A Diffusional Interphase in Layered Polyesters

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SYNOPSIS

The properties of the birefringent interphase in the laminates of unsaturated polyester resin were characterized using polarized microscopy and a birefringence compensation technique. The thickness of the interphase was found to depend on the casting conditions, and values ranging from 0.004 to 0.25 mm were observed. The location and dependence of the thickness on the curing conditions suggested that the interphase formed due to the diffusion of constituents from the liquid resin of the second layer into the previously cured layer. The index of refraction of the interphase was higher than that of the polyester above and below it. There was a sharp front marking a boundary of the interphase from the rest of the resin. These observations indicated characteristics of non-Fickian interfacial diffusion. Qualitative estimation of the birefringence in the interphase by interference colors indicated the first-order optical retardation. The birefringence was hypothesized to be due to residual stresses resulting from the fabrication procedure. The birefringence was quantified using a Berek compensator to measure the stresses. The approximate stress values were found to be in the range of 10–40 MPa. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

An interphase between two layers or phases is a region of finite thickness having properties different from the bulk properties of the surrounding regions. It plays an important role in the performance of layered or multiphase materials. The interphase between two thermoplastic materials forms due to the interpenetration of the molecules across an interface, when brought in contact above their glass transition temperature.[1] In fiber-reinforced composites, the physical or chemical interactions between fibers and a polymer matrix lead to the development of an interphase region on the matrix side.[2] While numerous studies have been performed on the interphase in thermoplastic polymers or fiber-reinforced composites, the interphase formation in layered thermosetting polymers has not received much attention.

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Thermosetting polymers, especially unsaturated polyester resins, are widely used as matrix materials in polymer composites and large parts are fabricated by lay up techniques. The examples include composite boats, automobile parts, showers, and hot tubs.[3] Thermosets are also used in the manufacture of multichip modules of integrated circuits using a spin-coating procedure.[4] The key characteristic of these fabrication techniques is that the part is built in layers and the time delay in casting two successive layers could vary based on the production cycle. There are several events that may occur at the interface: The interfacial bonding develops upon formation of chemical linkages between the previous layer and the newly applied layer.[5] The loss or polymerization of the monomer at the surface of the previous layer could occur, often leading to poor interfacial adhesion.[6] The constituents of the liquid resin of the fresh layer, before curing, could diffuse into the network of the partially or fully cured previous layer. This event may alter the interfacial properties. The birefringence in the interphase may indicate residual stresses that could become additive to the external stresses and degrade the laminate property.[7] Thus, the knowledge of the interfacial interactions is important to optimize the macroscopic properties of the layered structures targeted for specific applications.

Recently, two research groups have reported on their observations of a birefringent zone in resin-rich regions of fiber-reinforced polyester and between layers of polyesters.[8,9] However, the origin and the properties of this layer were not conclusively understood. We have conducted a study to determine the origin of the interphase, to characterize the properties of the interphase, and to define its role in the performance of the layered structure. Thickness and stress were two macroscopic properties chosen to be quantified. In this article, we report the key features of the interphase, suggesting the importance of the interphase. Subsequent articles will define the growth kinetics of the interphase and will analyze the evolution of stresses during the interphase formation.

MATERIALS AND METHODS

Laminate Fabrication Procedure

General purpose orthophthalic polyester resin (Aristech Chemical Corp., Pittsburgh, PA) was used to fabricate the layered structure. Fixed amounts of benzoyl peroxide (Cadox 40E, Akzo Chemical, Chicago, IL) and *n*-*n*-dimethylaniline (Eastman Kodak, Rochester, NY) were added to the resin as a catalyst package to cure the liquid resin. The curing was performed between two glass plates covered by mylar sheets and separated by spacers of the thickness desired for the layer. Then, after a fixed time of curing, another layer was cast on the previously cast first layer. Following this procedure, several two-layer sheets were prepared for various gelation times and time delay in casting two layers. The degree of crosslinking of the casting was not measured. However, the conditions of the gel time of the resin and the curing time after gelation are reported and variations in their values represent different degrees of crosslinking in the polyester casting.

Microscopic Observations

Thin cross sections of the layered sample were cut and observed under the Leitz optical microscope in plane and polarized light. The thin section was immersed in an index of refraction oil ($n = 1.51$) during observation, and the interphase was examined for thickness, birefringence, and differences in the index of refraction. The thickness measurement for the samples was made using an optical micrometer. Other distinct features developed around the interphase were also examined.

Birefringence Analysis

The order of birefringence in the interphase was qualitatively estimated based on the interference colors produced in the thin section when viewed in polarized light.[10] The magnitude of the birefringence was measured using a compensation technique and Berek compensator. In this technique, a compensator crystal of known birefringence is placed in the light path in such way that when rotated it produces the phase difference opposite to the phase difference produced by the stresses present in the thin section. Hence, all birefringence can be canceled by the manipulation of the axis of rotation of the crystal. By measuring the angle of rotation needed to produce the null condition, the strength of the birefringence produced by the stress can be measured. We used the Berek compensator with a calcite crystal which can measure birefringence up to 4 orders. More details about this technique and measurement procedures can be obtained from the literature.[11,12]

RESULTS AND DISCUSSION

Examples of Birefringent Interphase

The presence of the birefringent interphase in the fiber-reinforced polyester boat hulls, constructed by lay up techniques, is illustrated in Figure 1. The layer is distinctly visible in plane light as shown in Figure 1(a) and becomes even more dramatically visible in polarized light as seen in Figure 1(b). Two strongly birefringent and distinct interphases were observed when a three-layer polyester structure was fabricated using a lay up technique, as shown in Figure 2. The location of the interphase was determined by careful peeling of the two-layer structure, and it was observed that the interphase forms at the interface between layers but it is completely within the layer that was cast first. There was no difference in thickness or birefringence of the interphase before and after peeling.

Significance of Birefringence

Castings of unsaturated polyesters have a randomly oriented crosslinked network.[13] The loss of monomer during curing could produce a surface inhibition layer with oriented surface molecules causing birefringence. However, cross sections of single-cast sheets of the polyester resins showed only negligible birefringence which is due to shrinkage stresses induced during curing. The interphase illustrated in Figure 2 is highly birefringent and must be produced only by the stresses resulting from the fabrication procedure. Two causes were hypothesized: Either the restricted swelling of the first layer during absorption of the liquid resin constituents of an added wet layer to induced swelling stresses or due to the curing of the second layer on top of the first layer, curing shrinkage stresses were transmitted in the interphase.

Thickness of the Interphase

Casting of a single-layer polyester sample did not show the presence of a birefringent zone. However, the immersion of a single-layer polyester in a liquid resin produced similar birefringence in the sample and the thickness of the birefringent zone increased with immersion time. The observations confirmed that the interphase formed due to the diffusion of the liquid resin of layer II into the solid polyester (layer I) and birefringence was generated partly by swelling stresses until the liquid resin cured and diffusion stopped.

The cross sections of various two-layer polyester samples cast under different conditions are shown in Figure 3. Figure 3(a) illustrates a case where the interphase is not birefringent and the examples in Figure 3(b) and (c) have interphases of different thickness. Thus, experiments under various casting conditions produced interphases of the thickness in the range of 0.004–0.25 mm. Observations of interfacial diffusion between the layers have been reported for a variety of systems.[14,15] The diffusion of the crosslinking agent from the liquid epoxy resin into the epoxy network was observed by Sporer and Robertson[14] during their study on the bonding between thermally aged epoxies. Brown et al.[15] investigated the diffusion of polyamic acid into the partially or fully imidized polyimide (layer I) and discovered the strong dependence of the diffusion of polyamic acid into the polyimide on the degree of curing of layer I. Similarly, in our case, conditions of lower crosslinking of layer I and slower curing of layer II increased the thickness of the interphase, and the thickness was independent of the thickness of the first or second layer.

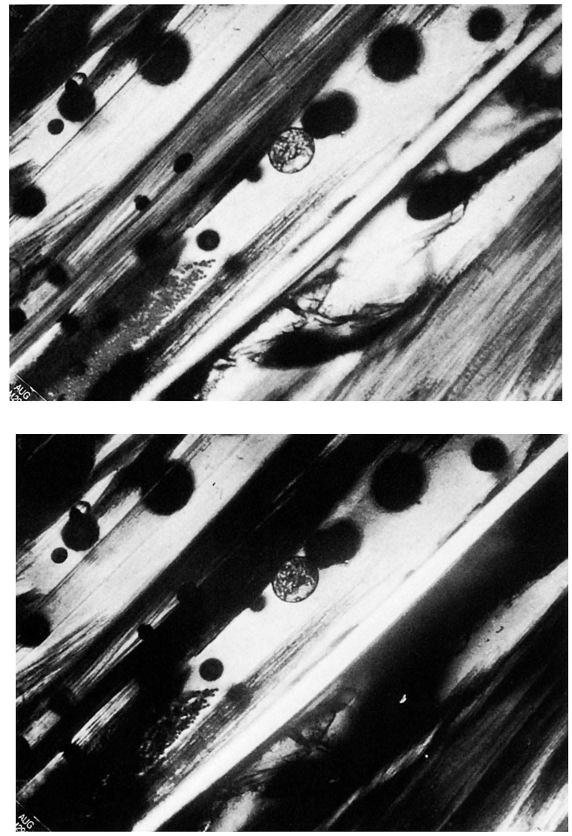

(a)
(b)

Figure 1 The birefringent interphase in a boat hull section observed in (a) plane light and (b) polarized light. Magnification: 35×.

The index of refraction of the interphase was higher than that of the polyester above and the below, thus proving that it has a different chemical composition than that of the surrounding polyester. In most samples, there was a sharp front between the interphase and the remaining part of the resin, marking a boundary of the interphase. This behavior represents characteristics of Case II or non-Fickian-type diffusion mechanism, and it was observed for the higher crosslinking density of layer I. Conversely, in a few samples, a sharp boundary was not observed in plane light, and the condition appeared when the interfacial diffusion occurred in a lightly crosslinked layer I. Thus, two key parameters, degree of crosslinking of polyester layer I and the time for which the second layer remains liquid, should determine the interphase growth kinetics, diffusion mechanism, and ultimate thickness of the interphase. More analysis of the interphase development and an experimental correlation predicting the thickness of the interphase are discussed in detail separately.[16]

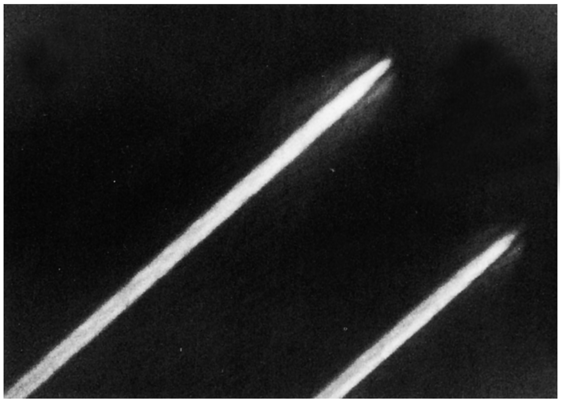


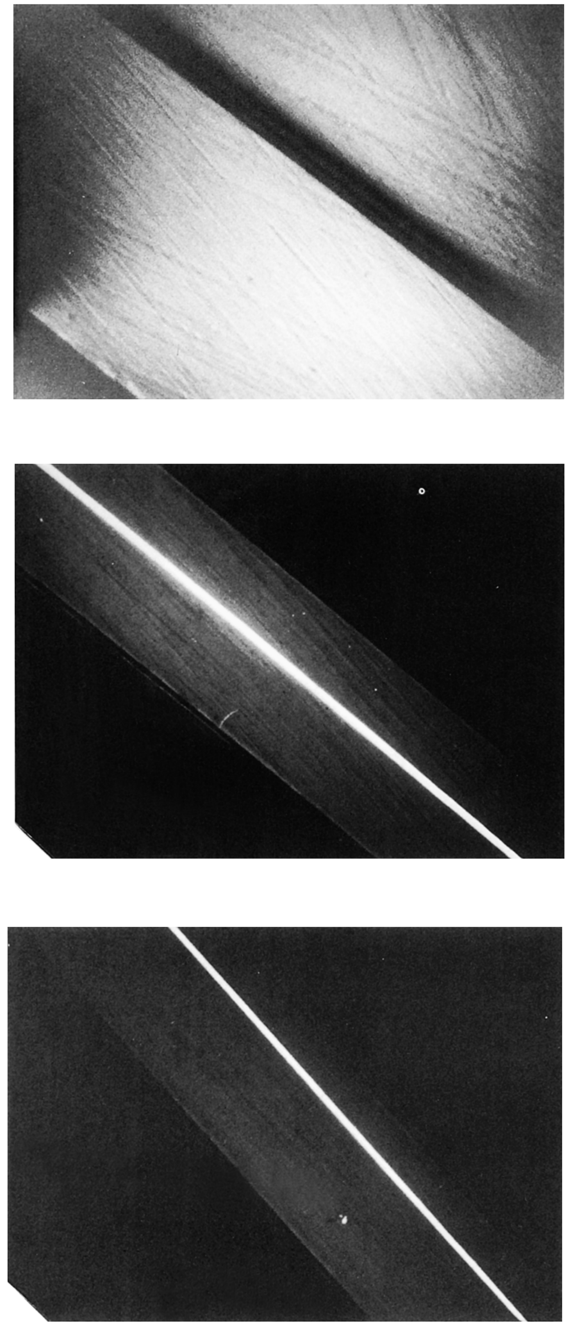
Figure 2 Birefringent interphases in a three-layer specimen. Magnification: 35×.

Case II transport is a specific type of anomalous transport, first defined by Alfrey et al.[17] Among numerous studies on this diffusion mechanism, the theory proposed by Thomas and Windle elucidates the most characteristics of Case II diffusion.[18] This type of diffusion behavior is relaxation-controlled, and segmental changes associated with chain relaxation develop significant stresses in the swelling polymer. These stresses have been observed by polarized light microscopy and quantified by birefringence measurement.[19,20]

Thomas and Windle observed birefringence in partially swollen samples and proved that the mechanical conditions lead to compressive stresses in the swollen gel.[19] They measured the birefringence profile across the swollen layer and found a sharp decrease in the values behind the front. In earlier studies, Gurney[20] and Robinson[21] also observed a similar decrease behind the front to a nonzero value. In our system, the added second layer remains liquid only up to the gel time, thus limiting the diffusion time, and it ultimately cures to a crosslinked network on top of the first layer.

Birefringence in the Interphase

The birefringence developed before gelation of the resin indicated swelling stresses. The fast vibration direction of birefringence was parallel to the interface and the slow direction was perpendicular to the interface. Thus, the index of refraction was low parallel to the interface. Using the Berek compensator and the knowledge of mechanical conditions of samples during diffusion, the compressive stresses in the interphase were confirmed. On both sides of the interphase, the compensation direction changed, indicating a stress of the opposite sign (tensile) to that of the interphase. Curing of the second layer on top of the first layer did not change the vibration directions, but showed dramatic changes in the magnitude of birefringence. From these observa-



(a)

(b)

(c)

Figure 3 Illustration of the difference in interphases, resulting under different casting conditions of two layers. In (a), the interphase show no birefringence but a thick black zone, while in (b) and (c), the birefringent interphase has different thickness. Magnification: 35×.

tions, it was concluded that both swelling stresses and curing stresses produce birefringence in the interphase. The example of the nonbirefringent interphase represents a condition for which significant diffusion occurred, but the stresses were not sustained due to a very low degree of crosslinking.

In polarized light, the birefringence in the interphase produced interference colors corresponding to the first order (optical retardation values less than 550 nm). Using the Berek compensator, the birefringence in the interphase of various samples was measured. For example, interphases in Figure 3(b) and (c) yielded values ranging from 40×10^{-5} to 100×10^{-5}. Birley et al.[9] obtained the birefringence of 53.6×10^{-5} when the interphase was developed due to a 2 h delay in casting. These values of birefringence are one order of magnitude higher than those observed in the single-layer casting of different polyester resins.[9] As the stress optical coefficient of the material in the interphase was not known, it was not possible to calculate accurate values for the stress. The values of stress optical coefficients for stretched sheets of polyester resin have been observed to be in the range of $2.2\text{–}3.5 \times 10^{-11}$ Pa^{-1}. Using this range of values and the stress-optics law, the calculations of principal stresses yielded the range of 10–40 Mpa.

This range is of the same order of magnitude as the residual stresses generated at the interface between reinforcement and the matrix.[22,23] The analysis of the birefringence during the growth of the interphase is presented elsewhere.[24]

CONCLUSIONS

During casting of two successive layers of the polyester resin, a birefringent interphase develops due to the diffusion of the constituents of the liquid resin into the partially or fully cured previously cast resin layer. The ultimate thickness is strongly dependent on the curing conditions. It is not affected by the thickness of the two layers. The index of refraction difference between the interphase and the rest of the resin is produced by diffusion and the resulting changes in composition. The birefringence in the interphase is first order and it is generated by a combination of swelling and polymerization shrinkage stresses.

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