

Mechanism of Low Profile Behavior in Unsaturated Polyester Systems

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Synopsis

The mechanism by which low profile character is achieved in unsaturated polyester systems has been investigated. Using techniques of microscopy, data are developed that support a model in which micro stress cracking is induced to relieve stress promoted by polymerization shrinkage. Thus the strain is accommodated internally in a molded part, rather than through macroscopic shrinkage of the article.

INTRODUCTION

The plastics industry has recently shown strong concern over the development of zero- or low-shrink, crosslinkable polyester resins for use in engineering composites. These highly filled (glass fiber, calcium carbonate, etc.) resin systems are usually compression molded to form a variety of automotive parts, from hood scoops and fender extension to front end panels. Using these materials, substantial weight and labor savings may be realized compared with metal components.

Prior to the low-shrink innovations, crosslinkable polyester-styrene systems yielded extremely strong and chemical resistant molded parts, but these suffered from rough surfaces (high profile), deep sink marks opposite structural ribs, and difficulty in maintaining close tolerances to machined molds. For these reasons, an inordinate amount of labor was required to obtain acceptably smooth decorative finishes. These problems have been traced in a large part to resin shrinkage (7-10%) during cure. More recently, with the advent of so-called "low profile" and low-shrink systems, much of the problem has been alleviated, and in many cases it is now possible to obtain suitable products directly from the mold.

The typical low-shrink/low-profile sheet molding (SMC) or bulk molding (BMC) compound contains a highly reactive unsaturated polyester as a crosslinking agent (XLA), a thermoplastic polymer as a low profile additive (LPA), and styrene (S). This resin system comprises about 20-25% of the SMC while the remainder consists of 45-50% of particulate filler (calcium carbonate, etc.) and 25-30% of chopped glass roving. There are also smaller amounts of catalyst, chemical thickening agents (magnesium oxide, etc.), and release agents.¹⁻⁷

As the importance of the phenomenological aspect of low profile systems has grown the mechanism by which desirable properties are obtained has become of more interest and several related papers have recently appeared.¹⁻⁷

In the present paper, we will be concerned only with the resin system and the mechanism by which low-shrink and low profile behavior occur.

Walker⁴ has recently enumerated many of the factors that appear to be related to development of low profile character. These are listed as follows:

1. Use of low profile additive systems reduces the gross shrinkage of the molded part and may even result in zero shrinkage or an overall expansion.

2. With low profile systems, surface roughness due to "fiber pattern" or microirregularity is significantly reduced.

3. With these systems, castings are opaque and show areas containing a multitude of microvoids.

4. Very reactive polyester systems are used, and a substantial polymerization exotherm seems necessary for effective performance.

5. Effective systems contain a larger proportion of styrene than usually required.

6. Although there appear to be specific constraints on the nature of the crosslinking polyester portion of the system, there seems to be considerable latitude in the choice of the thermoplastic low profile additive.

From these basic observations, several workers have speculated on the driving force for development of low-shrink behavior, and there appear to be several possible explanations for observed phenomena. Perhaps the most prevalent view is that the polymerization exotherm vaporizes styrene monomer providing voids that compensate for shrinkage. However, at realistic molding temperatures (140–150°C) and pressures (1000 psig), it seems unlikely that monomer would volatilize (at 200°C, the vapor pressure of styrene is ca. 50 psig⁴). Other possible simple explanations also fail to correlate all facts.

At this point we wish to introduce data that indicates that a major factor for low profile behavior is strain relief through microscopic stress cracking.

Polymerization shrinkage is thus compensated by internal void formation rather than macroscopic shrinkage of the molded part. Thus shrinkage and "high profile" are avoided. This mechanism is most closely approximated by a recent suggestion of Rabenold.⁵

The most common low profile resin system presently available is a two-phase mixture of two polymers in styrene solvent. We will discuss this system in detail. There are also available single-phase and multiphase systems which will be reported on later but in which the basic behavior is similar to that in the two-phase systems.

THE TWO-PHASE LOW PROFILE POLYESTER SYSTEM

The two-phase system is comprised of 40% (by weight) of a propylene glycol-fumaric acid polyester that serves as a crosslinking agent (XLA), 13% of polymethacrylate copolymer as a thermoplastic low profile additive

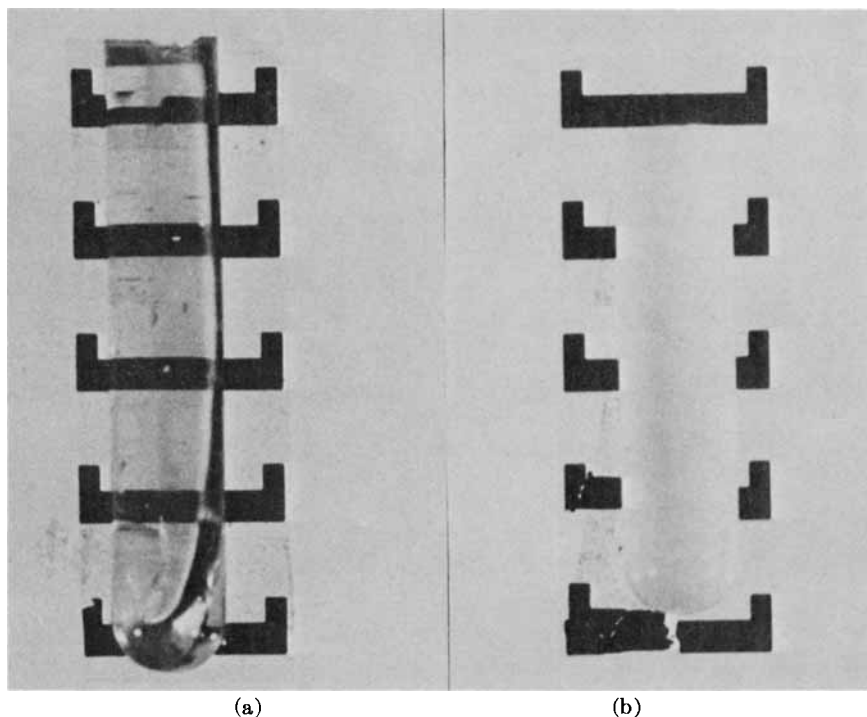


Fig. 1. Typical molded crosslinked (a) and low-profile (b) polyester.

(LPA), and 47% styrene (S). These components are not completely soluble in each other and on thorough mixing form a two-phase dispersion consisting of 50–100 μ liquid globules (phase D) in a continuous medium (phase C). A 40:60 ratio (vol) of phase D:phase C is found on permitting separation to occur. Analysis of the two phases by nuclear magnetic resonance shows the compositions to be as follows:

	Phase D	Phase C
% XLA (wt)	27	49
% LPA (wt)	21	2
% S (wt)	52	49

As noted above, on vigorous mixing phase D is dispersed as 50–100 μ globules in the continuous phase C. This structure is easily observed under the light microscope (*vide infra*). On heating the catalyzed (benzoyl peroxide), dispersed system in a test tube at 80°C (atm. pressure), the mixture slowly warms and shows a substantial polymerization exotherm raising the internal polymer temperature to 180°C. At about 150°C, the casting turns white and opaque, and this character is representative of the totally cured casting (see Fig. 1). If the procedure is carried out in a compression mold at 150°C and 1000 psig, more appropriate molding conditions, similar changes are observed. This is in contrast to the clear moldings obtained with non low profile systems (Fig. 1).

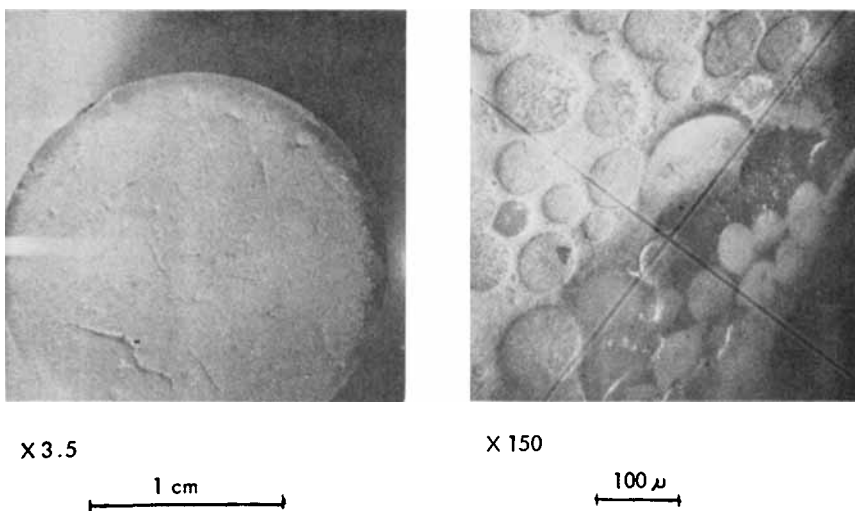


Fig. 2. Cured two-phase, low profile polyester system.

Examination of a polished cross section of such a casting shows a retention of the two-phase character. Figure 2 shows the 10–100 μ spherical globules in a cross section. These appear to be filled with minute voids which account for the white, opaque appearance.

We were particularly interested in observing changes in this system at various points in the cure cycle with minimum perturbation of the process. The hot-stage microscope was found to be particularly useful for this purpose. In this work, a sample of the catalyzed, dispersed system was placed between microscope cover slips on the hot stage and the temperature was raised to 200°C over a period of about 10 min.

A series of photomicrographs using transmitted light show observations made at appropriate intervals as depicted in Figure 3.

The sequence of events observed during this simulated curing cycle are:

1. At room temperature, we observe inhomogeneity with 10–100 μ globules dispersed in a continuous phase.

2. On heating to 118°C (3.4 min), the system partially cures, becomes immobile, and close examination of the globules shows that they are no longer homogeneous. Very fine particles (1 μ diameter) have precipitated within their volume. This point is more easily observed at higher magnification as in Figure 4.

3. On heating to 141°C (4.4 min), there is apparently little change. However, the small areas, A, appear black. These photomicrographs were taken using transmitted light, and these "dark" areas appear white using reflected light. In fact, the black areas represent sites where void formation has occurred and light is diffracted. The small black area on the elongated globule is of particular interest. It appears at the interface of the globule and the continuous matrix. It is not totally evident from these

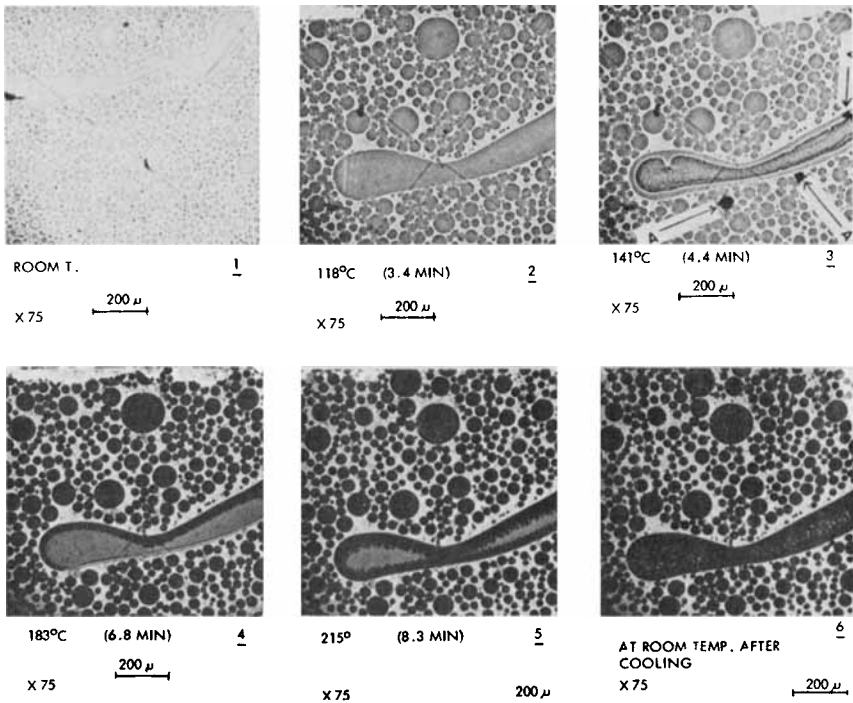


Fig. 3. Microscopic examination of the cure cycle for the two-phase, low profile polyester system as observed on a programmed hot stage microscope.

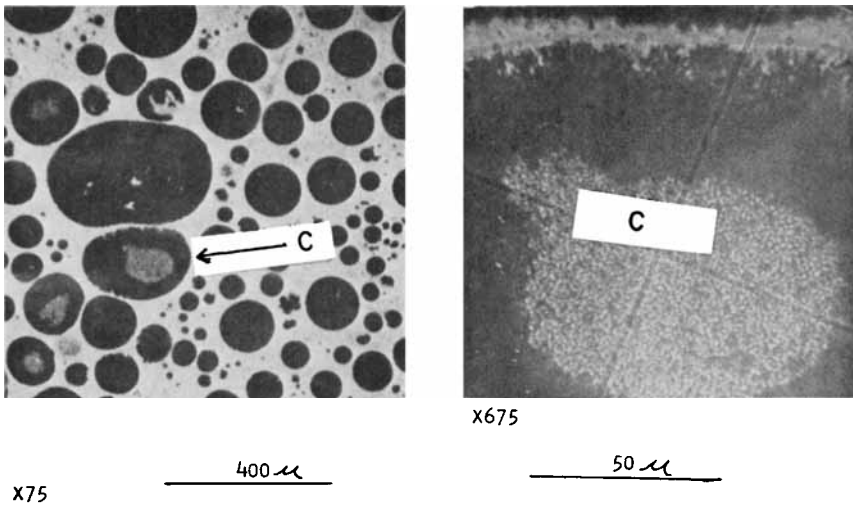


Fig. 4. Particulate structure of the two-phase, low profile polyester system.

pictures, but it appears as if much of the void formation is initiated at such interfaces.

Another pertinent observation concerning the interface at this stage of the cure can be seen in Figure 5, where a similar sample at the same state of cure is observed under polarized light. The photomicrograph on the left, 3A, is similar to picture 3 of Figure 3. That on the right, 3B, shows the same area with plane polarized light and a crossed polar. The areas at the *interface* of globule and continuous phase show substantial light transmission that reflects molecular anisotropy in these regions. We interpret this as indicative of strain in the matrix caused by polymerization shrinkage.

4. Continuing in Figure 3, at 183°C (6.8 min) almost all of the globules have developed voids as shown by lack of light transmission. The elongated globule is still transparent to a large extent, but the progress of void formation along the interface may be noted.

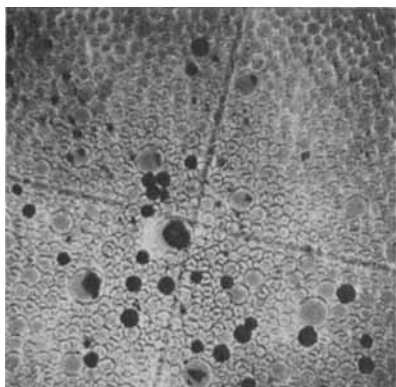
Observations in Figure 5 show the effect of void formation on interfacial strain. Examination of a sample at a stage of cure similar to that in picture 4 shows no birefringence around the void-filled globules. (The void filled globules appear light because light randomly diffracted is not totally blocked by the crossed polar.) Those globules that do not show voids still exhibit birefringence and strain at the interface. It appears from these photographs that void formation relieves strain introduced by polymerization shrinkage.

5. Picture 5 of Figure 3 shows that raising the temperature to 215°C effects little general change. However, there is some additional void formation in the elongated globule. Maintaining this temperature for 5–10 min gives no further change.

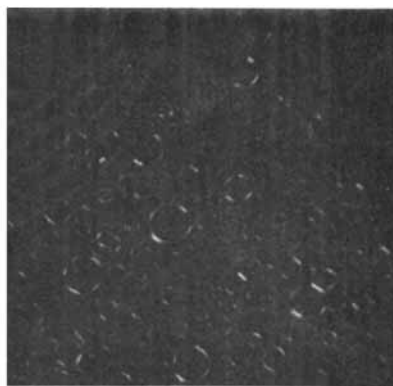
6. Finally, on cooling to room temperature, we observe additional void formation within the elongated particle.

Further evidence regarding the microstructure of this system has been gathered using scanning electron microscopy and observing a fresh fracture surface of a cured polymer sample. Photomicrographs are shown in Figure 6. Pictures 1 and 2 show an untreated surface at 100× and 10,000× magnification respectively. In picture 1, the structured 10–100 μ globules and the homogeneous continuous phase may be seen. Picture 2 shows the interior of one of the globules and the 1- μ bead structure. These beads seem fused and covered with a thin smooth coating. The fissures approximately 1 μ in breadth are also observable, although some seem to be filled. Pictures 3 and 4 show similar magnifications of a fracture surface that has been leached for 72 hr with chloroform. The low-magnification photograph shows topology similar to that of the untreated surface. Higher magnification of the globule interior shows 1- μ beads that have a rough surface. It appears as if a soluble coating contributing to the smooth appearance had been washed off the surface and out of the interstices leaving a more open, porous structure.

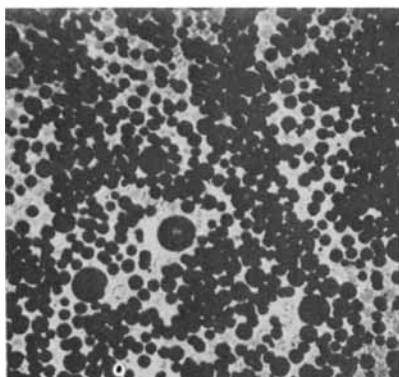
These data are in agreement with information inferred from work using the light microscope. Thus, the 10–100 μ globules in the cured



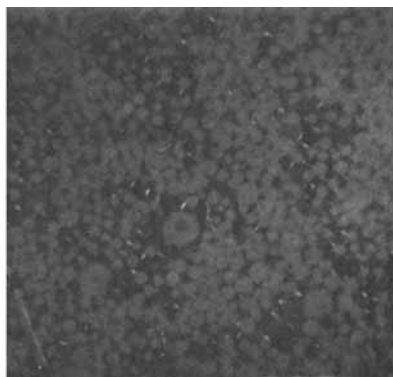
CURED TO 130°C **3A**
 ORDINARY TRANSMITTED LIGHT
 X 75 200 μ



CURED TO 130°C **3B**
 PLANE POLARIZED LIGHT AND
 CROSSED POLARS
 X 75 200 μ



CURED TO 150°C **4A**
 ORDINARY TRANSMITTED LIGHT
 X 75 200 μ



CURED TO 150°C **4B**
 PLANE POLARIZED LIGHT AND
 CROSSED POLARS
 X 75 200 μ

Fig. 5. Examination of the cure cycle for the two-phase, low profile polyester system using plane polarized trans method light and a crossed polar.

sample contain a 1- μ bead structure covered by a smooth coating and interspersed with a number of channels and fissures. The 1- μ beads are insoluble in chloroform and probably crosslinked, but the smooth coating may be washed off and is composed of thermoplastic low profile additive. This has been confirmed in leaching studies where 16% of the total weight of polymer was removed with boiling chloroform. Nuclear magnetic resonance spectra indicate that the soluble material is predominantly low profile additive. Thus, most of the low profile additive is susceptible to solubilization and not crosslinked or entrapped.

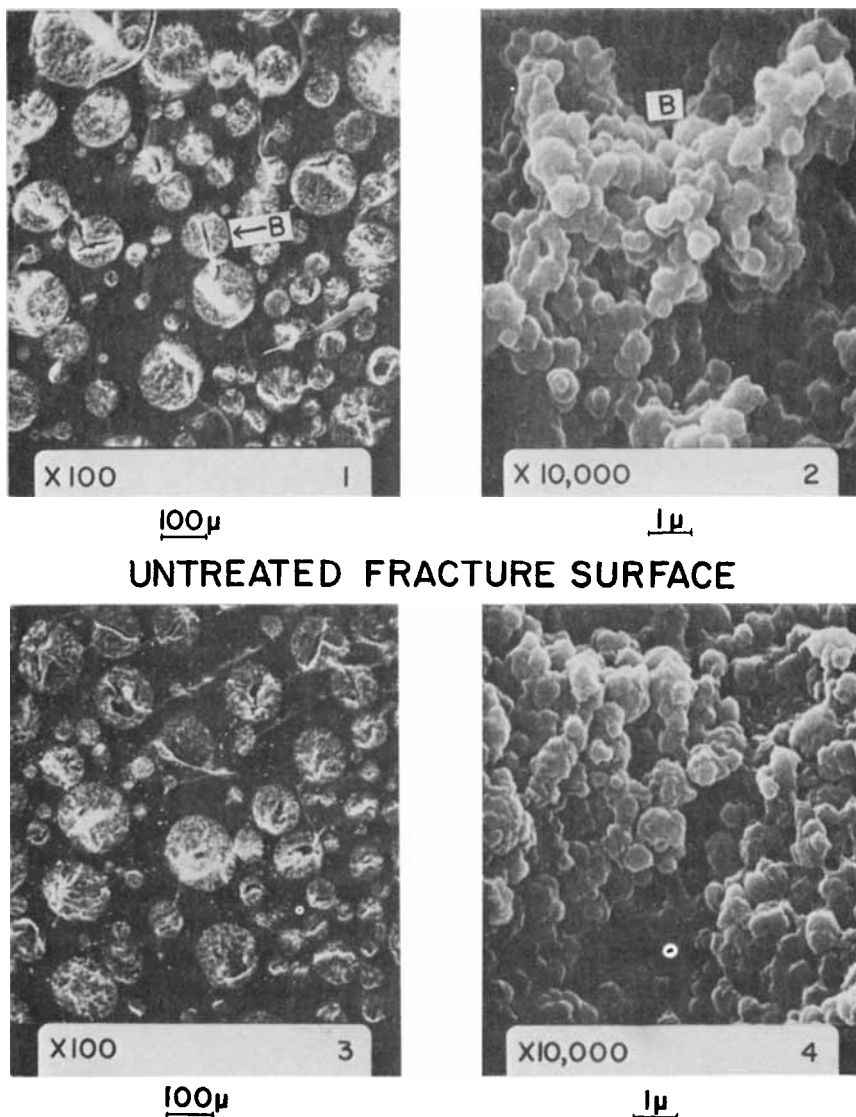


Fig. 6. Scanning electron photomicrograph.

The above represents the experimental data from which we wish to derive a mechanism for low profile behavior as follows:

1. At room temperature, this system is comprised of two phases: a dispersed phase of 10–100 μ globules comprised of 27% XLA, 21% LPA, and 53% S, and a continuous phase containing 49% XLA, 2% LPA, and 49% S.

2. On heating to ca. 120°C; (a) crosslinking polymerization occurs in the continuous phase contributing to shrinkage; (b) styrene monomer ex-

pands thermally to counteract polymerization shrinkage; (c) crosslinking polymerization occurs between XLA and S in the dispersed phase; 1- μ beads of this crosslinked material separate out of the LPA. Thus, the dispersed phase of 10–100 μ globules is in fact comprised of 1 μ crosslinked beads dispersed in a continuous matrix of LPA (containing still some styrene and unsaturated polyester).

3. On continued heating to 140°C, these polymerization processes continue. As monomeric styrene is consumed the thermal expansion of this monomer no longer compensates for polymerization shrinkage, and strain develops within the system. This appears to be concentrated at the globule–continuous phase interface.

4. On further heating to ca. 150°C with continued polymerization, strain increases to a point where stress cracking is initiated at the globule–continuous phase interface. Once initiated, the stress cracking propagates through the weak LPA interstitial matrix among the 1- μ beads in the globule. This stress cracking substantially relieves strain and introduces the observed void formation that compensates for overall shrinkage.

5. Continued heating to 215°C effects little further change. However, on cooling back to room temperature, thermal contraction introduces additional strain which is relieved by further stress cracking as observed.

The above sequence seems to accommodate all observed facts and explains the low profile behavior as a function of strain relief by microstress-cracking through a weak interstitial matrix of LPA rather than being manifested as macroscopic shrinkage of the molding.

The preceding represents a rationalization of the mechanism of low profile behavior in this two-phase system. We have also examined single- and multiphase systems and find that parallel mechanisms may be proposed, although details differ because of the different physical structure. Data on these systems will be presented at a later date.

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