## Mechanism of Low Profile Behavior in Unsaturated Polyester Systems

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# Mechanism of Low Profile Behavior in Unsaturated Polyester Systems

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The mechanism of low profile, low shrink behavior in single- and two-phase unsaturated polyester systems has been investigated. The curing process of several compositions has been followed by optical microscopy at various heating rates, fracture surfaces of cured samples have been observed using scanning electron microscopy and some of their physical properties have been measured. A mechanism is proposed, based on data obtained in this work and additional published data, which consists of shrinkage reduction in the continuous phase by thermal expansion of styrene and other constituents and in the dispersed phase by void formation.

## INTRODUCTION

In the past few years, reinforced polyesters have increased their market penetration in a wide variety of applications such as transportation, industry and construction. Reinforced polyesters are very attractive materials having such properties as high strength to weight ratio, high chemical resistance, low heat conductivity, freedom of design and low tooling costs. Further expansion in the use of these materials has been limited by their high polymerization shrinkage causing difficulty in m olding to close dimensional tolerances, surface

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irregularities and sink marks opposite structural ribs. The common volume shrinkage during the curing cycle is in the range of 5–10%.

Recently, several unsaturated polyester systems have been developed, which yield molded parts that are "ready for painting". Such systems have been designated as "low profile" and/or "low shrink" materials. These systems consist of, in addition to various fillers, additives and reinforcing materials and thermoplastic polymers, e.g. acrylics,[1] poly(vinyl acetate),[1] cellulose acetate butyrate,[2] polystyrene,[1] etc. It is important to emphasize that the low shrink compounds consist of highly reactive unsaturated polyesters and larger proportions of styrene than in regular polyesters. In addition, all moldings based on low profile compositions are opaque.

The curing kinetics, the mechanism of the low profile behavior and the structure of the cured system have been the subject of several recent reports.[1–7]

Volumetric changes during the cure cycle of a low shrink polyester system (Rohm and Haas Paraplex p-19) as a function of time have been followed using a high-pressure dilatometer.[4,5] In a conventional system the following was measured: at first there is thermal expansion followed by shrinkage as a result of polymerization and a small amount of thermal contraction. After the polymerization ends, the system, while cooling to room temperature, continues to shrink resulting in total volume shrinkage of 7.1%. Under the same reaction conditions, the low shrink system exhibits, after the thermal expansion and just before the polymerization shrinkage, an additional small expansion peak. The expansion is pressure and temperature dependent namely, raising temperature and/or lowering pressure cause an increase of that peak, whereas lowering temperature and/or raising pressure can eliminate it. In this system the polymerization shrinkage is quite small and after cooling to room temperature the resulting total volume change is even an expansion of 2.8%.

Some authors[4–7] assume that the polymerization in the continuous phase is faster than that in the dispersed phase; the latter gives mainly homopolymerization of styrene. They suggest that as a result of the heat evolved during the curing reaction, the free monomer, located in the dispersed phase, prevents shrinking by its sufficiently high vapor pressure. In addition, as the system's temperature increases, the dispersed phase expands resulting in a decrease in the shrinkage of the continuous phase. The dispersed phase has a sponge-like structure as a result of both, diffusion of monomer to the continuous phase during its crosslinking and homopolymerization and shrinkage. Other workers[8] who followed the curing cycle using optical microscopy and observed the cured samples using scanning electron microscopy, support the above-suggested mechanism. Walker[9] assumes also void formation but he adds that the mechanism may be expansion of the voids under the influence of the styrene vapor pressure. However, surface tension considerations would predict much smaller voids than observed.

Boos *et al.*,[10] using dilatometry, calorimetry and swelling experiments, suggest that the total volume changes during crosslinking are mainly controlled by temperature. They show in their work that at high enough temperatures even a conventional polyester system does not shrink. Hence, the function of the thermoplastic low shrink additive is to lower the crosslinking temperature at which no shrink or even expansion occurs. This effect can be also accomplished by using other additives having high thermal expansion coefficients or by using initiators with different decomposition temperatures.

The effect of the thermoplastic low shrink additive characteristics, in addition to its incompatibility with the thermosetting system, has been also studied.[1] Poly(methyl methacrylate), poly(vinyl acetate) and polystyrene have been used as additives. The main two relevant properties in which the three polymers differ are glass transition temperature $(T_g)$ and thermal expansion coefficient $(\alpha)$. It has been observed that the polymer with the lowest $T_g$ and highest $\alpha$ among the three polymers namely, PVAc, is the most effective low shrink additive.

Pattison *et al.*[3,11] have published two comprehensive works on the mechanism of low profile behavior of unsaturated polyester systems. In their first paper[3] they have investigated a two-phase system consisting of propylene glycol-fumaric acid polyester (XLA-40% w), acrylate copolymer (LPA-13% w) and styrene (S-47% w). Analysis of the two phases formed upon mixing the three materials shows that the dispersed phase consists of 27% XLA, 20% LPA and 53% S whereas the continuous phase contains 49% XLA, 2% LPA and 49% S. The main additional processes taking place during curing are the following: upon heating, XLA and S are crosslinked in the dispersed phase and separate out of the LPA as $1\mu$ beads. On continued heating, as the styrene is consumed, the polymerization shrinkage can no longer be compensated by the styrene, and stresses develop within the system resulting in cracking. The cracks are probably initiated at the two-phase interfaces and propagate through the LPA. In their second report Pattison *et al.*[11] examined an initially single-phase system. The general behavior has been observed to be similar to the two-phase system except for the $1\mu$ crosslinked resin beads precipitating out from the continuous phase followed by stress cracking all over the material and not within a separate phase.

In summary it can be said that no satisfactory explanation of the low profile/low shrink behavior of unsaturated polyester systems has yet been substantiated; however, there are a number of hypotheses which partially explain the process in different ways. The mechanism is complex because of the different processes which take place in both continuous and dispersed phases. In the present work, single- and two-phase low shrink polyester systems were studied, their curing cycle was followed, their end structure was examined, few of their properties were measured and the influence of their composition and their rate

of curing was observed. The purpose of the present work was to elucidate and better understand the mechanism of the scientifically intriguing and technologically important low shrink behavior of unsaturated polyester systems.

## EXPERIMENTAL

### Materials

The curing process of two principally different systems has been studied. One system consisted of one phase and the other of two phases prior to their cure. The single-phase system was prepared in our laboratory whereas the two-phase system is a commercial material.

The unsaturated polyester was prepared by the following procedure: A 2 liter reaction flask fitted with mechanical stirrer, graduated distillation trap topped with a condenser, thermometer and nitrogen-inlet tube, was charged with 6.3 moles (5% excess) propylene glycol, 4.5 moles maleic anhydride and 1.5 moles phthalic anhydride. The reaction temperature was raised to 180°C and maintained at that temperature until the acid number dropped below 50. Following the cooling of the polyester to 90°C, styrene was added to yield a composition of 45% styrene and 55% unsaturated polyester. To obtain a single-phase low shrink polyester, several thermoplastic materials were tested as soluble additives at concentration of 5% in the polyester described above. The following materials were tested: low molecular weight polystyrene ($M_n = 6300$, $M_w = 36000$), poly(methyl methacrylate) (Diakon, LO-937, CA-603, MG-101, ICI), cellulose acetate butyrate (C.A.B.465E, Eastman Kodak), polyamide (Rilsan B ATO Chemie) and polyvinyl acetate ($M_w = 45000$, BDH Chemicals). The polyester-additive mixtures were examined for homogeneity by optical microscopy at a magnification of $400 \times$. Single-phase system was obtained only with the polyvinyl acetate (PVAc). It was found to be soluble in the polyester up to a concentration of 15%. A concentration of 10% was selected for the present study.

As a representative two-phase low shrink polyester, Rohm and Haas Paraplex P-19D[2] was selected. It is a two-component resin system based on Paraplex p-340 and Paraplex p-701, which is an acrylic polymer/styrene monomer syrup. The two liquid components must be blended just before their use. According to Rohm and Haas technical data, minimal shrink and optimum surface profile are obtained when a composition based on 60 parts Paraplex p-340 and 40 parts Paraplex p-701 is used.

In the course of the present study the following techniques have been utilized:

*Optical microscopy* The curing process of the polyester systems was followed using a Mettler hot stage microscope, model FP-52. A sample of initiated

polyester system was placed between two microscope cover glasses on the hot stage and the temperature was raised at a constant desired rate. Photomicrographs were taken at selected time intervals during the heating cycle. In addition, fracture and specimen surfaces of crosslinked samples were examined with a reflection light microscope.

*Electron microscopy* Fracture surfaces were also examined using a scanning electron microscope—TV MINI SEM, ISI International Scientific Instruments.

*Electrical properties* Volume resistivity of crosslinked samples was measured with a Keithley 610 Multi Range Electrometer using a 6105 resistivity adapter and an OA regulated high voltage supply.

*Ultrasonic energy absorption* The absorption of ultrasonic energy in crosslinked samples was measured by using Sonatest UFDI with a Sperry RG 162 crystal at 5 MHz.

*Density* The density of various samples was measured by the flotation method.

## RESULTS

The two components of low shrink Paraplex P-19D, namely Paraplex p-340 and p-701 (in the recommended ratio of 3:2), form, after thorough mixing, a phase dispersion consisting of 0.015–0.15 mm in diameter droplets dispersed in the continuous phase. This structure is easily observed under an optical microscope, as can be seen in Figure 1. The large smooth areas seen in Figure 1 are the result of coalescence of several droplets. Such areas are convenient to better follow the curing process.

Upon heating such a sample, which contains also 1% t-butyl peroctoate, at a rate of 10°C/min, the clear droplets change first to opaque (at 125°C) followed by the appearance of black areas (at 154°C) resembling growing branches (see Figure 2). As the temperature increases up to the studied maximum of 220°C, the dark areas continue to expand until the branched structure covers almost the whole area of the dispersed phase (see Figures 3 and 4).

Using a different initiator, 1% butanox M-105 (Akzo's methylethylketone peroxide—50% active), the general behavior of the Paraplex P-19D system is similar to that of the previous one. The changes are similar to, but not as pronounced as those with t-butyl peroctoate. At 105°C the droplets begin to opacify and at 240°C the dispersed phase is still not all black. Not before
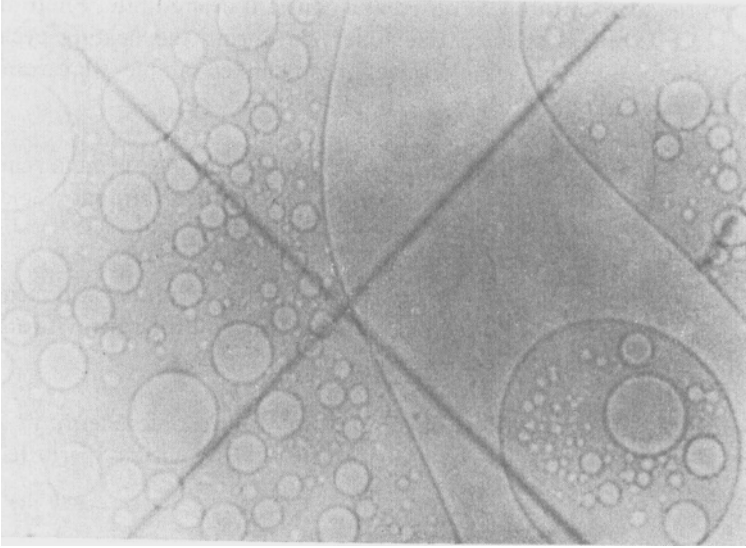
FIGURE 1   Optical micrograph of two-phase low profile polyester consisting of 60%
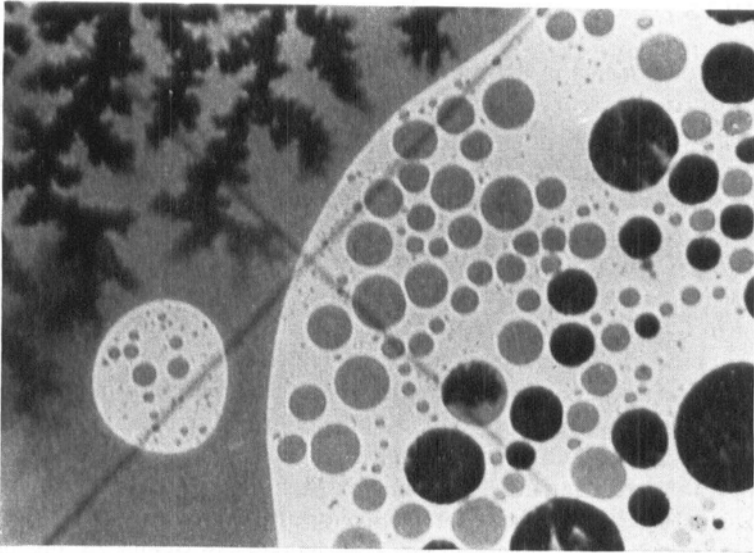Paraplex 340, 40% Paraplex 701 and 1% Trigonox 42 (125 ×).



FIGURE 2   As in Figure 1, heated to 154°C at a rate of 10°C/min (125 ×).
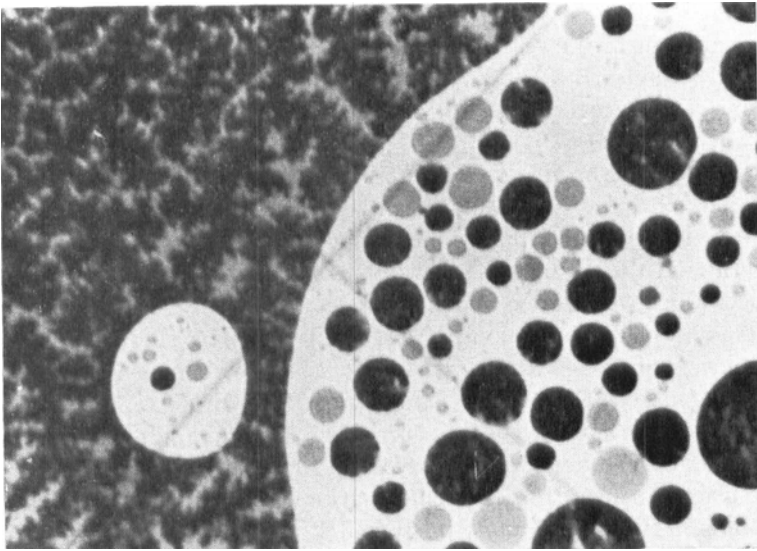
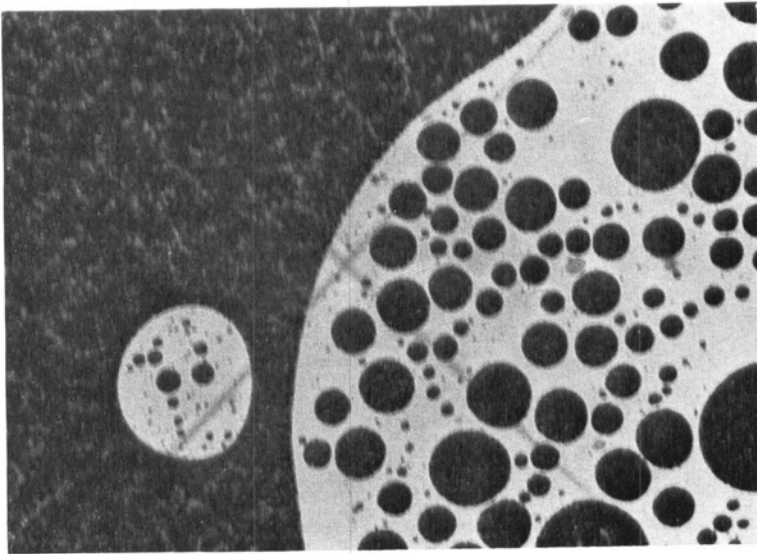FIGURE 3    As in Figure 1, heated to 160°C at a rate of 10°C/min (125×).



FIGURE 4    As in Figure 1, heated to 220°C at a rate of 10°C/min (125×).

cooling to 50°C and reheating did the dispersed phase turn all black (see Figure 5).

The addition of an accelerator, 0.25% cobalt naphthenate, to the first described Paraplex P-19D system, shifts the changes to occur at lower temperatures, the process rate is higher, so that the dispersed phase is completely black already at 200°C.

By lowering the heating rate from 10 to 3°C/min, the residence time was prolonged and the system could reach higher degrees of cure at lower temperatures. For example, the droplets changed from transparent to opaque already at 97°C. There are no significant observed differences between the final products which were heated at different rates.

Two additional compositions of Paraplex P-19D were studied. The system consisting of 68% p-340/32% p-701 and 1% t-butyl peroctoate behaves similar to the previously described 60/40 Paraplex P-19D system, except for the higher temperatures at which the changes occur. The darkening, for example, begins at 207°C and even after several minutes at 220°C not all of the droplets have turned black. An interesting different behavior was observed for a composition consisting of 50% p-340, 50% p-701 and 1% methylethylketone peroxide. Upon heating at a rate of 10°C/min at about 100°C, the initial two-phase system becomes homogeneous (see Figure 6). Upon further heating, at 125°C,
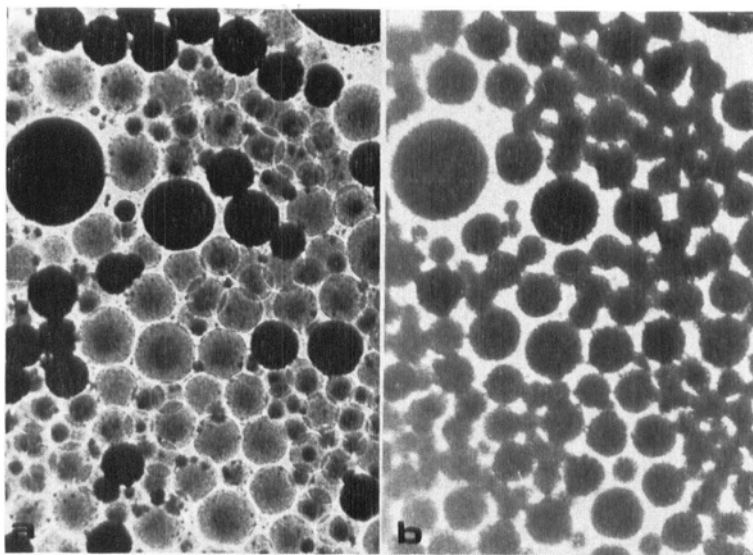


FIGURE 5   Optical micrographs of two-phase low profile polyester consisting of 60% Paraplex 340, 40% Paraplex 701 and 1% Butanox 105, heated to 240°C (a) followed by cooling to 50°C and reheating to 240°C (b) at a heating rate of 10°C/min (125 ×).

black areas consisting of granular structure can be observed (see Figure 6) and at 160°C the whole area turns black. The changes take place all over the sample and not only in discrete droplets. It seems that above a certain temperature the system behaves as a single-phase low shrink polyester. This type of system will be discussed next.

A single-phase system consisting of home-made polyester (45% styrene), 10% PVAc and 1% t-butyl peroctoate was studied. Upon heating, the homogeneous system turns from a clear to an opaque one consisting of granular structure. At 130°C the typical black areas appear all over the sample (see Figure 7). On continued heating, the black areas grow in size and at 180°C the whole sample is already black. This behavior is similar to the above described one for 50/50 composition of Paraplex P-19D.

It is interesting to note at this point the effect of the additive compatibility with the polyester system. Compatibility of the thermoplastic additive with the polyester system was determined using optical microscopy at a magnification of 400×. It was observed that 10% PVAc is compatible whereas PMMA and PS are not. However, mechanical loss spectra of the 10% PVAc/polyester system show two peaks which shed doubt on the actual compatibility of the two. Nevertheless PVAc can be considered to be more compatible than PMMA or PS with polyester and compounds containing PVAc show single-phase behavior whereas compounds containing PMMA or PS show two-phase behavior.

Atkins et al.[1] also tested the three different low profile additives namely, PVAc, PMMA, and PS. Comparison of the ability of the thermoplastics to control shrinkage shows the poly(vinyl acetate) to be superior. The authors explain this superiority to be related to the thermal coefficient of expansion
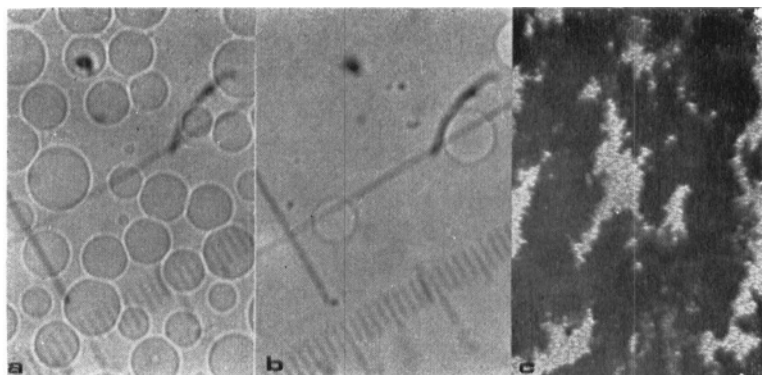


FIGURE 6   Optical micrographs of two-phase low profile polyester consisting of 50% Paraplex 340, 50% Paraplex 701 and 1% Butanox (a) heated to 40°C, (b) heated to 90°C, (c) heated to 137°C, at a rate of 10°C/min (185×).
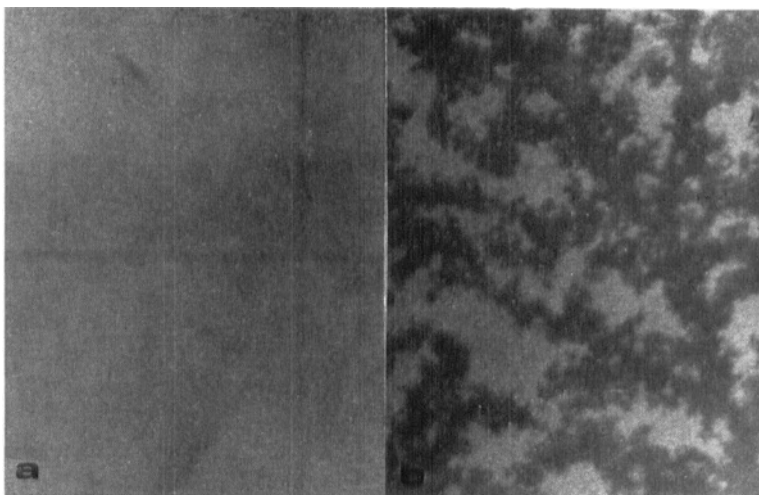
FIGURE 7   Optical micrographs of single-phase low profile polyester with 45% styrene, 10% PVAc and 1% Trigonox 42, (a) heated to 40°C, (b) heated to 130°C at a rate of 10°C/min (125 ×).

and glass transition temperatures, the thermoplastic-polyester-styrene compatibility and polarity. The facts mentioned in Atkins' work are in accord with our proposed mechanism.

In addition to the thin films prepared for observation of the curing process, several bulk samples were prepared so that physical properties could be measured and fracture surfaces examined. The fracture surface of Paraplex P-19D (60% p-340; 40% p-701) with 1% MEK peroxide and 0.1% cobalt naphthenate crosslinked at ambient temperature is shown in Figure 8. The two-phase separation is clearly seen as well as the internal structure of the dispersed phase. The same structure is also characteristic to samples prepared from a home-made single-phase system containing 10% PVAc as the low shrink additive.

In order to clarify the observations described above (optical and scanning electron microscopy) two physical properties which should be sensitive to structural changes, namely volume resistivity and ultrasonic absorption, were measured. Volume resistivity measurements were performed in accordance to ASTM D257-61 and the results are shown in Table I. Ultrasonic energy absorption was measured at a frequency of 5 MHz, using samples all 4 mm thick. The absorbed energy is estimated from the relative amplitude of the two observed peaks, after adjusting their amplitudes so that the first peak amplitude be 100%. The results are summarized in Table I.
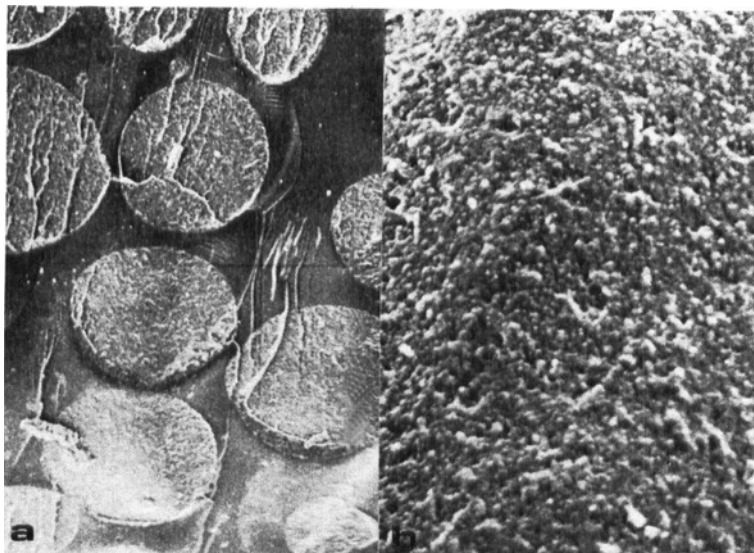
FIGURE 8   Scanning electron micrograph of fracture surfaces of low profile polyester consisting of 10% Paraplex 340, 40% Paraplex 701 and 0.1% cobalt naphthenate cured at ambient temperature, (a) 125×, (b) 625×.

TABLE I

Volume resistivity and ultrasonic energy absorption of various polyester compositions

| Sample[a] | Crosslinking temperature | Volume resistivity ohm–cm | UEA[b] log amplitude | UEA[b] linear amplitude |
|---|---|---|---|---|
| Paraplex P-340 | 25°C | $8.0 \times 10^{16}$ | 47% | 10% |
| 60/40 Paraplex P-19D | 25°C | $3.4 \times 10^{17}$ | 40% | 7% |
| 60/40 Paraplex P-19D | 150°C | — | 32% | 3% |
| Home-made polyester containing 45% styrene | 25°C | $6.0 \times 10^{15}$ | — | — |
| Home-made polyester containing 45% styrene and 10% PVAc | 25°C | $4.1 \times 10^{16}$ | — | — |

[a] All samples catalyzed with 1% MEK peroxide and 0.1% cobalt naphthenate.
[b] Ultrasonic Energy Absorption.

## DISCUSSION

Low profile, low shrink polyesters, single- and two-phase systems, were studied at several compositions, with two different initiators, with and without a promoter and at different heating rates.

The three studied compositions of Paraplex P-19D consist of 50:50, 60:40 and 70:30 ratios of Paraplex p-701 respectively. According to Rohm and Haas recommendations, as the molding produced is larger, the ratio p-340/p-701 should be higher. In the present work it has been observed that as this ratio increases, the size and amount of black areas seen in the optical microscope and formed upon curing increase. Assuming that these black areas represent sites of void formation[3-8] resulting in diffraction of light, it can be concluded that as the ratio of p-340/p-701 increases, more voids are formed upon curing and the shrinkage is lower.

A study of the effect of the type and concentration of initiator on the low shrink behavior shows that in systems initiated by t-butyl peroctoate, significantly more of the dispersed phase turns black upon curing than in systems initiated by methyl ethyl ketone peroxide (the first one is recommended by Rohm and Haas, although "other peroxides are also acceptable"). Hence, in systems initiated by t-butyl peroctoate, upon curing, more voids are formed and their behavior as low shrink polyester is more efficient. Decreasing the initiator concentration from 1% to 0.1% resulted in a partially cured system consisting of much less blackened dispersed phase. The influence of cobalt naphthenate on the curing process is as expected, namely curing at higher rates and lower temperatures than without the accelerator. However, the final product appears to be similar to the one cured without the accelerator.

It has been observed that the curing process is influenced by the heating rate. Lowering the heating rate results in the beginning and completion of curing at lower temperatures. Although there are no significant differences in the amount of black areas observed in samples heated at the rates of 3 and 10°C/min, it seems as if the higher rate of heating results in a darker dispersed phase. This is probably due to relaxation processes which can take place at the lower curing rate.

Observations of fracture surfaces of identical systems cured at different temperatures, by scanning electron microscopy show that the voids in samples cured at the higher temperatures appear deeper and larger than those formed at the lower temperature.

An attempt was made to prove that the blackening of the dispersed phase, as is observed in the optical microscope, is a result of void formation. Resistivity measurements show differences among the various polyester systems, although in the expected direction but not large enough to be explained by void formation. Supporting data were obtained by ultrasonic energy absorption measurements, showing that the low shrink system (with voids) absorbed more energy than the regular one (without voids). In addition, assuming that voids are formed as a result of stress cracking, changes in the curing process affecting the stresses should also influence the shrinkage. For example, samples cured at a lower temperature shrink more and their ultrasonic energy absorption is

lower than that of the same composition cured at a higher temperature. As mentioned above, at lower curing rates some of the formed stresses can probably relax.

After summarizing our observations the following mechanism of the low shrink behavior of the two-phase unsaturated polyester systems is proposed:

1) The initial system exists as a two-phase mixture at room temperature. The continuous phase consists of the polyester, styrene and some of the thermoplastic additive. The dispersed phase consists of the thermoplastic additive and polyester in styrene.

2) Upon heating, crosslinking begins to take place in the continuous phase while the dispersed phase remains fluid since crosslinking in the latter is much slower than in the continuous phase. As a result, the concentration of unreacted styrene in the continuous phase decreases with time causing some migration of styrene from the droplets into the continuous phase. Crosslinking of the continuous phase would cause the system to shrink but thermal expansion of the monomeric styrene and thermoplastic additive, plus the styrene vapor pressure act to cancel out the shrinkage.

3) As the reaction in the dispersed phase begins, the polyester which has been crosslinked is no longer soluble in styrene and thus precipitates out of the solution. This is seen in the photomicrograph as a change from clear to opaque droplets.

4) On further heating, polymerization in the dispersed phase continues. Styrene, which is apparently in excess of the amount needed for crosslinking, can homopolymerize causing shrinkage of the droplet. The overall shrinkage tendencies coupled with the different thermal expansions create stresses within the droplets. The stresses increase upon further raising the system's temperature. The high unsaturation of the polyester generates a rigid material and causes, as a result of the developed stresses, microcracking rather than elastic deformation. These microcracks create voids which compensate for the polymerization shrinkage.

5) After polymerization in both phases is completed, further heating or cooling only results in thermal expansion or contraction. This can cause additional stresses and microcracking, but in much lower magnitudes than in the previous process.

It is therefore seen that there are two main mechanisms operating to reduce the shrinkage: (a) Polymerization shrinking of the continuous phase is compensated for vapor pressure of styrene and the thermal expansion of the other constituents; (b) Polymerization shrinking of the dispersed phase is compensated for by void formation in the dispersed phase.

This mechanism is supported also by dilatometric measurements of conventional and Paraplex P-19 resins during cure.[4,5] The volume vs. time curve of Paraplex P-19 consists of an extra peak which is a result of void formation, causing the sample to expand. After the first expansion peak (related to thermal expansion) there is some contraction, which is interpreted to occur when the curing of the dispersed phase begins. This contraction causes also stresses and thus crack formation. Increasing the cure temperature and/or decreasing the pressure results in an increase in this extra peak height while decreasing the temperature and/or increasing the pressure can even eliminate it.[5] This is clearly a result of the curing temperature and pressure dependence of the stress formation process. Polymerization at low temperatures minimizes thermal expansion resulting in no expansion differentials which can cause stress. At high pressures, greater stresses are needed in the material to create cracks and voids, hence the stresses generated are insufficient for this purpose.

The applicability of the proposed mechanism to low shrink behavior in single-phase systems was also studied. In single-phase systems there is only one polymerization rate but, nevertheless, its behavior is very similar to that of two-phase systems. The earlier polymerization shrinkage in the single-phase due to polyester crosslinking is also compensated for by thermal expansion of the other components. As the polyester shrinks further, stresses are induced throughout the system and the behavior is similar to that in the dispersed phase of a two-phase system. In this case, however, there is void formation throughout the sample. The high reactivity of the polyester raises its glass transition temperature assuring a rigid system and as a result crack formation and voids which compensate for the shrinkage of the polyester.

The advantage of the two-phase low profile polyester over the single-phase is in its mechanical properties. The continuous phase in the two-phase system is crack free and thus will have better properties than the single-phase material having cracks and voids throughout it. The single-phase system is superior in its ability to control shrinkage due to the larger volume of voids which develop through the whole material.

## Acknowledgement

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