

## Mechanism of Low-Profile Behavior in Single-Phase Unsaturated Polyester Systems

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### Synopsis

The mechanism of the low profile behavior in certain single-phase polyester systems has been examined. It appears that as polymerization occurs, crosslinked beads ( $<1\mu$ ) of polymer separate from the bulk solution. As the temperature rises, liquid monomer expands, counteracting polymerization shrinkage. As shrinkage surpasses expansion towards the end of polymerization, stresses are induced in the system. These are relieved internally by a series of micro cracks in the continuous matrix of the polymer rather than, as in ordinary systems, through macroscopic shrinkage of the molded part.

Industrial interest in "low profile" reinforced polyester systems has been continually increasing over the past years. These types of resin systems provide not only low profile (a highly uniform, smooth surface without imperfections such as fiber pattern, etc.) but also excellent reproduction of mold dimensions and maximum dimensional stability in subsequent use applications. Thus, it is possible to directly mold high-gloss, close-tolerance parts without costly finishing steps. These systems differ from the usual crosslinking polyester compositions in that they incorporate a small amount (10-20%) of a thermoplastic polymer in the formulation to effect the desired low-profile behavior. The mechanism by which this low-profile behavior occurs and the structure of the cured composition has been the subject of several recent publications.<sup>1-10</sup> We have reported<sup>8</sup> the results of a study on a system which consists of two phases in the uncured liquid state. That study suggests that the low-profile character is the result of releasing polymerization-induced stress through a process of microstress cracking rather than through manifestation as macroscopic contraction or shrinkage. Ehnert et al.<sup>9</sup> have developed similar data on both the two-phase and a homogeneous system, as well as a pigmentable low-profile resin. These data are in essential agreement with our experiments,<sup>8</sup> but our work with the microscope suggests a more detailed mechanistic interpretation.

In the present paper we will discuss the mechanism of low-shrink and low-profile behavior in the homogeneous, single-phase system. Several different single-phase systems have been investigated, and all seem to show similar characteristics. Some aspects of the behavior differ from those of the two-phase system previously reported on,<sup>8</sup> but the principal processes responsible for the desirable low-profile character are very similar.

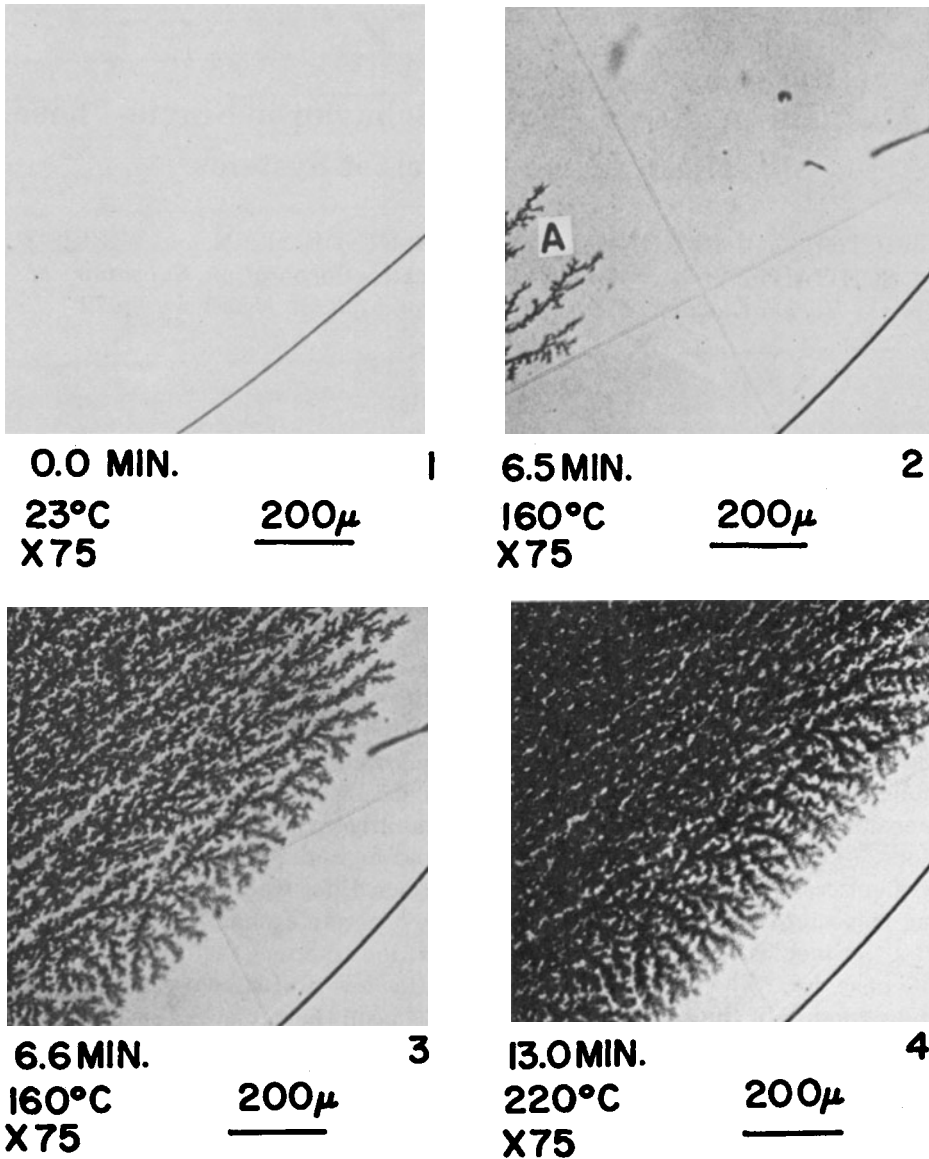


Fig. 1. Microscopic examination of the cure cycle for the single phase low-profile polyester system as observed on a programmed hot stage.

The homogeneous system that will be considered here is comprised of 28 wt-% of an unsaturated polyester (propylene glycol, 0.9 moles; maleic acid, 0.1 mole phthalic acid) as the crosslinking agent (XLA), 12 wt-% poly(vinyl acetate) as a low-profile additive (LPA), and 60% styrene monomer (S). Data on the low-profile behavior of formulations of this resin system are well documented.<sup>9</sup>

In our studies, the liquid resin system was used with 1 wt-% tertiary butyl perbenzoate as a catalyst. On curing this clear, homogeneous mixture under heat and pressure, the resultant casting is white and opaque. Cross sections of the casting are visually homogeneous even at high magnification. This is

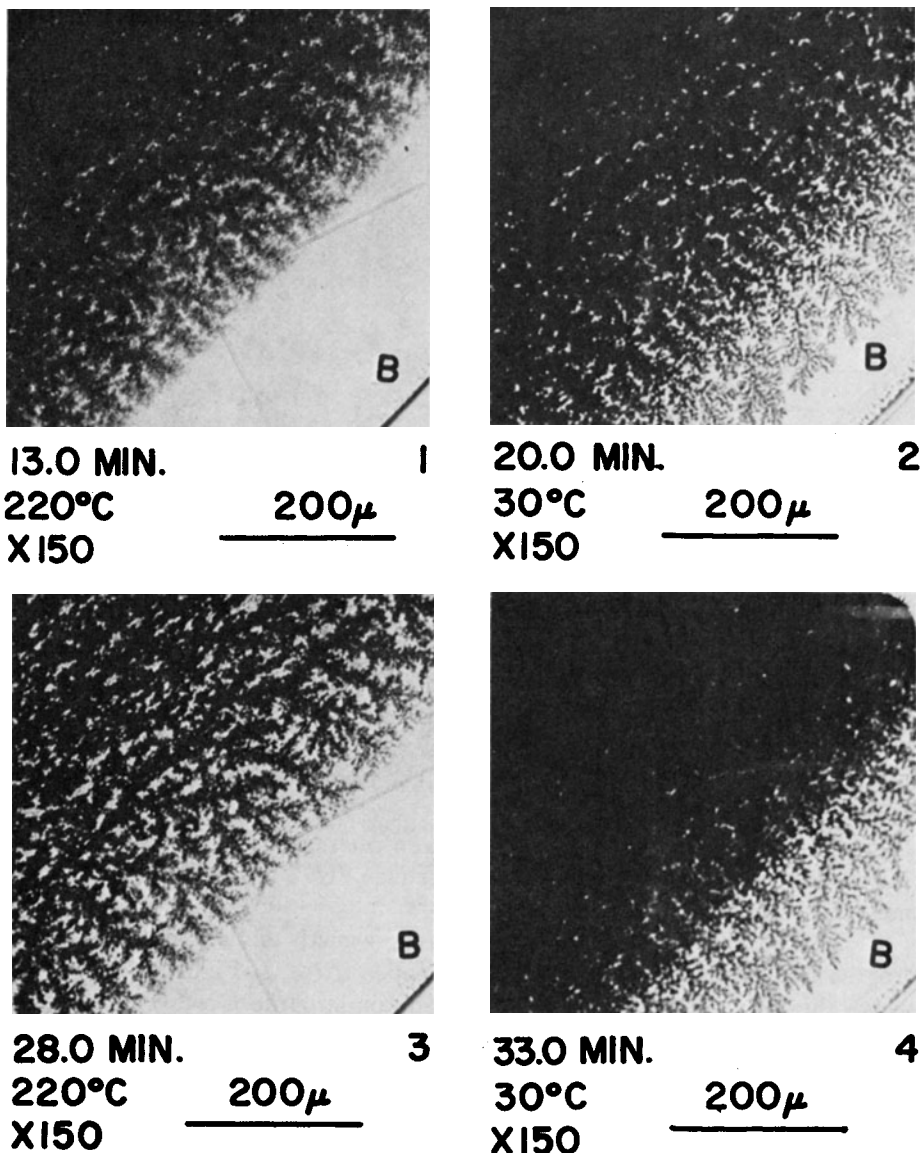
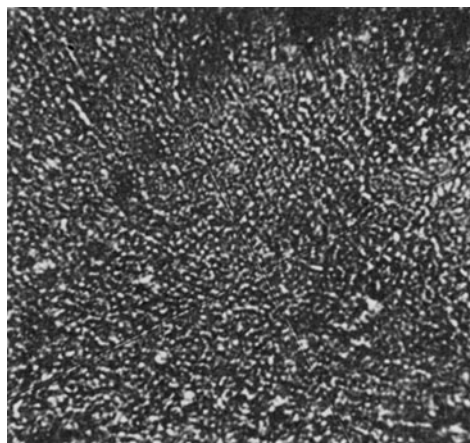


Fig. 2. Continuation of the microscopic examination of the cure cycle for the single phase low-profile system as observed on a programmed hot stage.

in contrast to the nonhomogeneous character of the two-phase systems. However, as noted in previous papers,<sup>1-10</sup> the white, opaque appearance seems to be characteristic of most, if not all, low-profile systems.

In order to fully understand the sequence of physical events occurring during the cure cycle, we have elected to study examples of the unfilled resin system curing under the simulated conditions of the hot-stage microscope. A drop of catalyzed resin solution (*vide supra*), catalyzed with 1% tertiary butyl benzoyl peroxide was placed between microscope cover slips and heated on the hot stage at a predetermined rate such that a temperature of ca. 200°C was reached after 10 min. The sample was monitored using the microscope



**4.0 MIN.**  
 $\sim 130^{\circ}\text{C}$   
**X 675**

**20 $\mu$**   
 \_\_\_\_\_

Fig. 3. Bead structure of the single phase polyester system.

(transmitted light), and photographs were taken at significant times. Observations made in this manner are presented in Figures 1, 2, and 3. Each of the pictures shows significant physical changes and will be discussed in sequence below:

1. The first picture in the series (Fig. 1) shows the homogeneous nature of the liquid resin system.

2. On heating to  $130^{\circ}\text{C}$  (4 min), a second phase may be noted. This is a fine dispersion of beads of ca.  $1\ \mu$  diameter (see Fig. 3 for an example at high magnification).

3. At  $160^{\circ}\text{C}$  (6.5 min), a rapid dendritic growth of fissures is observed progressing across the field of the microscope. Area A, Figure 1, picture 2, shows these fissures advancing. These photomicrographs were made using transmitted light, and diffraction at the fissure surfaces causes the dark appearance. These same areas appear white when viewed in the usual manner with reflected light.

4. Picture 3, Figure 1, shows the progress of the fissure network throughout the sample at  $160^{\circ}\text{C}$ , while picture 4 shows further growth at  $220^{\circ}\text{C}$ . On extended heating at  $220^{\circ}\text{C}$  or on heating to high temperatures, little additional change is noted. In Figure 2 we will examine the same area as in Figure 1, but at a somewhat higher magnification.

5. Picture 1 of Figure 2 was made at the same point as picture 4, Figure 1. Picture 2 of Figure 2 shows the effect of cooling the sample to room temperature. Note areas B that show substantial secondary extension of the dendritic fissure network. This is most obvious at B, but is also evident throughout the sample.

6. Picture 3, Figure 2, shows the effect of reheating the sample to  $220^{\circ}\text{C}$ , causing a regression of the secondary fissure structure. Picture 4 shows the effect of cooling that again induces the secondary fissures. This secondary phenomenon seems quite reversible on a macroscopic scale.

In addition to examination of the cure cycle using ordinary transmitted light, we have also done a parallel study using plane polarized light and a crossed polar. This was an attempt to detect birefringence caused by anisotropy in areas under stress caused by polymerization. In our previous study with the two-phase, low-profile polyester system,<sup>8</sup> this was observed, and its appearance and disappearance on fissure formation was an important part of our rationale of the mechanism of low-profile behavior. In the present case, no birefringence was observable, but it might be expected that birefringence in this case should be present in individual areas much less than  $0.1 \mu^2$  and would not be observed using visible light.

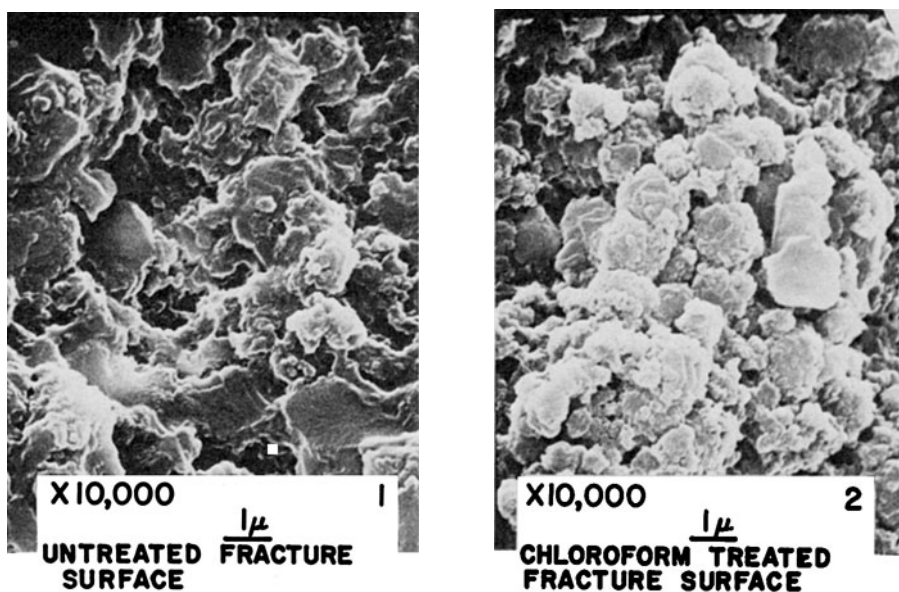


Fig. 4. Examination of fracture surface of cured low profile polyester.

Information regarding the final structure of the cured specimen has been obtained using solvent extraction and scanning electron microscopy. A sample of the cured, unfilled resin from a molded specimen was extracted with boiling chloroform in a Soxhlet extractor for 40 hr. The extract was concentrated and a quantitative recovery of the low-profile additive was made. Identification of the extract was made using NMR spectroscopy. This extraction procedure transformed the rather tough low-profile polymer system into a friable solid.

Examination of these samples by scanning electron microscopy is instructive, as shown in Figure 4. Observations of fracture surfaces with and without chloroform treatment are shown at high magnification. In picture 1, the nonleached fracture surface of the molded specimen, note that the area appears to be composed of a structure of  $0.2\text{--}1.0 \mu$  beads that are fused together or covered by a smooth coating. Small fissures in the structure are noted. These correspond to the cracks observed in the samples examined under the light microscope. Picture 2 (Fig. 4) is a similar view of a fracture surface that has been thoroughly leached with chloroform. By this process, all of the low-profile additive was extracted. Note the character of the surface is more

open and comprised of 0.1–1.0  $\mu$  beads that are rough. The bead structure is intact, but the smooth coating has been washed off.

On the basis of the above data, we may rationalize a mechanism for the low-profile behavior of this single-phase, low-profile system that is also consistent with that proposed for the two-phase system already published.<sup>8</sup>

The steps in the rationale may be presented as follows:

1. The initial mixture of styrene, unsaturated polyester, and low-profile additive is homogeneous.

2. On heating to ca. 130°C, there is simultaneous copolymerization of the unsaturated polyester and styrene resulting in contraction and a counteracting thermal expansion of styrene monomer.

3. At about 130°C, the crosslinking polymerization has progressed to a point where beads of crosslinked resin (1  $\mu$  or less in diameter) separate from the styrene–low-profile additive solution.

4. As polymerization continues, styrene is consumed leaving a matrix of low-profile polyester. During this phase of cure, polymerization is effecting a contracting stress, and there is little styrene monomer present to counteract it by thermal expansion.

5. As these stresses increase, they are relieved by crack formation that progresses through the weak matrix of low-profile additive. This obviates the need for relief of the internal stress by macroscopic contraction of the molding as a whole, as observed in the ordinary crosslinking polyester system.

6. On cooling the cured hot molding, stress due to thermal contraction of the resin is induced. This is relieved, as observed, by extension of the fissure network, and, as expected, this secondary extension is reversible with heating and the resultant thermal expansion.

The above sequence of events seems to be consistent with observed phenomena and with our proposal of a mechanism in other systems. In addition to explaining the low-profile and low-shrink behavior in these novel systems, the mechanism and morphology are also important in understanding the problem of pigmentability in the conventional low-profile systems. We plan to publish results of studies in these areas in the near future.

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