Interfacial Diffusion in Layered Polyesters

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SYNOPSIS

Microscopic observations of cross sections of laminates of unsaturated polyesters revealed a birefringent zone (interphase) at the interface. Several observations associated with this interphase were made that predicted either beneficial or detrimental effects of the presence of the interphase in the laminate. A study was conducted to identify the origin and to characterize the properties of the interphase. It was proven that the interfacial diffusion of uncured liquid resin into the previously cured resin formed the interphase. The significant effect of the curing of the second layer on the thickness of the interphase was evident. The diffusion kinetics was dependent on the laminate preparation conditions. A correlation was developed that predicts the properties of the interphase based on crosslinking density of layer I and gel time of the resin of layer II. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In polymeric composite materials such as laminates and blends, the physical and chemical properties are strongly influenced by the structure of the interface (or interphase) region that is formed by the contact of different or similar polymers. The interdiffusion of molecules across an interface has been demonstrated as the main mechanism for the adhesion between polymeric layers.[1,2] It has been proven that the degree of interdiffusion and diffusion kinetics depend on the contact time, temperature, presence of solvent, and properties of the materials in contact.[1,3-5] The adhesion between different polymers can be best secured by the reinforcement of the interfacial region by an increase in the thickness of the interphase and intermolecular forces.[6-8] During the formation of the layered structure, there is a possibility of molecular orientation, swelling of the host polymer, and alterations in the surface crosslink density or compositional and morphological gradients near the interface.[9,10] When the adhesion between layers is attempted by initial application of solvent, the result can be plastisization of the interface causing a weaker bond.[9] In composite ma-

terials, zones of imperfect bonding and zones containing shrinkage stresses have been found in the interphase between matrix and reinforcing fiber, and the formation of the interphase involves a complex interplay of physical and chemical factors related to composite performance.[10-12] Considering the importance of the properties of the interphase it becomes necessary to gain knowledge of the interpolymer interactions.

Recently, we reported on a well-defined birefringent zone (interphase) located near the interface between two layers of unsaturated polyesters.[13] Earlier Birly et al.[14] also observed a similar boundary layer in polyester laminates formed from the same or different resins. The interphase was very thin and visible only under a microscope. Thickness of the interphase was different depending on the laminate preparation conditions. The index of refraction of the zone was different from the adjacent bulk material. The disk cracks that had formed upon supersaturation of the laminate with water did not propagate through the interphase; instead they were deflected at the interphase boundary. This phenomena indicated the possibility of the cracking delamination during the application. The delayed nucleation of cracks in the region surrounded by two birefringent interphases suggested the role of the interphase properties on the diffusion kinetics. Also stresses, such as bending or flexural, could be concentrated at the interphase and the magnitude

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higher than the material strength could lead to the failure. The polyester laminates often suffer poor interfacial bonding demanding the knowledge of the interfacial interactions.[15]

These observations warranted a study on the origin and the properties of the region. In this article we demonstrate that birefringent interphase is caused by the diffusion of the constituents of the freshly applied liquid layer II into previously partially or fully cured layer I. The events occurring during the growth of the interphase are discussed and the thickness of the interphase, that is diffusion distance, has been correlated with the characteristics of the crosslinked polyester network and process conditions.

EXPERIMENTAL

Materials

General purpose orthophthalic polyester resin was obtained from Aristech Chemical Co. (Pittsburgh, PA) and was used as received. The styrene content of the resin was 42%, and ethylene glycol was used to build the polyester that had equal parts of maleic and phthalic acid. Benzoyl peroxide (BPO, 40% as a paste, suspension in phthalate plasticizer, Cadox 40E, Akzo Chemicals Ltd., Chicago, IL) and n-n dimethyl aniline (Eastman Kodak Co., Rochester, NY) were used as an initiator and a promoter, respectively.

Methods

Polyester Resin Samples

A single sheet of polyester resin was cast between two glass plates. The plates were covered with Mylar® sheets, and spacers were put between glass plates to control the thickness of the casting. The resin was catalyzed with 2% BPO and 0.3% dimethyl aniline. The gel time ($L1$) of this resin for this catalyst composition was found to be 22 min. The casting was cured for a definite period of time (T). Subsequent curing of the sheet was prevented by putting the casting at low temperature. Three sheets were cast by using the same catalyst amount but cured for different times. The different curing times produced different crosslinking densities in the castings. In the following discussion these three sheets will be referred to as systems A, B, and C to represent curing time of 1, 5, and 24 h, respectively. Thus, system A has the lowest and system C has the highest degree of crosslinking.

Diffusion of Liquid Polyester Resin

For experiments, square samples of 1 × 1 in. were cut from the cast sheets of A, B, and C and each sample was immersed in liquid polyester resin in a separate bottle. The resin was not stirred during the experiment to duplicate the experimental conditions set for the catalyzed resin diffusion study. At definite time intervals one sample was removed; the resin sticking to the sample was wiped off and a thin cross section was cut from the middle of the sample. The section was observed under the microscope in plane and polarized light. The diffusion of the resin into the network produced a birefringence in the penetrated region and also a change in the index of refraction occurred in that zone. The thickness of the region was measured using an optical micrometer; and during the measurement, the section was immersed in refractive index oil (n = 1.51) to eliminate surface interference of defects caused by cutting. All the thickness results are reported in millimeters. The sharp boundary of the interphase was often visible in plain light, but thickness measurements were not always possible due to the presence of microcracks formed during the cutting of the thin section. No difference in the thickness was observed in either measurement technique.

Diffusion of Catalyzed Polyester Resin

To study the diffusion of catalyzed resin, the above described procedure was followed. However, the samples were immersed in liquid resin catalyzed by initiator and promoter. In this condition the resin remained liquid only until gelation and during this time the resin on the sample could be wiped off before sectioning and observation. After gelation it was converted to a crosslinked solid network, thus a layer II was formed on top of the layer I. Each layer I sample of systems A, B, and C was tested with catalyzed resin as layer II having three gel times ($L2$) of 10, 22, and 45 min. These different gel times were obtained by using BPO in 1, 2, and 3% levels, and the promoter content was kept constant to 0.3%.

Thickness of Interphase as a Function of Network Characteristics

To observe the changes in thickness of the interphase as a function of crosslinking density of layer I and the gel time of layer II, a layer II was cast onto a sample of layer I in a petri dish and covered by a Mylar sheet. The thickness of layer II varied from 20 to 40 mil. The sheets of layer I of different cross-

linking densities were produced by variations in gel times ($L1$) and curing times (T). The gel time of layer II is termed as $L2$. $L1$ and $L2$ were selected to be 10, 22, and 45 min. Curing times were chosen to be 0.5, 3, 10, and 24 h. The casting and curing were performed at room temperature. After 24 h of curing of both layers, a thin section of the two layers was cut by using a diamond saw (Isomet, Buehler Supplies) and the section was observed under the Leitz optical microscope in plain and polarized light.

RESULTS AND DISCUSSION

Diffusion Kinetics

Liquid Polyester Resin Diffusion

The diffusion of liquid polyester resin into the cured polyester network produced a birefringent zone in the penetrated region and thickness of the zone increased with longer exposure to liquid resin. In Figure 1, changes in the thickness of the interphase with time are shown for systems A, B, and C. The diffusion rate and mechanism were distinctly influenced by the degree of curing, that is degree of crosslinking of polyester. With the variations in the crosslinking of polyester samples, the diffusion mechanism shifted from case I to case II diffusion. These variations are demonstrated in Figure 1. When the sample was cured for 1 h (system A), the resin diffused into the sample following a rate law of thickness = $0.01303 [\text{time}]^{0.515}$. The diffusion of resin in samples cured for 5 h (system B) followed the rate law: thickness = $0.00104 [\text{time}]^{0.94}$. It has been proven that the penetrant diffusion into a crosslinked or a glassy polymer causes segmental changes associated with chain relaxation and swelling of the polymer. The restriction on the swelling imposed by adjacent dry regions induces stresses on the material that are manifested as birefringence, as we have observed here, in polarized light.[16-18]

The samples cured for 24 h (system C) showed a different diffusion behavior. Up to 45 min of exposure to liquid resin, no birefringence was observed in the cross section. However, samples with longer exposure showed a distinct birefringence and thickness of the front increased with more exposure. The maximum thickness of the penetration was 0.022 mm after 2 h of exposure to liquid resin.

This incubation time must have been caused by a different surface structure produced due to styrene loss from the sample during postcuring. This outward diffusion would produce a thin tensile layer of styrene depleted polymer on the surface.[19] Only
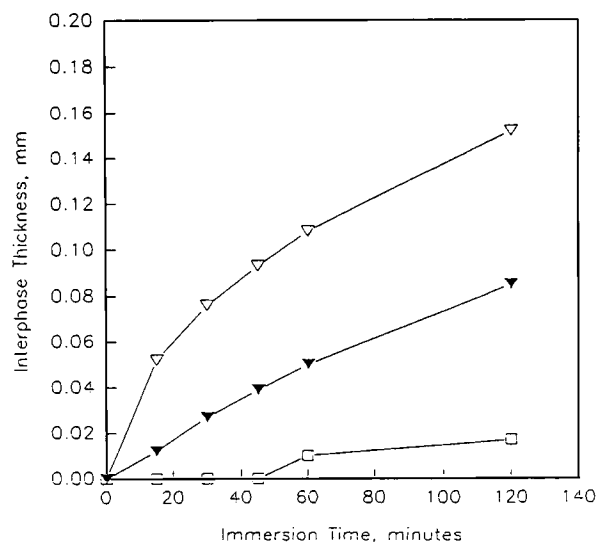

Figure 1 Interphase thickness of polyester samples cured for (▽) 1 h, (▼) 5 h, and (□) 24 h due to immersion in liquid resin.

when the styrene in that layer is replaced, could the compression (swelling) layer begin to form. This hypothesis concerning the incubation layer was tested using pure styrene liquid and a postcured polymer layer. The sample was immersed in the liquid, weighed over 15 min, and checked for diffusional birefringence. Immediately upon immersion, the sample gained weight but there was a lag time of 30 min before the compressional birefringent layer began to form. Initially, the birefringent front moved at a higher rate and then approached linear kinetics causing the anomalous diffusion mechanism.

Catalyzed Resin Diffusion

In practice, layered polyester structures are formed using catalyzed resin and there the diffusion kinetics is of practical importance.[20] Catalyzed resin is converted to a crosslinked network after the gelation of the resin. The gel time is fixed by the amount of the catalyst at the beginning of the crosslinking reaction. At the gel time, low molecular weight polyesters and styrene monomers are consumed in the formation of the network, and the diffusion of the unreacted monomers to the interface is impeded. The composition of penetrant at the surface of layer I is fixed by the partial pressure of the penetrant in layer II; but as gelling proceeds, the amount of free styrene decreases as it forms polystyrene crosslinks in the polyester. Hence the gel time of the liquid resin (layer II) is an important parameter that determines the time during which diffusion into layer I may occur. The change of interphase thickness with time

during immersion in catalyzed resin is shown in Figures 2 and 3. For comparison liquid resin diffusion in the similar layer I samples is also shown. The diffusion of the catalyzed resin also produced a birefringent zone similar to the one observed during the liquid resin diffusion.

The results for system A are presented in Figure 2. It is clear that catalyzed resin diffusion follows a rate law identical to liquid resin diffusion early in the experiment. However, the diffusion thickness growth is limited due to the solidification of layer II after the gel times of 22 and 10 min, respectively. For higher gelation time, a higher thickness of the diffusion zone was observed.

Jump in Thickness at Gelation

Upon gelation of the second layer, an increase in the thickness of the interphase was observed. This observation is clearly apparent in the samples for 24 h (Fig. 3). No birefringent front zone appeared in the sample when exposed to liquid resin until after the incubation period of 45 min. When the resin of layer II cured after 45 min, the sudden appearance of a birefringence zone (0.018-mm thickness) was observed. A similar appearance was also noted when catalyzed resin gelled in 22 and 10 min. Thus, these cases represent the appearance of the interphase only after the gelation. Shrinkage is associated with the curing of the resin in layer II. This shrinkage can produce a compression on the surface of layer
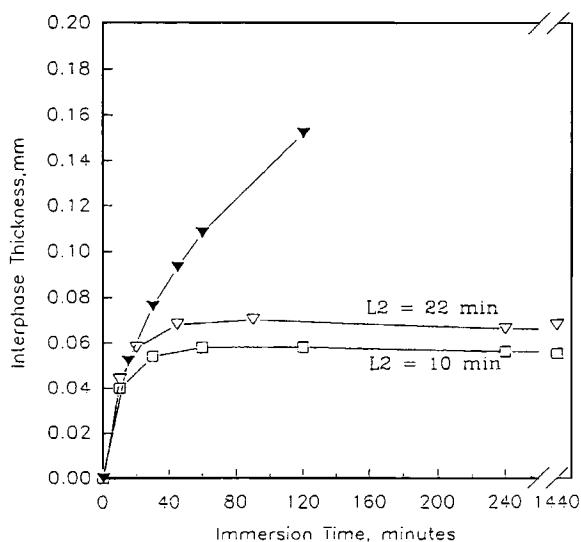

Figure 2 Interphase thickness with time of immersion in (▽, □) catalyzed resin and (▼) liquid resin. Layer I samples were cured with gel time ($L1$) of 22 min and curing time (T) of 1 h. The gel times of the catalyzed resin were set to 22 and 10 min.
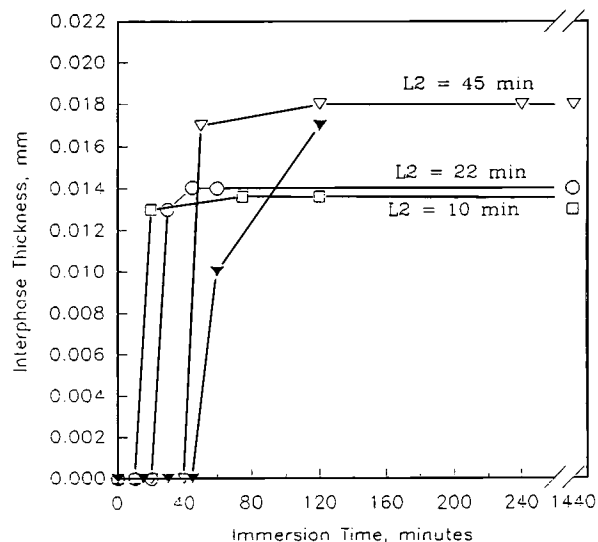

Figure 3 Interphase thickness with time of immersion in (○, ▽, □) catalyzed resin and (▼) liquid resin. Layer I samples were cured with gel time ($L1$) of 22 min and curing time (T) of 24 h. The gel times of the catalyzed resin were set to 45, 22, and 10 min.

I. If a diffusional compression is just beginning to form in layer I, it can be enhanced by the cure shrinkage.

Evidence of Polymerization in Interphase

An alternative explanation is that the curing of the components in the diffusional layer takes place. As layer I gels, free radicals at the interface promote the polymerization of styrene absorbed into the interphase. Finally, a combination of both mechanisms could result in the enhanced thickness of the diffusion layer when layer II cures. Under this scenario, as layer II cures, the shrinkage further stresses the diffusional layer. The penetrant styrene then forms polystyrene links that add stress and lock in those produced by the curing of layer II. This later scheme explains the persistence of the stress in layer I even after layer II is stripped from it after complete solidification of both layers. The analysis of the birefringence in the interphase will be discussed in detail in our subsequent article.

Interphase Thickness and Network Characteristics

It was shown earlier that the interphase thickness depends mainly on the degree of crosslinking of the polyester network (layer I) and the gel time of the freshly applied liquid resin (layer II). A definite increase in the thickness after the gelation of layer II was also observed (Fig. 4). The diffusion mechanism
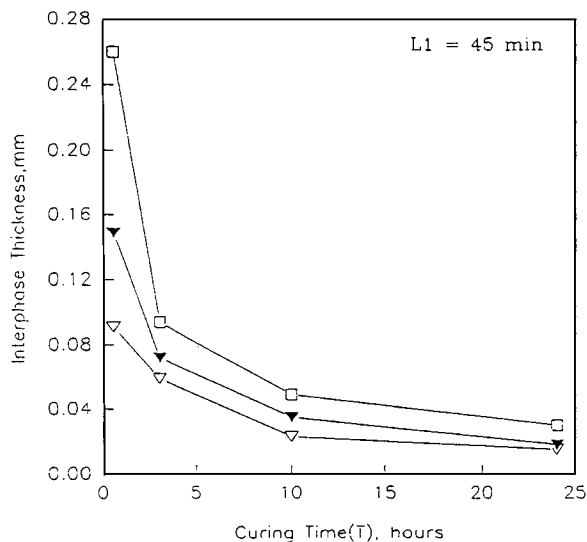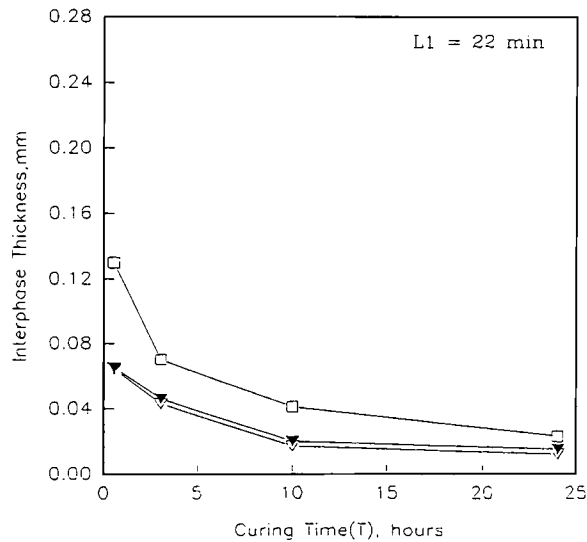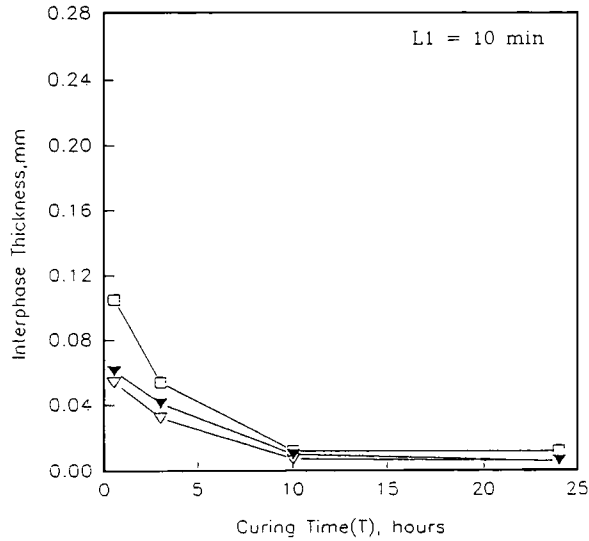
was also dependent on the crosslinking density of layer I. To predict the interphase thickness, a correlation is necessary that can satisfactorily reflect all the effects behind the development of the interphase. Hence, the interphase thickness was measured for different network characteristics of layer I and layer II. The different degrees of crosslinking obtained were changed by variations in the gel and postcuring times ($L1$ and T).

In Figures 4(a–c) the thickness of the interphase formed at various degrees of curing of layer I is illustrated, for gel times of layer II of 10, 22, and 45 min, respectively. It indicates that for a fixed gel time of layer II, the thickness of the interphase decreases with increasing curing of layer I. The thickness reduces significantly within a few hours of curing of layer I and it remains more or less constant with further curing of layer I, regardless of gel time of layer II.

Experimental Correlation and Prediction of Interphase Thickness

All the experimental results have indicated that the thickness of the interphase was higher for the longer gel time of layer I ($L1$), but the magnitude decreases with increasing postcure time (T). When the gel time of the layer II ($L2$) is longer the thickness is also higher. Hence the thickness of the interphase was analyzed as a function of $L1 * L2/T$. The results are illustrated in Figure 5. The curve drawn through the data is a best fit to a logarithmic equation. The equation for this curve is

$$\text{Thickness} = 0.0274 \left[\frac{L1}{T} * L2 \right]^{0.5} \qquad (1)$$

where $L1$, T, and $L2$ have units of time in minutes and thickness is in millimeters. The data for ($L1 * L2/T$) values of less than 40 were used to generate the best fit curve shown in Figure 5. An extension of the curve to a value of 70 predicts an interphase thickness of 0.23 mm. To achieve such a value takes an experiment in which $L1$ and $L2$ are at their maximum of about 50 min for each variable and T is a minimum. That value is approximately 30 min because lower values lead to Fickian diffusion and a diffusion front no longer existed. After several

Figure 4   Thickness of the interphase, as a function of the curing time of layer I, when layer II was cast. The gel times of layer I were: (a) 10 min, (b) 22 min, and (c) 45 min. The gel times of the layer II were: (∇) 45 min, ($\blacktriangledown$) 22 min, and ($\square$) 10 min.
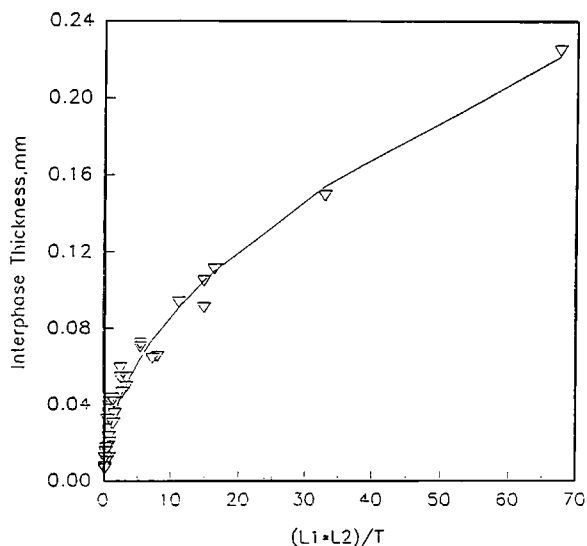
Figure 5   Analysis of the thickness of the interphase as a function of $(L1*L2/T)$. The solid line depicts the curve fit representing eq. (1).

attempts, experimental data were obtained, and as indicated by the data point in Figure 5, the model prediction is excellent. The residual standard deviation is 0.0074.

Significance of Eq. (1)

$L1$ and T in eq. (1) define the degree of crosslinking. Higher values of $L1$ over T are obtained for samples with lower crosslinking density. The knowledge of the exact relationship of the gel time $(L1)$ and curing time (T) to crosslinking density would allow the above equation to be written to directly reflect the effect of the degree of crosslinking of layer I on the thickness.

CONCLUSIONS

The diffusion of catalyzed liquid polyester resin into a previously cast polyester layer forms the birefringent interphase at the interface. The birefringence is produced due to the swelling stresses generated during diffusion. The diffusion mechanism depends on the degree of crosslinking of layer I that is defined by the gel time and curing time. The thickness of the interphase is dependent on both the degree of crosslinking of layer I and the gel time of layer II. At gelation of the liquid resin of layer II a crosslinked network forms that should stop subsequent diffusion of the resin. However, a certain jump in the thick-

ness of the interphase occurs upon gelation, indicating the effect of curing. The effect of curing is clearly evident when there was no noticeable diffusion and birefringence before the gelation of the resin and only upon gelation a birefringent interphase of certain thickness formed. This observation predicted the changes in the magnitude of birefringence in the interphase due to additional curing or shrinkage stresses. The thickness of the interphase can be predicted based on the correlation developed during this study.

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