

# Irreversible Effects of Hygrothermal Aging on DGEBA/DDA Epoxy Resin

G. Z. XIAO, M. E. R. SHANAHAN

Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux, B. P. 87, 91003 Evry Cedex, France

Received 10 October 1997; accepted 14 December 1997

**ABSTRACT:** Irreversible hygrothermal aging effects on DGEBA/DDA epoxy resin were studied by FTIR, gravimetric tests, and DMTA. The results show that water immersion at 50, 70, and 90°C leads to the introduction of carbonyl groups in the resin and chain scission of the crosslinked structure. These irreversible structural changes induce the addition of water to the polymer initially and weight loss of the material eventually. They also lead to the irreversible decrease of the glass transition temperature of DGEBA/DDA. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 363–369, 1998

**Key words:** DMTA; epoxy resin; FTIR; hygrothermal aging; irreversible effects; water

## INTRODUCTION

Epoxy resin-based composites and adhesives are often used for structural applications where their long-term properties are of primary importance. Consequently, a great deal of effort has been devoted to evaluating and characterizing their performance under various deleterious conditions, particularly in a humid environment at elevated temperature. It is well recognized that epoxy resins can suffer substantial losses in their properties, particularly mechanical, following the pick-up of water.<sup>1–8</sup> The glass transition temperature,  $T_g$ , is lowered by the absorption of moisture.

Although some workers have found<sup>6,9</sup> that water absorption induced more or less reversible degradation (plasticization), prolonged hygrothermal aging may lead to irreversible damage of the resin due to susceptibility of the polymer to hydrolysis, oxidation, and change of the effective average crosslinked molecular weight. In a previous investigation,<sup>10</sup> we have found that water, at

90°C, can attack the crosslinked chains in an epoxy resin, causing chain scission and the leaching of segments.

To improve our understanding of these irreversible degradation effects, we studied the hygrothermal aging of a model epoxy resin at 50, 70, and 90°C. This article reports some of our results concerning irreversible aging effects as observed on the Fourier transform infrared (FTIR) spectrum, from water absorption and desorption, as well as with the glass transition temperature.

## EXPERIMENTAL

### Sample Preparation

A model epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) and dicyandiamide (DDA) without fillers was studied. The material was supplied by CECA S. A. France. This resin was cured by maintaining the polymer at a temperature of 140°C for 1 h after heating from ambient temperature at a rate of 3°C/min. Both DSC and DMTA studies confirmed that the resin was fully cured under these conditions by leading to a maximum

Correspondence to: M. E. R. Shanahan.

possible value of  $T_g$ . Moreover, FTIR analysis confirmed that there was no residual, unreacted curing agent, or epoxide groups in the cured resin.<sup>10</sup> Thin films (of about 0.15-mm thickness) were prepared for FTIR analysis, while plates cut from the cured polymer with the dimension of ca.  $30 \times 30 \times 1.2$  mm were employed for water-absorption and -desorption tests and small samples with the dimensions of ca.  $18 \times 5.5 \times 1.5$  mm were prepared for DMTA analysis and swelling tests.

### FTIR Analysis

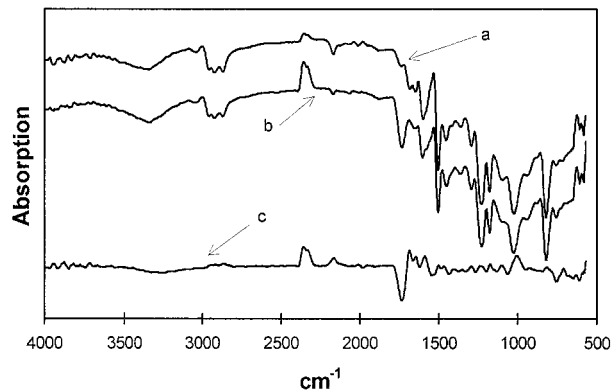
A Bruker IF25 spectrometer from Bruker Analytische Messtechnik GmbH was employed for the FTIR analysis. The spectra were recorded from 4000 to 500  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

Thin films of the cured resin were analyzed by using a Golden Gate single-reflection diamond ATR accessory. Aged samples were prepared by immersing the thin films in water for 1 month at 50, 70, and 90°C, respectively, and then fully dried.

### Water Absorption and Desorption

For the gravimetric part of this study, specimen weight was determined using a Mettler AT250 analytical balance which was accurate to  $\pm 0.05$  mg. Before aging, the samples were dried in a desiccator at 40°C and weighed periodically until the percent weight change was less than 0.08% per week. The weight of the dry resin was then recorded as the initial weight of the resin ( $W_0$ ). The samples were then placed in distilled water at 50, 70, and 90°C, respectively. Both absorption and absorption plus desorption tests were conducted:

- (a) Absorption: At different time intervals, samples were taken out, dried superficially, weighed, and then returned to the water. For each temperature, the average of three samples was taken.
- (b) Absorption plus desorption: After immersing in water for a given period, some samples were taken out and dried at their initial aging temperature and subsequently further dried at 70 and 90°C depending on the sample. Each drying process was only stopped when a good estimation of the final equilibrium weight after desorption could be obtained.



**Figure 1** Effect of aging on the FTIR spectrum of DGEBA/DDA epoxy resin: (a) before aging; (b) 30 days in 90°C water, then fully dried; (c) difference spectrum =  $b - a$ .

Weight change was found to be negligible during the time required for weighing, even after prolonged exposure to water.

### DMTA Studies

The glass transition temperature ( $T_g$ ) of the polymer in its various conditions was obtained by employing a DMTA (Metravib Viscoanalyser) in the tension mode. The effective testing length of the samples was controlled at 9.8 mm by using a gauge. Tests were run from room temperature to 250°C with a temperature increasing rate of 10°C/min. The values presented for unaged resin are the average of five samples. Those for the aged polymer are taken from one or two samples, depending on availability.

The results of the  $T_g$  were correlated to the swelling of the resin during aging. Sample volume was calculated from length, thickness, and width measurements made with micrometers accurate to  $\pm 0.001$  mm. For each specimen, the thickness and width were calculated as the average of five measurements, one near each end, and three at approximately equidistant positions along the length. Length was determined from the average of six measurements by turning around the sample. Dimensional changes were made ca. 2 min after removal from the water.

## RESULTS AND DISCUSSION

### Aging Effects on FTIR Spectrum

Figure 1 shows the FTIR spectra of the cured DGEBA/DDA epoxy resin film before aging and

**Table I** Tentative Assignment of Major Bands in the Infrared Spectrum of DGEBA/DDA Epoxy Resin

Positions ( $\text{cm}^{-1}$ )	Assignment
3342	—OH, —NH stretching
3100–2800	—CH <sub>3</sub> , and —CH <sub>2</sub> — stretching
2168	Nitrile
1736	C=O
1681	C=N
1650	N—H bending
1604, ~1581	Quadrant stretching of the benzene ring
1504	Semicircle stretching of <i>p</i> -disubstituted benzene
1454, 1384	C—H bending of aliphatic groups
1360	—OH bending (or C—H of aliphatic secondary alcohol)
1293	Twisting mode of —CH <sub>2</sub> — groups
1227	Stretching mode for aromatic ether
1178	C—C stretching of the bridge carbon atom between two <i>p</i> -phenylene groups
1034, 1029	Stretching of the <i>trans</i> forms of the ether linkage
824	<i>p</i> -Phenylene groups

after 1 month of immersion in water at 90°C followed by complete drying. For reasons of comparison, their difference obtained by digital subtraction is also shown in this figure. Table I gives our tentative assignment for the main absorption that appears in the spectrum for the unaged resin. The table indicates that the bands in the cured resin are readily assigned to specific functional groups, and changes in their intensities or positions can provide information on specific interactions involved during hygrothermal aging.

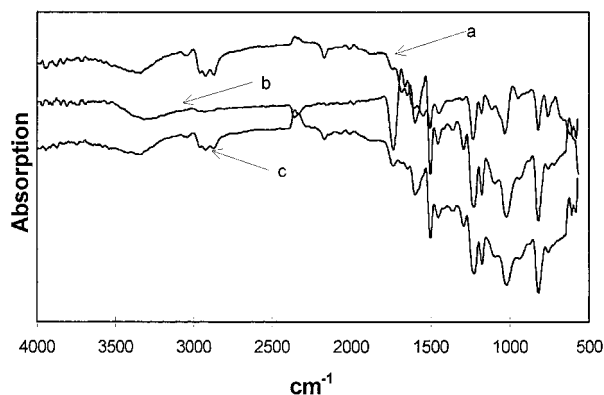
Apparently, aging irreversibly enhances the absorption at  $\sim 1736 \text{ cm}^{-1}$  and to a significant extent. This band can be assigned to carbonyl groups, as discussed in ref. 10. In addition, there is a decrease of the two bands associated to nitrogen-containing groups at 1681 and 1650  $\text{cm}^{-1}$ , with the disappearance of the 1681  $\text{cm}^{-1}$  band. Since there is no excess of the hardener, the effects can only be due to the modification of the main-chain structure.

From the difference spectrum, it can also be seen that the intensity of the absorption at 3342  $\text{cm}^{-1}$  is slightly increased after aging. As this absorption is due to O—H and N—H stretching and intermolecular hydrogen bonds, this suggests strongly that hygrothermal aging induces hydroxyl and amine groups into the epoxy chains.

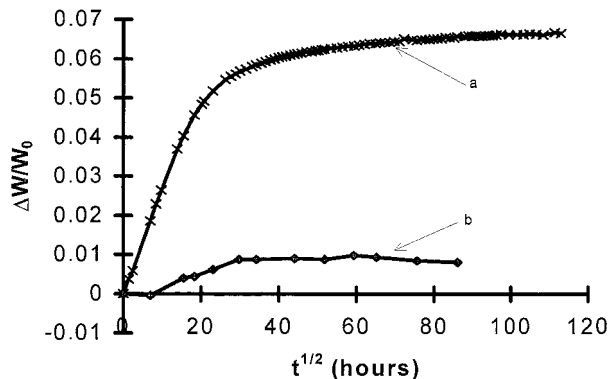
Some other changes of the spectrum due to aging can also be observed from the difference spectrum. The C—H stretching vibrations in the 3100–2800  $\text{cm}^{-1}$  region decrease slightly after aging. The absorption band related to nitrile

groups at 2168  $\text{cm}^{-1}$  also decreases. Hygrothermal aging at 50 and 70°C has similar irreversible effects on the FTIR spectrum of the DGEBA/DDA epoxy resin, as shown in Figure 2.

In previous work,<sup>10</sup> we found that DGEBA/DDA epoxy backbone chains can be cut during water immersion at 90°C, and then segments leach out. The leached substances contain the —NH—C≡N structure, —OH groups, and a higher proportion of C—N, N—H, and —C=O groups. In correlating these findings with the results shown above, we may conclude that hygrothermal aging at all three temperatures studied leads to the introduction of carbonyl groups in the resin and the loss of some nitrogen-containing



**Figure 2** Spectrum of DGEBA/DDA epoxy resin aged at different temperatures: (a) before aging; (b) 30 days in 50°C water then fully dried; (c) 30 days in 70°C water then fully dried.

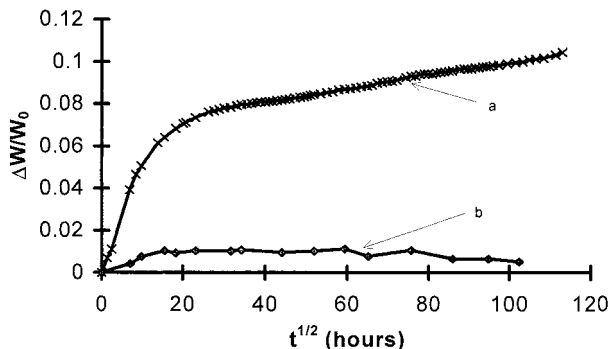


**Figure 3** Relative weight change of epoxy resin,  $\Delta W/W_0$ , versus square root of water immersion time,  $t^{1/2}$ , at 50°C: (a) before drying; (b) after drying.

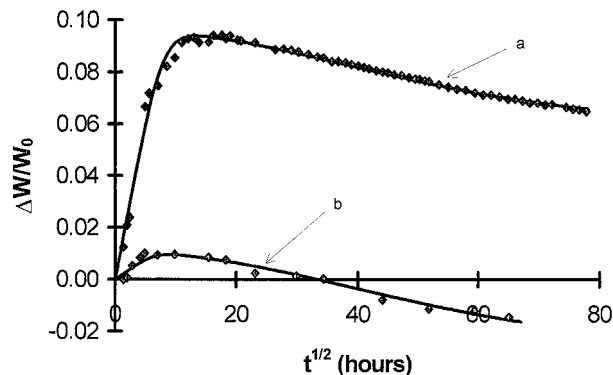
functional groups, accompanying the scission of some crosslinked chains. In the following, we study the effects of these irreversible structural changes on the behavior of water absorption and desorption as well as on the glass transition temperature of the resin.

#### Water Absorption and Desorption

Figure 3–5 show the absorption and the absorption/desorption curves for the DGEBA/DDA epoxy resin during hygrothermal aging, respectively, at 50, 70, and 90°C. For samples aged in 50 and 70°C water (see Figs. 3 and 4), as can be seen from the absorption curves, water uptake initially increases essentially linearly with the square root of aging time (although some very slight sigmoidal behavior<sup>11</sup> is present), then the absorption rate appears to decrease (on a  $t^{1/2}$  scale). Final saturation seems to be difficult to attain. These observations indicate that the final absorption stages are delicate to observe. Adamson<sup>12</sup> commented that this phenomenon may re-



**Figure 4** As for Figure 3, but aging at 70°C.

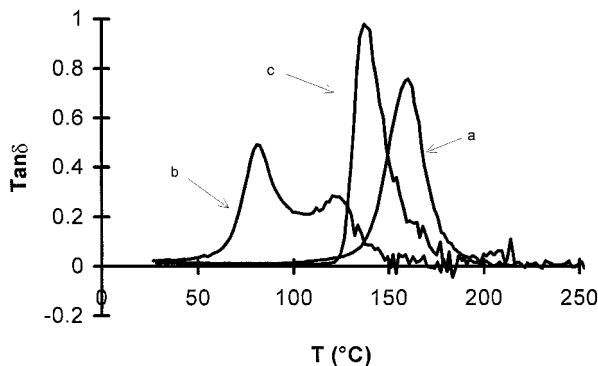


**Figure 5** As for Figure 3, but aging at 90°C.

flect the difficulty with which water enters the highly crosslinked microgel particles or micelles within the resin, while the two-phase model suggests that it is due to the reversible trapping of water by certain functional groups in the resin.<sup>13</sup> Interestingly, all the absorption/desorption curves show the following trend (this is particularly clear at 90°C): The residual weight change as a fraction of initial weight,  $W_0$ , tends to increase initially and then starts to decrease slowly. The overall behavior suggests irreversible trapping of water and degradation of the polymeric structure during hygrothermal aging.

For the case of aging at 90°C, as presented in Figure 5, the absorption curve shows that the resin also increases weight reasonably linearly with the square root of aging time initially, but starts to lose weight after attaining a maximum value, even though the observed absorption was not accompanied by any visible damage to the material except color change. From the absorption/desorption curve, it can also be clearly seen that the residual weight increases initially and that this is then followed by a reduction which leads eventually to a net weight loss. It is quite possible that this weight loss effect could also occur at the lower temperatures, but not in the time scale studied due to slower kinetics.

Since hygrothermal aging introduces oxygen-containing groups into the DGEBA/DDA epoxy resin and cuts the crosslinked chains, as discussed above and in the literature,<sup>14,15</sup> in qualitative terms, the absorption and absorption/desorption behavior in Figures 3–5 might suggest the following scenario: Initially, the polymer absorbs water, of which a fraction reacts chemically, causing the addition of oxygen-containing groups and chain scission. In the early stages, these reactions lead simply to the chemical addition of water



**Figure 6** Effect of hygrothermal aging on the  $\tan \delta$  versus  $T$  relationship of DGEBA/DDA epoxy resin: (a) before aging; (b) after aging in 90°C water for 15 days; (c) after aging in 90°C water for 15 days, then complete drying.

which will be unable to leave upon drying. A weight increase therefore follows, even after drying. However, after the number of chemical reaction sites has increased, the probability of a given intercrosslink chain being cut in two (or more) places increases, thus facilitating separation and subsequent leaching of the detached segments from the network. This leads to weight loss: slight in the case of absorption alone but consequent in the case of absorption followed by desorption. In addition, a temperature increase could facilitate the leaching of the scission products.

#### Aging Effects on Glass Transition Temperature

Bulk epoxy resin was aged in 50, 70, and 90°C water and then tested by DMTA to obtain the effects of aging on the glass transition temperature ( $T_g$ ). Figure 6 presents typical loss tangent,  $\tan \delta$ , versus temperature,  $T$ , curves for the DGEBA/DDA epoxy resin before and after hygrothermal aging. For the unaged sample, the dynamic glass transition, defined by the temperature,  $T_g$ , at which the principal maximum in the loss tangent,  $\tan \delta$ , occurs, is about 159°C. The glass transition extends over about 60°C.

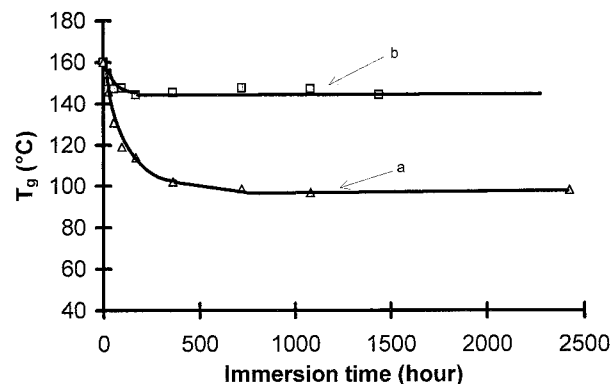
It can be seen that there is only one peak occurring in the test temperature range covered before aging. However, for the aged samples, a split and lowering of the  $\tan \delta$  peak are generally observed. This phenomenon has been noted previously.<sup>6,7,16–19</sup> The lower temperature peak is normally attributed to the “wet” part of the polymer, while the higher peak is somewhat controversial,

but is generally believed to be due to the drying of the sample during the test<sup>16</sup> and/or due to the dry part of the sample.<sup>6,7,16–19</sup> In our case, since small dimension samples were employed, both effects are expected. Here, we only consider the lower peak.

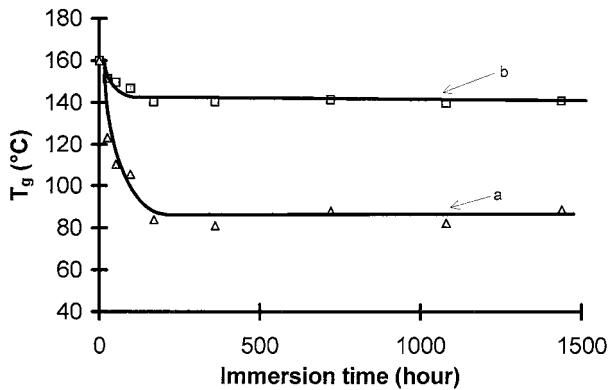
Interestingly, the  $\tan \delta$  versus  $T$  curve for the aged material does not recover its initial form, as before aging, after complete drying of the polymer. This can be seen in Figure 6. The results show that irreversible aging decreases the  $T_g$  of DGEBA/DDA by about 20°C. It is known that, in the epoxy resin, the glass transition temperature can be related to the crosslinked density.<sup>20,21</sup> With a decrease of crosslink density, the glass transition shifts to a lower temperature. Therefore, the DMTA results also confirm that chain scission occurs during hygrothermal aging.

Figure 7 shows the effect of aging time (in water at 50°C) on the glass transition temperature of the DGEBA/DDA epoxy resin before and after drying. The results show that water immersion induces both a partially reversible and partially irreversible decrease of  $T_g$ . Before drying, the  $T_g$  of DGEBA/DDA initially decreases with aging time, then approaches an asymptotic value of about 98°C. After fully drying, the change of  $T_g$  shows a similar trend, but with an asymptotic value about 144°C. Similar aging effects were observed at 70 and 90°C, as shown in Figures 8 and 9.

Table II summarizes the values of  $T_g$  after long-term aging. The results show that the  $T_g$  for both the wet and dry polymers decreases with increasing aging temperature. This result could be explained by the possibility that an in-



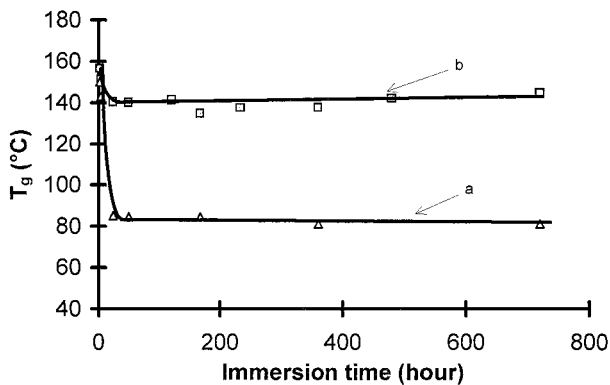
**Figure 7** Variation of  $T_g$  as a function of the water immersion time at 50°C: (a) before drying; (b) after drying.



**Figure 8** As for Figure 7, but aging at 70°C.

crease of aging temperature may well facilitate water diffusion into the resin and/or increase the likelihood of chemical reaction between water and the DGEBA/DDA epoxy resin.

Swelling tests were performed on DMTA samples in order to correlate the swelling of the polymer at the three temperatures, directly with the results of the  $T_g$ . The results are shown in Figure 10. Figure 10 shows the glass transition temperature (corresponding to the loss tangent maximum) versus the swelling of the polymer during water immersion. Both curves (corresponding to absorption and absorption/desorption) show the same trend: a decrease of  $T_g$  as swelling increases, followed by the approach of asymptotic values. These results suggest that the degree of swelling and  $T_g$  are directly related, since common curves are visible, irrespective of the temperature in question. This can be seen to be the case for aged and for aged and dried samples. This result may well indicate that the essential role of the temper-



**Figure 9** As for Figure 7, but aging at 90°C.

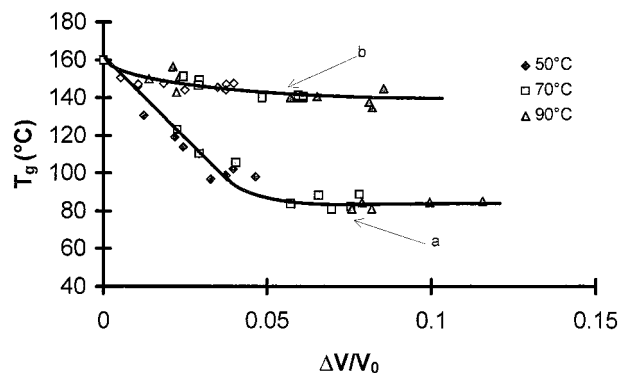
**Table II** Effect of Aging Temperature on the  $T_g$  of Water-saturated DGEBA/DDA Epoxy Resin

Aging Temperature (°C)	$T_g$ (°C)	
	Before Drying	After Drying
Before		158–160
50	~98	~144
70	~84	~141
90	~82	~140

ature increase is to accelerate the diffusion and swelling kinetics.

## CONCLUSIONS

1. FTIR studies have shown that hygrothermal aging at 50, 70, and 90°C induces irreversible changes in the molecular structure of DGEBA/DDA, with the introduction of carbonyl groups and chain scission.
2. These irreversible structural changes lead to the irreversible trapping of water in the polymer initially and weight loss of the resin eventually, as manifested by water absorption and desorption tests.
3. DMTA studies show that the glass transition temperature of DGEBA/DDA is (partially) irreversibly decreased after hygrothermal aging, hence, confirming the occurrence of chain scission. The experimental results also show that the decrease of  $T_g$  is swelling-dependent, the temperature increase only facili-



**Figure 10** Variation of  $T_g$  as a function of the swelling of resin during hygrothermal aging: (a) before drying; (b) after drying.

tating water diffusion and the swelling of the polymer.

The authors thank the French Ministry of Foreign Affairs and the Electricité de France (EDF), Centre des Renardières, for financial support and CECA S. A., France, for supplying the model resin. Use of the FTIR facilities at the EDF is gratefully acknowledged.

## REFERENCES

1. C. E. Browning, *Polym. Eng. Sci.*, **18**, 16 (1978).
2. E. L. MacKague, Jr., J. D. Reynolds, and J. E. Hal-kias, *J. Appl. Polym. Sci.*, **22**, 1643 (1978).
3. P. Moy and F. E. Karasz, *Polym. Eng. Sci.*, **20**, 315 (1980).
4. W. W. Wright, *Composites*, **12**, 201 (1981).
5. P. Peyser and W. D. Bascom, *J. Mater. Sci.*, **16**, 75 (1981).
6. C. Li, R. A. Dickie, and K. N. Morman, *Polym. Eng. Sci.*, **30**, 249 (1990).
7. B. De' Nève and M. E. R. Shanahan, *Polymer*, **34**, 5099 (1993).
8. M. P. Zanni-Deffarges and M. E. R. Shanahan, *Int. J. Adhes. Adhes.*, **15**, 137 (1995).
9. M. K. Antoon, J. L. Koenig, and T. Serafini, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1567 (1981).
10. G. Z. Xiao, M. Delamar, and M. E. R. Shanahan, *J. Appl. Polym. Sci.*, **65**, 449 (1997).
11. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, London, 1975.
12. M. J. Adamson, *J. Mater. Sci.*, **15**, 1736 (1980).
13. H. G. Carter and K. G. Kibler, *J. Comp. Mater.*, **12**, 118 (1978).
14. B. De' Nève and M. E. R. Shanahan, *J. Adhes.*, **49**, 165 (1995).
15. G. Z. Xiao and M. E. R. Shanahan, *J. Polym. Sci. Polym. Phys. Ed.*, **35**, 2659 (1997).
16. A. Chateauminois, B. Chabert, J. P. Soulier, and L. Vincent, *Polym. Comp.*, **16**, 288 (1995).
17. J. Mijovic and K. F. Lin, *J. Appl. Polym. Sci.*, **30**, 2527 (1985).
18. J. P. Soulier, R. Berruet, A. Chateauminois, B. Chabert, and R. Gauthier, *Polym. Commun.*, **29**, 243 (1988).
19. M. P. Zanni-Deffarges and M. E. R. Shanahan, *J. Adhes.*, **45**, 245 (1994).
20. L. Banks and B. Ellis, *Polymer*, **23**, 1466 (1982).
21. U. M. Vakil and G. C. Martin, *J. Appl. Polym. Sci.*, **46**, 2089 (1992).