water diffusion from the edge into an α-Al_2O_3/γ-APS/PE peel joint.

Fig. 9 Comparison of reduced peel width obtained from redrying experiments with the values predicted based on water diffusion for standard dried 2% γ-APS film after water exposure at 25°C.

Figure 1.

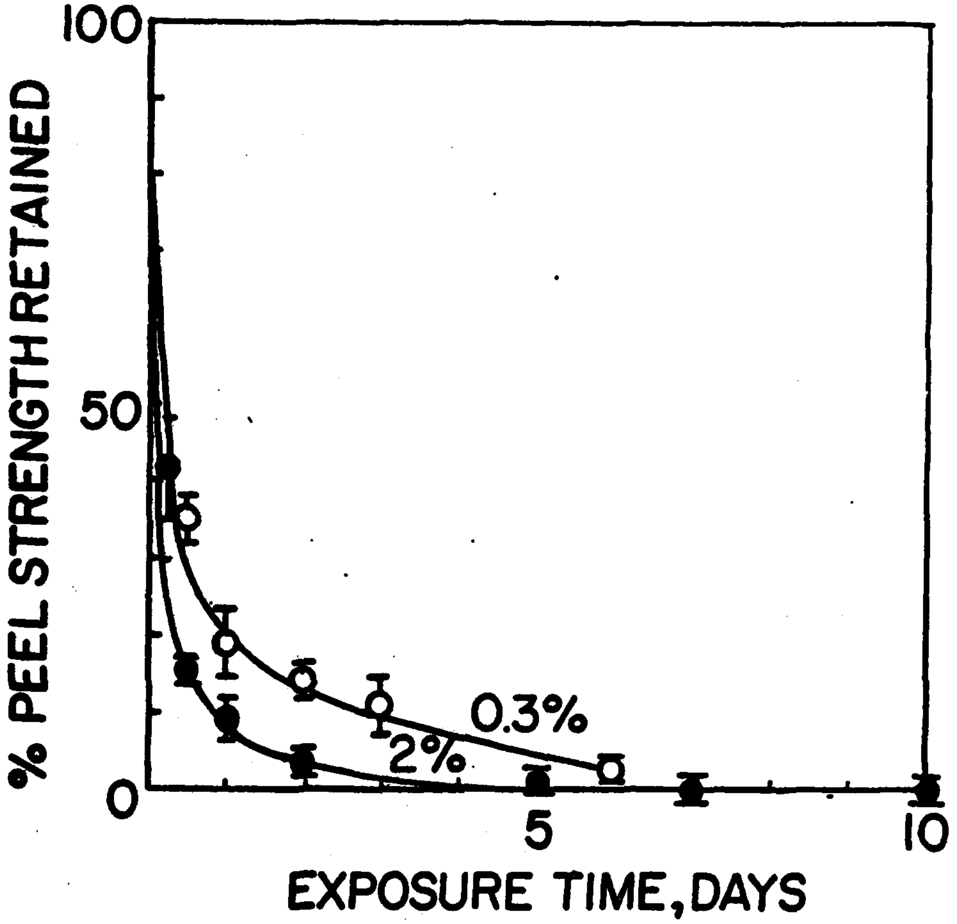


Figure 2.

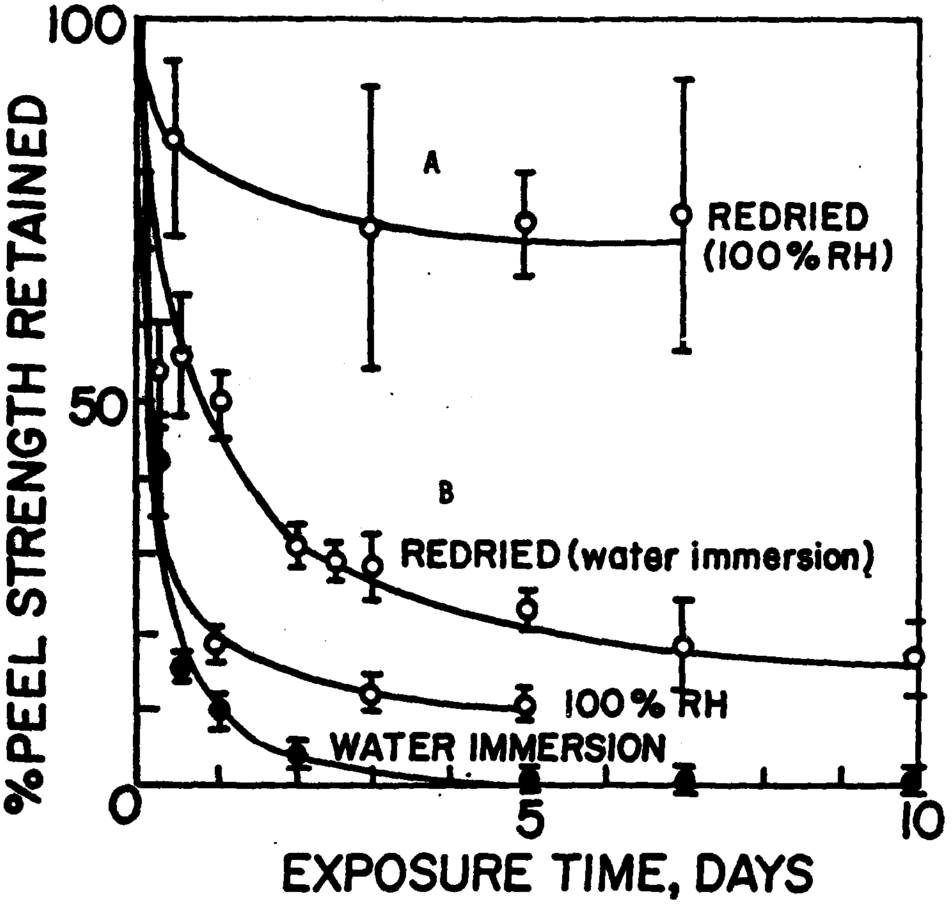

100
50
0
%PEEL STRENGTH RETAINED
0
5
10
EXPOSURE TIME, DAYS
A
REDRIED
(100% RH)
B
REDRIED (water immersion)
100% RH
WATER IMMERSION

Figure 3.

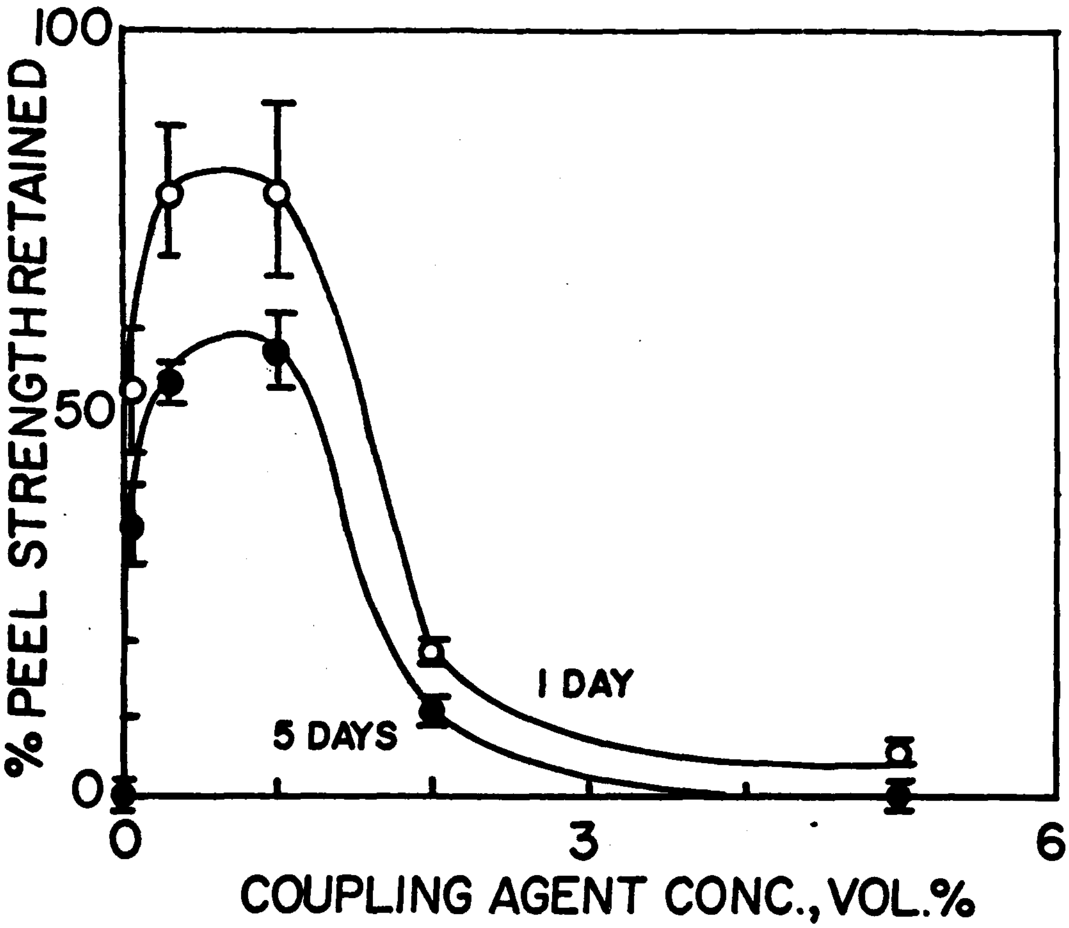
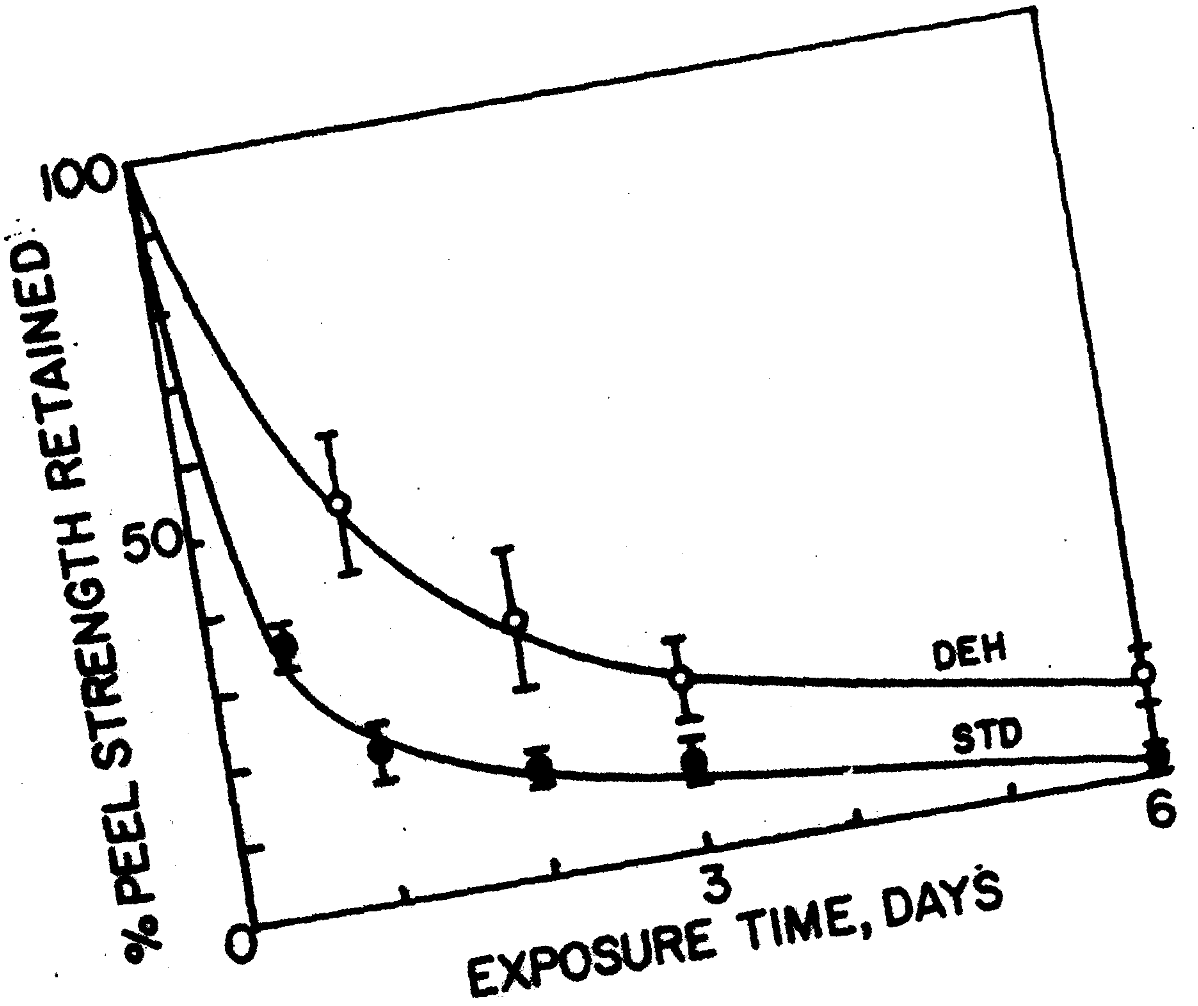
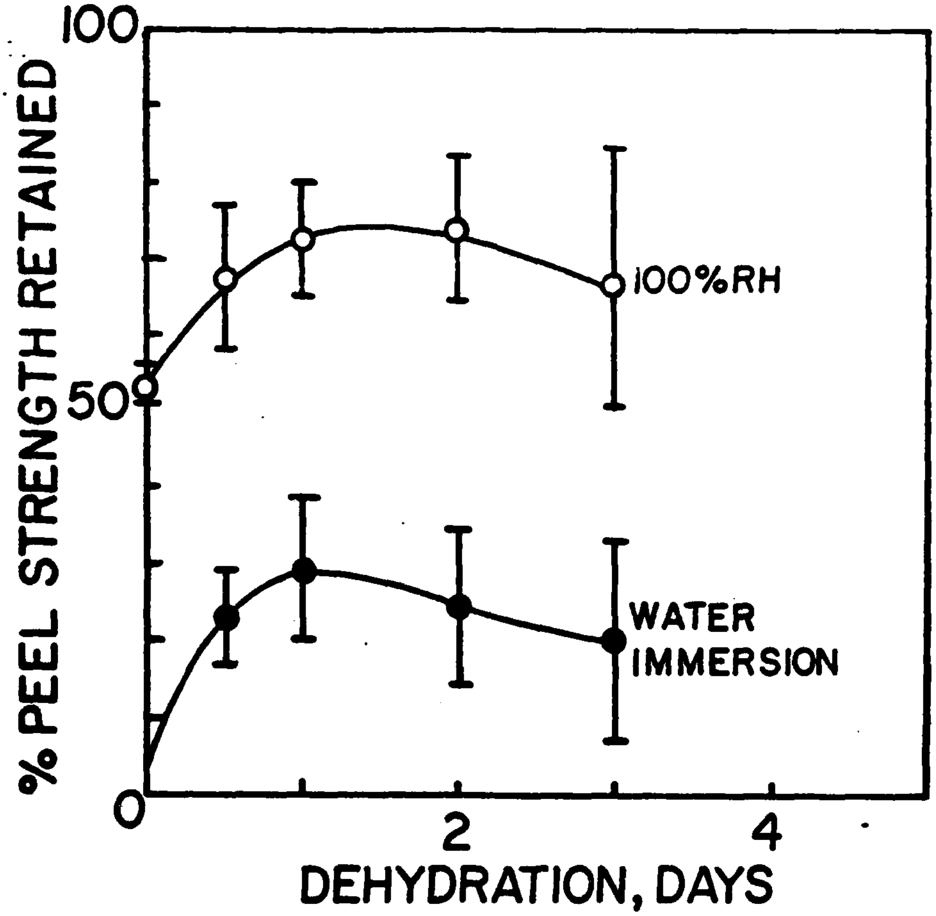

100
50
0
% PEEL STRENGTH RETAINED
0
3
6
COUPLING AGENT CONC., VOL.%
1 DAY
5 DAYS

Figure 4.



100
50
0
% PEEL STRENGTH RETAINED
3
6
EXPOSURE TIME, DAYS
DEH
STD

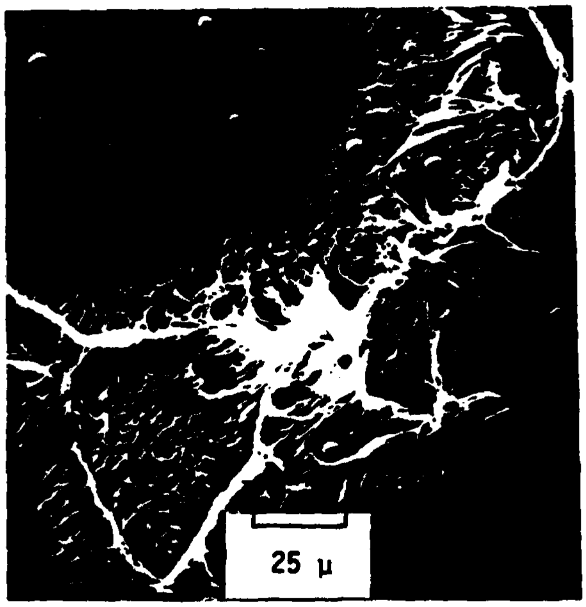
Figure 5.



100
50
0
% PEEL STRENGTH RETAINED
2
4
DEHYDRATION, DAYS
100%RH
WATER
IMMERSION

Figure 6.

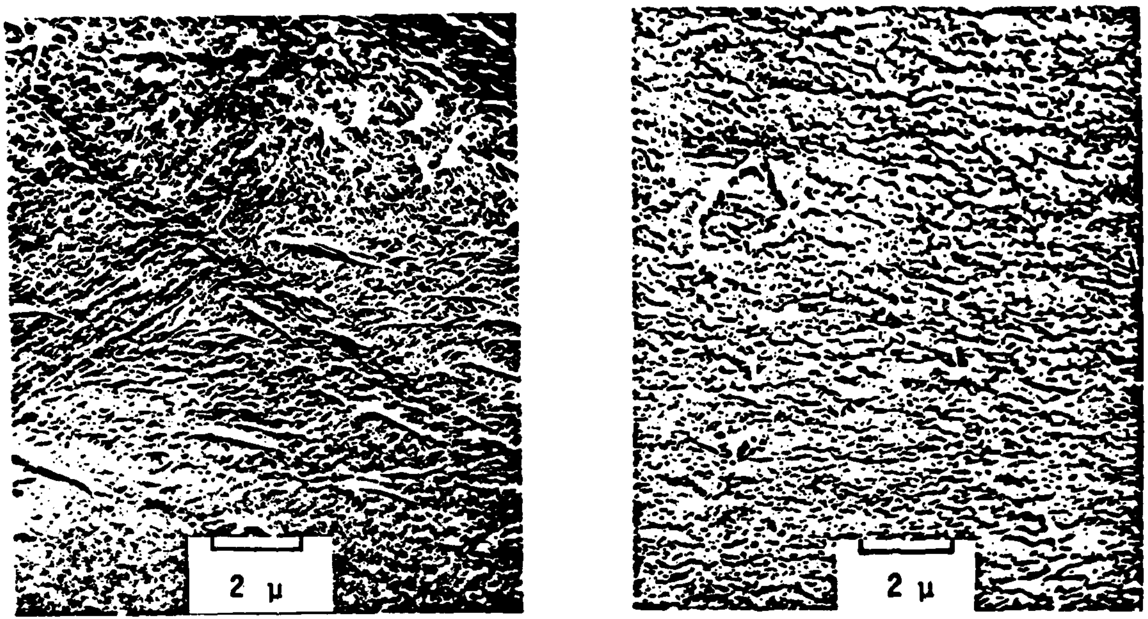
(A) α-Al_2O_3 side



(B) PE side

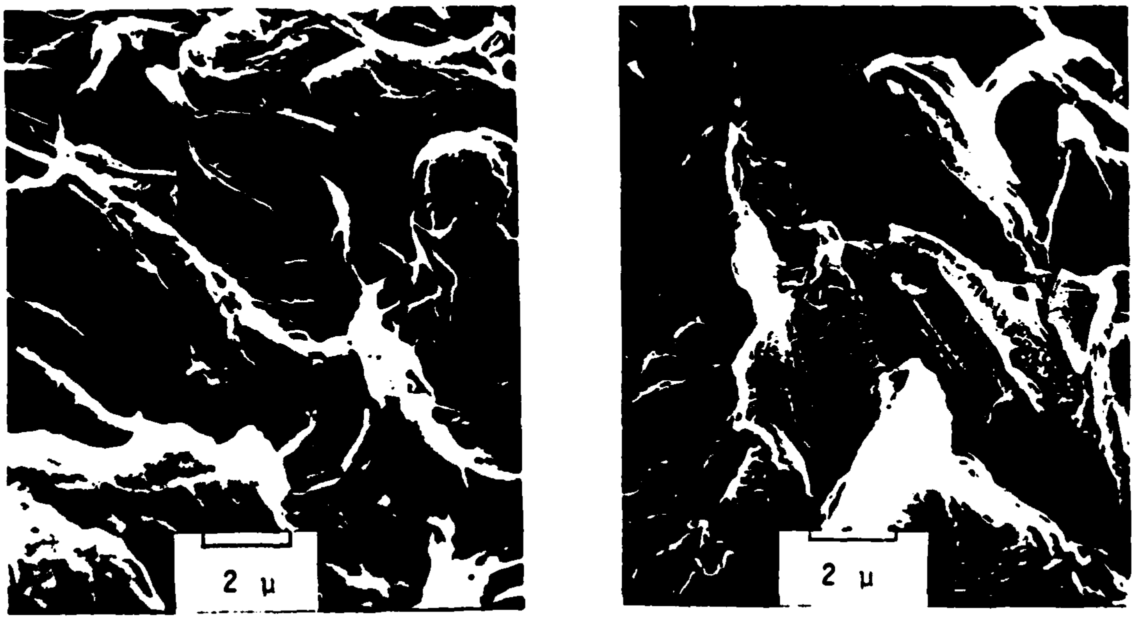
Figure 7.

(A)



α-Al_2O_3 side PE side

(B)



α-Al_2O_3 side PE side

Figure 8.

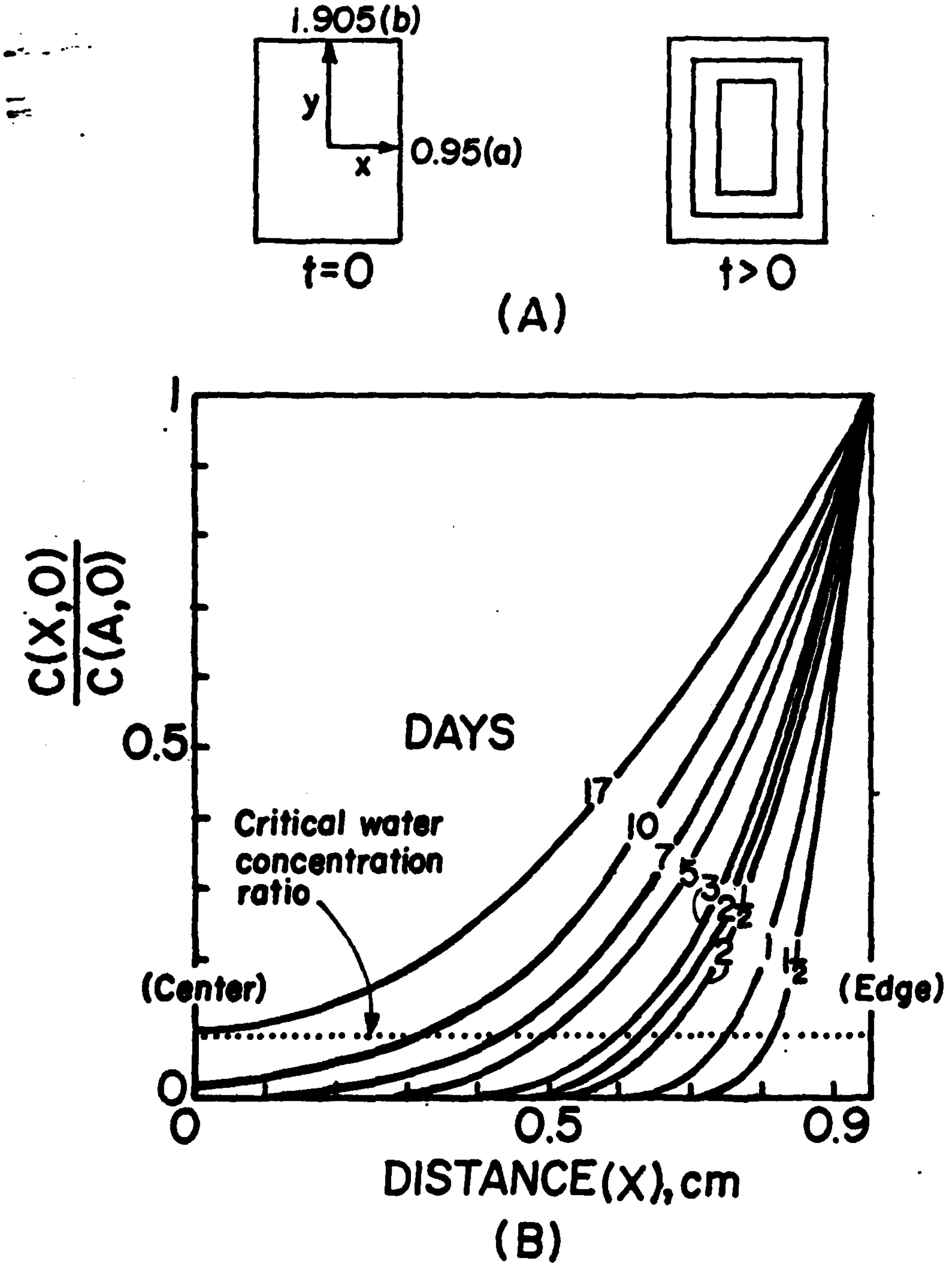
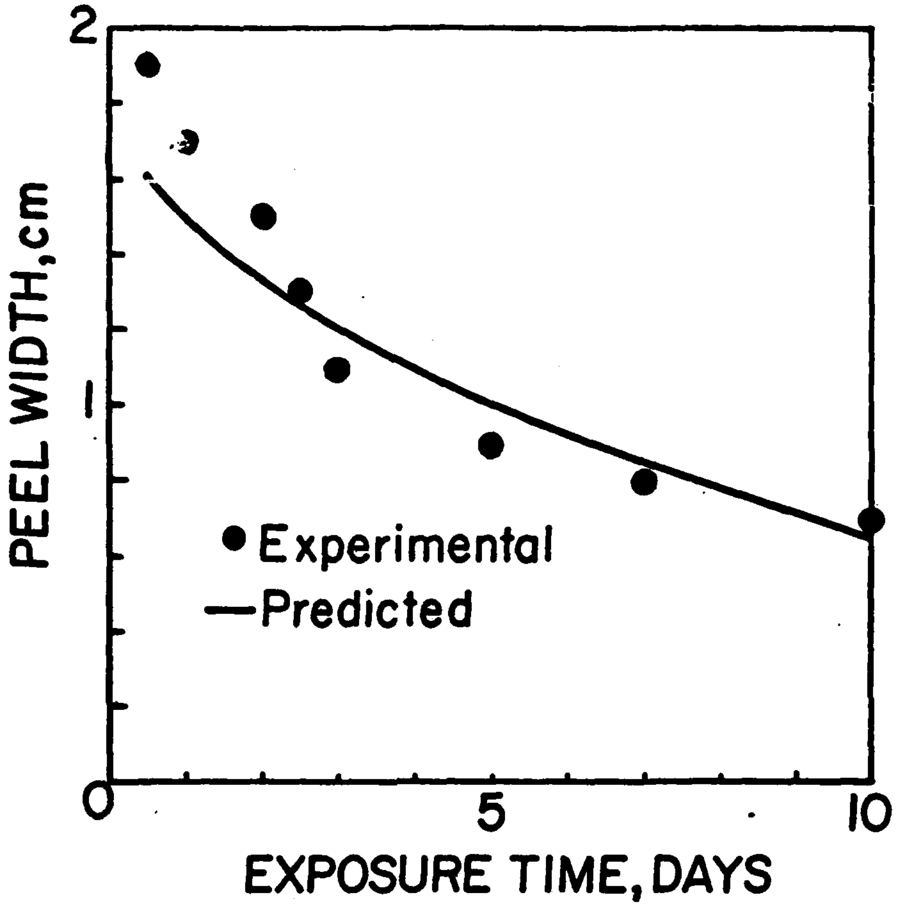

1.905(b)
y
x
0.95(a)
t=0
t>0
(A)
C(X,0)/C(A,0)
1
0.5
0
DAYS
17
10
7
5
3
2½
2
1
½
Critical water concentration ratio
(Center)
(Edge)
0
0.5
0.9
DISTANCE(X), cm
(B)

Figure 9.



PEEL WIDTH, cm
2
1
0
5
10
EXPOSURE TIME, DAYS
● Experimental
—Predicted

unclassified

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Adhesion promoters, organo silanes, γ-aminopropyl triethoxy silane, α-Al_2O_3/Polyethylene joint, durability, wet environment, failure analyses

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

~~We~~ is Investigated the durability of the joints (α-Al_2O_3/γ-APS/PE) in wet environment as a function of the γ-APS thickness, dehydration of γ-APS prior to joint formation and redrying the joint after a certain exposure. The joint strength measured by peel strength is found to decrease with exposure time in wet environment more rapidly in water than in 100% RH. →

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20. Abstract (continued)

With exposure time, the debonded area increases from the edges toward the central area of the joint. Relatively thin γ-APS treatment on α-Al_2O_3 appear to provide more durable joint than thicker γ-APS treatment resulting in an optimal thickness in the range of 0.3 ∿1% γ-APS concentration level. Dehydration of γ-APS lead to more durable joint with an optimal condition found between 1 ∿ 2 days of dehydration at 100°C in vacuum. Regardless of the γ-APS thickness and dehydration history, the failure in the debonded area seems to occur by the hydrolysis of γ-APS near α-Al_2O_3 side and by the deformation of polyethylene (cohesive failure) in the peeled area, as characterized by SEM and ESCA. The debonded area in the dried joint recovers little strength but in the bonded central areas, the strength is largely recovered, characterized by the extensive deformation of polyethylene. Diffusion of water in γ-APS near α-Al_2O_3 side rather than PE side can explain at least qualitatively most of the observed trends. Comparisons are made for the effects of γ-APS thickness and dehydration on the durability in wet environment and adhesion promotion in dry environment as well as on their respective failure mode.

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