## Microscopy of the Morphology in Low Styrene Emission Glass Fiber/Unsaturated Polyester Laminates

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ABSTRACT: Low styrene emission (LSE) unsaturated polyester resins are of interest in the context of increasing environmental concerns in the society. LSE resins have been developed to decrease styrene emission during the processing of composites based on unsaturated polyesters. In this article we applied a microscopy methodology to study morphology effects in laminates based on LSE polyesters. The study connects to the longer term objective to improve the understanding of how additives reduce styrene emission without imparting delamination resistance in composite laminates based on LSE polyesters. The major morphology differences between laminates made from different polyesters are discussed, including birefringent layers present as an interphase between different layers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1555–1562, 1999

**Key words:** microscopy; morphology; low styrene emission unsaturated polyester; glass fiber laminates

## **INTRODUCITON**

Unsaturated polyesters (UPE) resins are widely used as matrix materials in polymer composites. They are composed of an unsaturated polyester prepolymer, which is dissolved in styrene. Because the molecular weight of the prepolymers typically are in the range of 2000–5000 g/mol, the resin would be solid at room temperature if no styrene was present. The resin is transformed into a rigid, three-dimensional molecular network by a free radical polymerization of the styrene molecules with the double bonds in the unsaturated polyester prepolymer. Sufficient stiffness, strength, and toughness is obtained by the use of glass fiber reinforcement, and the final composite will exhibit a broad range of mechanical, chemical, thermal, and physical properties, depending on the constituents.  $^{1} \ \ \,$ 

Recent legislation has put pressure on the manufacturers of UPE resins to reduce the styrene emissions during manufacturing.<sup>2,3</sup> Although other reactive solvents, such as *p*-methylstyrene, vinyltoluene, or methyl methacrylate may be used instead of styrene,<sup>4</sup> this has not yet met with any commercial success due to increased price, limited availability, and largely unknown toxicological effects in industrial processing situations. If the styrene content is lowered to reduce styrene emission, the molecular weight of the polyester prepolymer must be reduced to maintain a sufficiently low viscosity of the liquid polymer mixture. This apparently leads to increased moisture absorption and inferior mechanical properties of the composite.<sup>5</sup>

A successful route to reduced styrene emission during hand lay-up has been the introduction of low styrene emission (LSE) polyesters.<sup>6–10</sup> In

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these resins, a wax or paraffin type additive is introduced that reduces styrene emission through the formation of a film layer at the top of the laminate. Wax mixtures, polybutyl acrylate<sup>11</sup> and paraffin wax combined with an attachment promoter such as linseed oil or dipentene<sup>9</sup> have been used. Typical amounts of wax added to the polyester have been in the range 0.1 to 2 wt %.

A problem often discussed is the increased risk of delamination with LSE polyesters. In standard polyesters this can occur if the laminate is left with an excess of resin on the surface for a long time, for example, over the weekend during a processing cycle. Delamination can also occur if the surface is contaminated with dust, or if the curing reaction proceeds too rapidly.<sup>12</sup> Air inhibition of the crosslinking reaction reduces the risk for delamination. As styrene evaporates from the laminate surface, the remaining polyester becomes undercured due to the inhibiting effect of oxygen on the crosslinking reaction. This creates a rubbery, tacky surface, to which the next laminate layer attaches efficiently with decreased delamination risk.<sup>13</sup> In LSE polyesters, where wax additives are used, no air inhibition occurs, and a hard, fully cured surface results. This may lead to lowered interlaminar adhesion, increasing the risk for delamination. This is one of the reasons why LSE resins were not so popular when they were introduced. This problem may be addressed by the use of adhesion promotors or bonding agents that have been developed by several producers. These compounds increase interlaminar adhesion while maintaining the decreased styrene emission.14

Shah and Rockett1<sup>13,15,16</sup> have discussed causes for delamination. According to them, styrene diffuses into the surface layer leading to polystyrene formation. This will prevent good interlaminar adhesion according to this hypothesis. As a second layer of polyester is added to an existing layer, a birefringent zone was observed to develop. It was suggested that the diffusion of styrene and polyester into the undercured surface of the first layer caused swelling stresses leading to the birefringence phenomenon observed as a thin specimen is viewed in polarized light. For an air-inhibited polyester, the thickness of this layer is in practice independent of the time before the second layer is applied. For a layer that is not air inhibited, the thickness of the birefringent layer decreases with increased waiting time.

The objective of the present study is to apply a microscopy methodology to study morphology ef-

fects in laminates based on LSE polyesters. Cross-sections of laminates are studied in transmitted polarized light. The study connects to the longer term objective to improve the understanding of how wax additives reduce styrene emission without imparting delamination resistance in composite laminates based on LSE polyesters.

## **EXPERIMENTAL**

## **Materials**

Three general-purpose orthophthalic polyesters from Neste Polyester were used without removal of the added inhibitors. The resin types included a standard non-LSE resin (I), an LSE resin (II), and a LSE resin (III) with higher crosslinking reactivity. The LSE resins contained a crystalline paraffine wax. The curing was done by adding 1.5 or 3 wt % of Butanox M50 (methyl ethyl ketone peroxide) from Akzo-Nobel. Scandinavian Glass Fibers MK12 glass mats (450 g/m<sup>2</sup>) were used as reinforcement.

### **Laminate Preparation**

Laminates of the size  $200 \times 300$  mm containing 30 wt % glass mats were prepared from each polyester. The lamination was done in two layers, simulating an actual laminating procedure. Three glass fiber mats were laminated in the first layer and cured for 2 h. An excess of resin was then poured over the surface and carefully distributed to form a film of approximately  $400-\mu m$ thickness. This was done to enhance the delamination effect. The second layer, consisting of three glass mats was laminated after a 72 h or 240 h delay, simulating an over-weekend or longer delay in lamination of a large structure such as a boat hull. The laminates were postcured for 24 h at 50°C before cutting into smaller specimens. Some of the laminates were also wedge opened in order to inspect the opened laminate surface for delamination.

#### **Microscopy Observations**

Cross-sections of the laminates were prepared by first cutting approximately 2 to 5 mm-thick sections. These were further cut to 0.2 mm thickness by using an Accutom diamond saw. Water was used as coolant, and the specimen was cut at 0.2 mm/min speed. The rotational speed of the saw was 400 rpm. The thin sections were finally polished to a thickness of 0.1 to 0.15 mm by standard metallographic procedures and SiC sandpaper.

To demonstrate the wax diffusion to the cured polyester surface, 60 mm-diameter specimens were casted out of neat polyester resin **II**. The thickness of the casting was 5 mm. The castings were cured in the same way as the laminates.

The specimens were studied under crossed polarizers with a Zeiss optical microscope. Some of the specimens were also studied by scanning electron microscopy (SEM).

## RESULTS

The cutting procedure with the Accutom was comparably straightforward, although some operator skills were required to obtain thicknesses as thin as 50–100  $\mu$ m. Key issues were straight-edged specimens and some experience in specimen fixation. Thin sections are advantageous, because transmitted light is used. No polishing procedure was required. Polarized light was used and the lower polarizator was rotated 45° with respect to the starting position for best results. This corresponds to a 90° difference in pass axes orientation between upper and lower polarizer. It was noted that sometimes an extra 45° sample rotation was necessary so that the birefringent layers would be observable. This is because of variations in specimen thickness. The key is how the specimen thickness is related to the half-wave thickness of the particular colors in white light, which give the desirable optical effect.<sup>17</sup> The specimen can then turn the axis of the linearly polarized light through 90° if the incident light makes an angle of 45° with the optical axis of the specimen. The light beam emerging from the specimen is then vibrating in the right direction to pass through the second polarizer. Birefringent layers and the wax particles can then be observed.

# Surface Characterization of Neat Polyester Castings

The reduction of styrene emission by wax additives is mainly explained as a film formation of the additive on the cured polyester surface. This is demonstrated in Figure 1, where a surface micrograph in reflected light is presented for a casting from neat polyester **II**. A large part of the surface seems to be covered by wax. The wax is present as larger particles connected by finger- or string-like entities. Between these wax strings



**Figure 1** Optical micrograph of the surface of neat casted polyester II. The wax covers approximately 50% of the surface as finger-like entities (reflected light, marker length 200  $\mu$ m).

and larger wax particles, the resin appears to be directly exposed to air. As the nonpolar wax is not completely soluble in the polar polyester, the wax will initially diffuse to the surface and form a film. As curing proceeds, the wax solubility in the resin decreases further. The wax forms particles and in this process, the string-like entities observed on the surface are created. Wax melting due to the exothermic heat from the crosslinking reaction may also be of large importance as the surface morphology is formed. Poor interlaminar toughness may then result if the resin applied in the next lamination step is unable to bond to the wax-covered surface. Although the wax covers the polyester surface to a large extent, wax additives cannot effectively prevent styrene emission in a real lamination operation. This is due to the fact that a lamination operation involves heavy rolling of the surface, which will break the covered surface. Styrene will thus evaporate through the rolled surface, and the decrease in styrene emission will not be as large as one could expect from the morphology in Figure 1.

# Laminates Containing No Wax Additive (Polyester I)

A micrograph of the cross-section of a laminate based on the conventional non-LSE polyester I with no wax additive is presented in Figure 2. The laminate was cured with 3 wt % Butanox M50, with a 10-day waiting period between the lamination of the layers. Fiber bundles are apparent as dark regions, typically measuring 1 mm by 70  $\mu$ m. Large resin-rich areas are present, and the



**Figure 2** Optical micrograph in polarized light of a laminate based on polyester **I** without wax additives. The curved birefringent line is the upper surface of the first laminated layer. The resin-rich layer can be seen between the curved and the straight birefringent lines (marked with arrows). Fiber bundles (A) and resin rich regions (B) can also be identified. (Marker length 500  $\mu$ m, specimen thickness 100  $\mu$ m.)

distribution of fibers is inhomogeneous. Two birefringent layers are apparent. The straight birefringent layer is the uppermost because the excess resin allows the formation of a plane surface. The birefringent layers in Figure 2 must be due to compressive stresses, most likely caused by styrene diffusion into the lower layer. Styrene from the applied upper layer can diffuse into the lower layer, as the surface is not fully cured, due to the oxygen inhibiting effect on the curing. Shah et al.<sup>13</sup> discussed styrene diffusion occurring when a polyester resin is applied on top of a cured polyester laminate. An interphase or diffusion region would then swell if it was unconstrained. However, an increase in volume cannot take place because the cured polyester is in the glassy state. Instead, compressive stresses are generated in the diffusion layer.

### Laminates Containing Wax Additives (Polyesters II and III)

The investigations were continued with the laminates based on polyester II, which contained wax. A representative micrograph is presented in Figure 3. This laminate was cured with 3 wt % Butanox M50 with a 3-day waiting period between application of the layers. Excess resin was also applied on the first layer. The matrix-rich layer is apparent at the center of the micrograph. The wax is observable as a second phase and has precipitated as particles. The possibilities of dust or voids constituting the second phase particles can be excluded because no second phase is apparent in the micrographs for specimens containing polyester I with no wax (see Fig. 2).

As polarized transmitted light is used, each micrograph will represent all wax particles through the specimen thickness. A thicker section will, therefore, result in a larger fraction of second-phase particles. Distinct birefringent layers are apparent in Figure 3. The straight birefringent layer represents the upper part of the resinrich layer. Distinct black streaks are present at both sides of the birefringent layers.

The wax particles are more apparent in the resin-rich region than in the rest of the laminate. The lower birefringent layer appears thicker (see Fig. 3). This was noted for several specimens of the same polyester. This can be empirically explained as a consequence of the shorter waiting time (2 h rather than 72 or 240 h) between the laminations of the layers. For the lower birefringent layer this leads to a lower degree of cure and to a thicker birefringent layer.

In Figure 4(a), micrographs of cross-sections from laminates based on polyester **III** are shown. This polyester contained wax, and was of higher



**Figure 3** Optical micrograph in polarized light of a resin-rich laminate based on polyester **II** with wax. The resin-rich layer can be seen between the birefringent lines (marked with arrows). Precipitated wax particles (C) can be seen in the resin-rich layer. (Marker length 500  $\mu$ m, specimen thickness 75  $\mu$ m.)

crosslinking reactivity than polyester **II**. The resin-rich layer is apparent at the center of the micrograph. Only one birefringent layer is present. Because the layer is straight, it represents the upper part of the resin-rich layer. The wax particles were larger for all laminates based on this resin compared with laminates based on polyester **II**.

A magnified view is presented in Figure 4(b). The shape and size of the particles is distinguishable because the thickness of this section is only 55  $\mu$ m. Particles often appear slightly elongated. A typical particle diameter is 20  $\mu$ m. It is not likely that elongated particles have been smeared out by the cutting wheel because the number of particles at the surface is only a small fraction of the total number of particles. The black streaks bordering the birefringent layers are distinct at higher magnification.

The lower birefringent layer was practically nonexistent in the specimens from the more reactive polyester III. The upper birefringent layer was always present with this resin. One may guess that the temperature in the 400  $\mu$ m-thick resin layer never goes as high as at the surface of the three layer laminate. The degree of cure may, therefore, be lower at the surface of the resinrich region. As a conclusion, the thickness of the surface layer later to become birefringent may depend on the degree of cure that correlates with curing time. This is in agreement with the work by Rocket et al. on standard polyester resins.<sup>13,15,16</sup>

It is very interesting to note details of the morphology of the wax in Figure 4(b) at the more irregular boundary between the glass mat and the matrix-rich region [marked with an arrow in Fig. 4(b)]. White wax regions are very close to each other as expected if the wax particles had joined and formed a region resembling a thin film. One can follow the film contours along the border between the glass mat and the matrix-rich region. This feature is not apparent at the birefringent layer. Conclusions regarding the volume fraction of wax are difficult to draw due to thickness variations between samples.

An SEM-micrograph of a laminate based on polyester **III** with wax is presented in Figure 5. The micrograph points to an interesting feature regarding the voids. The voids have an inner layer (ring-shaped in the micrograph) of different appearance than the base resin, possibly consisting of air-inhibited resin. No sign of a wax phase can be observed by scanning electron microscopy.

Although the laminates based on polyester II generally had smaller wax particles than laminates based on the higher reactivity resin III, it is not possible to conclude that the volume fraction of wax phase is smaller. This is because many particles may be too small to be resolved in an



(b)

**Figure 4** Polarized light micrographs of different magnification of a laminate based on polyester **III** with wax. The resin-rich layer (B) can be seen below the straight birefringent line. Fiber bundles (A) and wax particles (C) can be identified. The wax particles appear through the specimen. A wax film can be seen along the border of the glass mat and the resin-rich region (E). (a) Marker length 500  $\mu$ m; (b) marker length 200  $\mu$ m, specimen thickness 55  $\mu$ m.

optical microscope. In general, it appears that the chemical characteristics of the base polyester (solubility or reactivity) and the wax are the primary parameters determining the wax morphology. The following parameters were found secondary within the variations studied: peroxide content, amount of excess resin, waiting time between application of the resin-rich layer, and the second upper half of the laminate.

The effect of excess resin at the laminate surface on delamination resistance of glass mat laminates is of interest from a practical point of view. This can be discussed with Figure 6 as an illustration. Excess resin creates a flat upper plane



**Figure 5** Scanning electron micrograph of a polished surface from a laminate based on polyester **III** with wax. Fiber bundles (A) and voids (D) can be seen.

(see upper birefringent layer in Fig. 6), along which a delamination crack may propagate easily. In contrast, the path provided by the lower birefringent zone may still not delaminate easily even if adhesion is poor. The reason is that a crack that initiates at the lower birefringent zone needs to propagate along a highly tortuous path. The crack will, therefore, quickly grow into the laminate itself where the presence of glass fiber bundles will make crack growth extremely difficult.

#### Wedge-Opened Laminates

The morphology of three laminates that were wedge opened were also studied under polarized light. The fracture surface appearance from a side view is presented in Figure 7(a) and (b). In Figure 7(a), the material is based on polyester II containing wax. The crack grows into the laminate and the delamination resistance is high. The laminate based on polyester III with wax demonstrated low interlaminar toughness and is presented in Figure 7(b). The larger size of the wax particles in polyester III compared with polyester II is apparent. The crack in Figure 7(b) followed the straight, upper birefringent layer. Apparently, with LSE resins, the presence of a birefringent layer does not necessarily mean high interlaminar toughness. The birefringent layer only indicates diffusion from one layer into the other. In LSE resin-based laminates, wax effects may still lead to low interlaminar toughness.

## **CONCLUSIONS**

A procedure was developed by which the wax morphology and birefringent layer appearance through-the-thickness was characterized in glass mat laminates based on LSE unsaturated polyesters. The major morphology differences between laminates made from different polyesters were



**Figure 6** Optical micrograph in polarized light of a wedge-opened laminate based on polyester **II** with wax. The delamination crack (F) can be identified (marker length 500  $\mu$ m, specimen thickness 90  $\mu$ m).



(a)



Figure 7 Optical micrograph in polarized light of wedge-opened laminate based on (a) polyester II with high interlaminar toughness, and (b) polyester III with low interlaminar toughness. The thickness of the resinrich layer between the birefringent bands is about 400  $\mu$ m.

discussed, including birefringent layers. For the more reactive polyester III laminates, larger wax particles were found, compared with laminates made from polyester II. Also, in some laminates based on polyester III the contours of a wax film was present. One may also note that laminates based on the more reactive polyester III with wax additives demonstrated low interlaminar toughness. The morphology of wax at the surface of polyester II resin samples was also described. Regions without apparent wax coverage were present. The interlaminar toughness was satisfactory for laminates based on polyester II with wax additives. The solubility of the wax in the polyester, and the reactivity of the base polyester were the primary parameters determining the wax morphology.

This study shows that the morphology of unsaturated polyester laminates can be characterized by polarization microscopy. The procedure can with ease be used to improve the understanding of how wax additives affect styrene emission and delamination resistance in unsaturated polyester laminates.

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