

Heterogeneous Polymer-Polymer Composites. II. Preparation and Properties of Model Systems

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Synopsis

A two-stage emulsion polymerization procedure has been developed and used to prepare relatively uniform populations of heterogeneous acrylic latex particles (HLP). One class of particles (HLP1) can be described as composite materials comprising a glassy continuous phase and a rubbery discrete phase. Another class (HLP2) can be described (at high rubber content) as composite materials comprising a rubbery continuous phase and a glassy discrete phase. The phase structure of the HLP1 is sufficiently stable to allow fabrication of composites having a uniform spatial distribution of inclusions by direct compression molding. Although the observed particle structure of the HLP2 does not depend markedly on crosslinking, the phase structure and mechanical properties of compression moldings do. Crosslinking of the glassy stage appears to stabilize HLP2 phase structure during molding, while crosslinking of the rubbery stage favors phase inversion. The observed HLP2 particle structures and the morphology of molded HLP1 specimens are consistent with a shell-core model. It is found that the modulus and thermal expansion coefficient of many of these materials can be adequately described in terms of a simple theoretical model for the elastic and thermoelastic properties of particulate composites, provided that an interaction parameter interpreted as a maximum packing fraction is introduced.

INTRODUCTION

Many commercially important plastics are blends of incompatible polymers; high-impact polystyrene and many rubber and acrylic-modified poly(vinyl chloride) formulations are familiar examples. On the most elementary level, the physical properties of such materials are expected to follow simple volume-average mixing rules. More realistically, such physical parameters as phase geometry and morphology, which are characteristic of the composite itself rather than of its constituents, play an important role in determining composite properties. The effect of these parameters on viscoelastic properties has been discussed in a previous paper¹ on the basis of a theoretical model. Since the structure of conventional polymer blends is generally quite complex, it is difficult to assess the dependence of physical properties on individual parameters. Therefore, it is advantageous to develop model systems in which composite structure can be controlled.

This paper describes the preparation and properties of a number of acrylic polyblends prepared by multistage emulsion polymerization and

emulsion blending techniques. It has long been known that emulsion polymerization can yield heterogeneous products.² Indeed, synthetic polymer latexes can display heterogeneity on several levels.³ Thus, there may be interparticle variations in composition as well as intraparticle compositional gradients. Styrene-butadiene copolymerization, for example, can yield distinct and separable populations of particles having substantially different compositions.⁴ Also, a wide variety of intraparticle structural variations have been observed upon polymerizing styrene monomer in a styrene-butadiene latex.³ Although it has been suggested that styrene polymerizes more or less uniformly throughout rubber seed-latex particles,⁵ it has recently been demonstrated⁶ that even in the homopolymerization of styrene, the growing polymer particles are not homogeneous but consist of a polymer-rich core surrounded by a monomer-rich shell. In acrylic systems, it has been suggested on the basis of torsional modulus measurements that heterogeneous products are obtained in a two-stage polymerization.²

In this report, relatively uniform populations of heterogeneous particles, probably having a shell-core structure, are obtained by successive incremental addition of monomers in the emulsion polymerization of certain acrylic systems. The morphology of the latex particles and the physical properties of compression-molded specimens are examined.

EXPERIMENTAL

Polymerization and Molding Procedures

All polymers were prepared in emulsion employing commercial, low-inhibitor-grade acrylic monomers; sodium dodecyl sulfate and potassium persulfate were, respectively, the surfactant and the initiator used. For the two-stage incremental addition polymerizations, a seed latex was prepared starting with about 2 parts surfactant, 50 parts monomer, 2 parts initiator, and 700 parts water. Additional monomer (generally 100 to 400 parts) was added stepwise after initiation of the polymerization at 45°C. The rate of addition was adjusted to maintain the temperature at about 48° to 50°C. Upon completion of the first-stage polymerization process, 50 to 500 parts of a second monomer charge, of different composition, were added incrementally at a rate sufficient to maintain the temperature at 48° to 50°C. If additional surfactant was required to maintain the stability of the latex, it was dissolved in a small volume of water and added incrementally along with the second monomer charge. The polymerization was then taken to completion.

Two types of material were prepared by this procedure; both were intended to be polyblends comprising components of greatly different glass transition temperatures T_g . For convenience, the component of higher T_g is referred to subsequently as the glassy component, while that of lower T_g is referred to as the rubbery component. Unless otherwise noted, the glassy component was prepared from methyl methacrylate (MMA), while the rubbery component was prepared from a mixture comprising 95 mole-

% butyl acrylate (BA) and 5 mole-% 1,3-butylene dimethacrylate (BDMA). Heterogeneous latex particles in which the rubbery component was polymerized first are subsequently referred to as HLP1; particles for which the order of polymerization was reversed are referred to as HLP2.

Two additional types of material were prepared for comparison purposes. Physical blends were prepared by mixing latexes of separately polymerized glassy and rubbery components just prior to coagulation. Nominally random copolymers were prepared using essentially the procedure described for the HLP, except that the monomer feed composition was held constant throughout. Crosslinking monomers were omitted from the random copolymer formulations, but were included in the rubbery component of the physical blends.

Polymer solids were recovered by coagulation of latex in methanol; all products were washed repeatedly with methanol and water, isolated by filtration, and dried for at least 48 hr in vacuo.

Compression-molded sheets of about 0.060 in. in thickness were prepared using conventional procedures. Pressure was about 1000 psi; press temperature was chosen to ensure good fusion and ranged from room temperature for the more rubbery materials to 220°C for high molecular weight poly(methyl methacrylate) (PMMA). Good-quality surfaces were obtained by molding against photographic ferrotype tins treated with a light application of fluorocarbon release agent (Cadco Dry Lubricant Formula 61).

Electron Microscopy

Morphology of latex particles was examined in the transmission electron microscope. Specimens were prepared by spotting a highly diluted latex sample (ca. 0.01% solids in water) onto a parlodion substrate, shadowing with platinum at a 20° shadow angle, and coating with carbon. Microtomed thin sections of compression-molded specimens were also examined by transmission electron microscopy.

Thermal Expansion Coefficient

Thermal expansion coefficients were determined with the Perkin-Elmer Model TMS-1 thermomechanical analyzer. It was necessary to anneal the specimens before testing to overcome the effects of molded-in stresses; this was accomplished by heating the specimens to about 50°C above the T_g of the glassy component. Specimens were held at this temperature until dimensional equilibrium was attained and then cooled (at a rate equal to the test rate) to the desired minimum test temperature. Measurements of transition temperatures and expansion coefficients were made on the subsequent heating cycle with a programmed temperature rise of 5°C/min. Expansion coefficients could usually be reproduced to within 5%, transition temperatures of homogeneous materials, to within 5°C. The lower (rubbery component) transition temperature of heterogeneous

materials could not be accurately determined because of the small change in expansion coefficient at this transition.

Tensile Properties

Tensile properties were obtained using an Instron Universal Testing Machine. Tensile specimens of the usual dog-bone shape (length, 1.75 in., reduced gauge section 0.125 in. wide, nominal parallel gauge length 0.5 in.) were pulled at a cross-head speed of 0.02 in./min. Calculated values of modulus are based on an effective gauge length of 1 in., estimated on the basis of measurements using a clip-gauge extensometer.

For soft specimens, the modulus values reported are $|E^*|$, the absolute value of the complex dynamic Young's modulus, which were obtained using a Vibron Model DDV-II viscoelastometer. Temperature and frequency of measurement were 50°C and 110 Hz, respectively.

Optical Properties

Transmittance measurements were performed on specimens compression molded between photographic ferrotype plates. Measurements were made at 24°C against air using a Beckman Model DU spectrophotometer at 460 and 550 m μ . Refractive indices were determined using an Abbé refractometer following ASTM procedure D542-50. A saturated aqueous solution of zinc chloride was used as the contacting liquid.

RESULTS AND DISCUSSION

Morphology of Latex Particles and Molded Specimens

The particles produced by emulsion polymerization are usually perfectly spherical. The appearance of individual latex particles in the electron microscope is, however, dependent not only on the original shape of the latex particles but also on their composition and on specimen preparation conditions.³ During specimen preparation, polymer particles of sufficient rigidity maintain their spherical shape, while those of lower rigidity tend to flatten or spread and appear as oblate spheroids or spherical caps. Such differences in shape can be a useful guide to the composition of individual particles and hence to latex uniformity; they are readily revealed in the electron microscope by shadowing with evaporated metal. Heterogeneous particle structures can be studied directly by electron microscopy, provided there is a sufficient difference in density between the component phases. In some cases, structure is clearly revealed by shadowing.

When rubbery particles are used as seed latex particles for polymerization of MMA (i.e., for preparation of HLP1), there is a progressive and uniform change in the appearance of the particles. Figure 1 presents a series of micrographs obtained on latex specimens extracted at several stages of a two-stage polymerization. Very few new particles are formed during the addition of the second-stage monomer; also, the second-stage

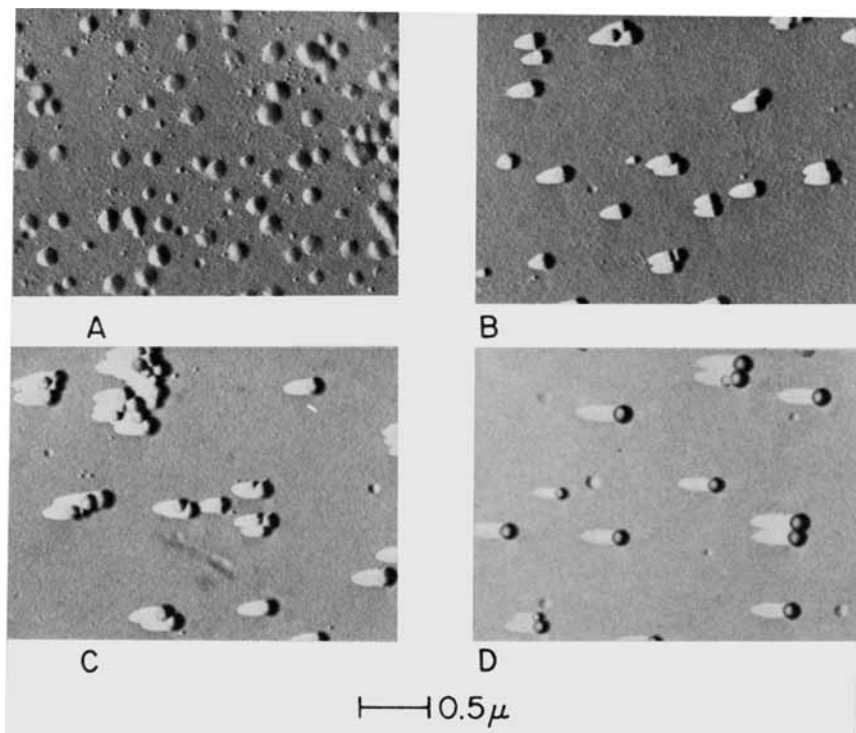


Fig. 1. Shadowed latex particles from various stages of an HPL1 synthesis: (A), rubber seed-latex particles; (B), (C), and (D), after addition of $1/3$, $2/3$, and all of the second-stage monomer. Final composition, 75G/25R.

monomer appears to be fairly uniformly distributed among the particles. The internal morphology of the particles is not, however, revealed. Direct examination of unshadowed HPL1 particles at high magnification (Fig. 2a) reveals what appears to be a shell-core morphology. However, a similar examination of homopolymer PMMA particles (Fig. 2b) reveals an essentially identical morphology. Microtomed sections of compression-molded specimens have also been examined by transmission electron microscopy; a preliminary exposure of the sections to xylene vapor results in the development of a uniform pattern of roughly spherical regions of about the same size as the rubber latex particles used as seed. (The original objective of the xylene treatment was simply to relax the sections to allow easier observation at high magnification. The observed enhancement of contrast is probably due to differential swelling of the two polymer phases.) The micrograph shown in Figure 3a was obtained on a xylene-treated 75G/25R HPL1 section; no structural features were observed in untreated sections. PMMA sections subjected to the same procedure displayed no texture. Figure 3b presents a micrograph of a xylene-treated 50G/50R physical blend section; the texture is much rougher, and there appear to be agglomerates of substantial size.

A broad range of HLP1 compositions has been prepared and studied in the electron microscope. Generally, the HLP1 display better dimensional stability than random copolymers of comparable composition. Also, the particles are generally uniform in appearance, and no details of internal

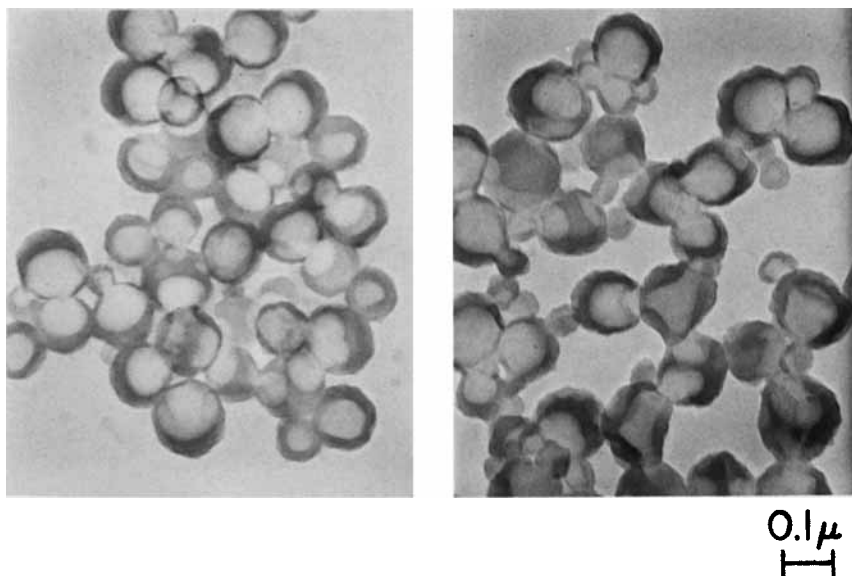


Fig. 2. Unshadowed latex particles of a 75G/25R HLP1 (A) and of PMMA (B).

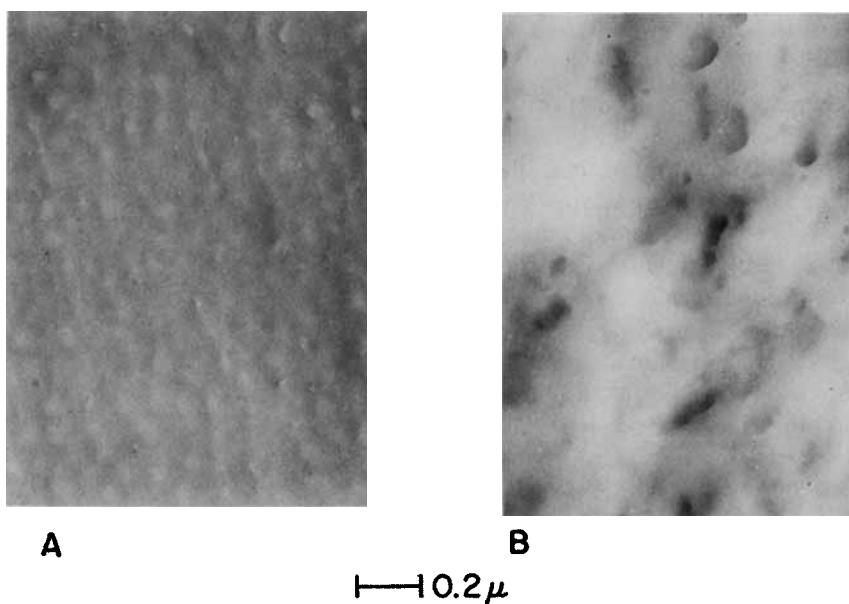


Fig. 3. Microtomed sections of compression-molded specimens: (A), 75G/25R HLP1; (B), 50G/50R physical blend.

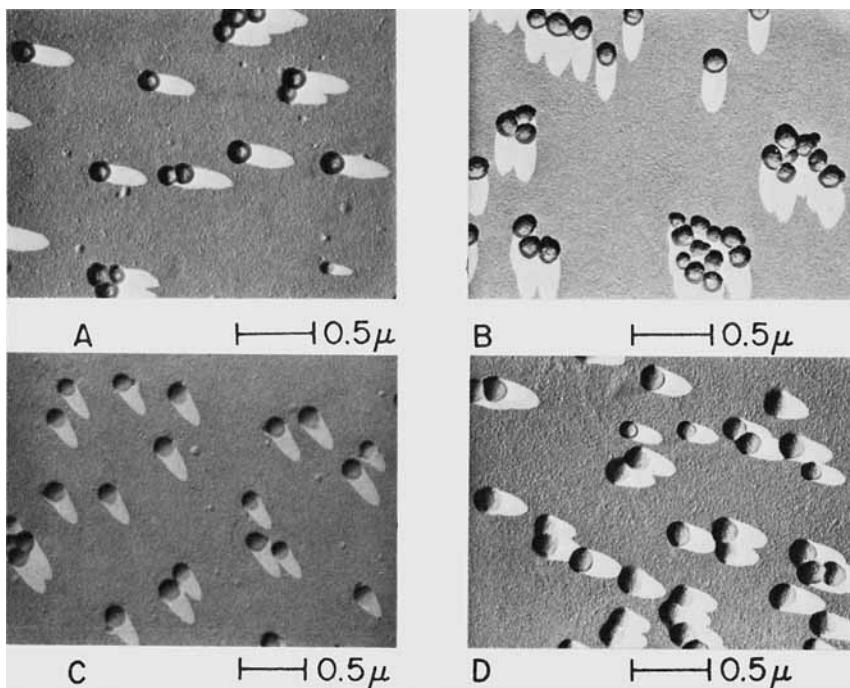


Fig. 4. Shadowed HLP1 latex particles: (A) and (B), 75G/25R; (C) and (D), 25G/75R; (A) and (C), first-stage monomer charge comprises 95 mole-% BA, 5 mole-% BDMA; (B) and (D), BDMA omitted from first stage.

morphology are revealed. An exception to these observations is noted at high rubber content (25G/75R): the observed morphology depends to some extent on the presence of a crosslinking comonomer in the first stage. As illustrated by Figure 4, the inclusion of a crosslinking comonomer in the rubber phase does not appear to make much difference at 75G/25R (Figs. 4a and 4b). At 25G/75R, the HLP1 particles based on crosslinked rubber particles (Fig. 4c) are uniform in appearance and are relatively dimensionally stable (random copolymers of comparable composition are similar in appearance to the rubber particles of Fig. 1a). Those based on uncrosslinked rubber particles (Fig. 4d) are less uniform; most are comparable to the particles of Figure 4c, but some are similar to the HLP2 discussed subsequently. It is not possible to state whether the variation in structure results during polymerization or later, during specimen preparation.

Figure 5 presents micrographs of a series of HLP2—particles prepared by polymerization of rubbery component monomers on a glassy seed latex. The particles of Figures 5a and 5c are based on a crosslinked glassy seed latex (prepared from a mixture containing 95 mole-% MMA and 5 mole-% BDMA); the second-stage monomer charge consisted of BA. The particles of Figures 5b and 5d are based on a PMMA latex; the second-stage monomer charge consisted of 95 mole-% BA and 5 mole-% BDMA.

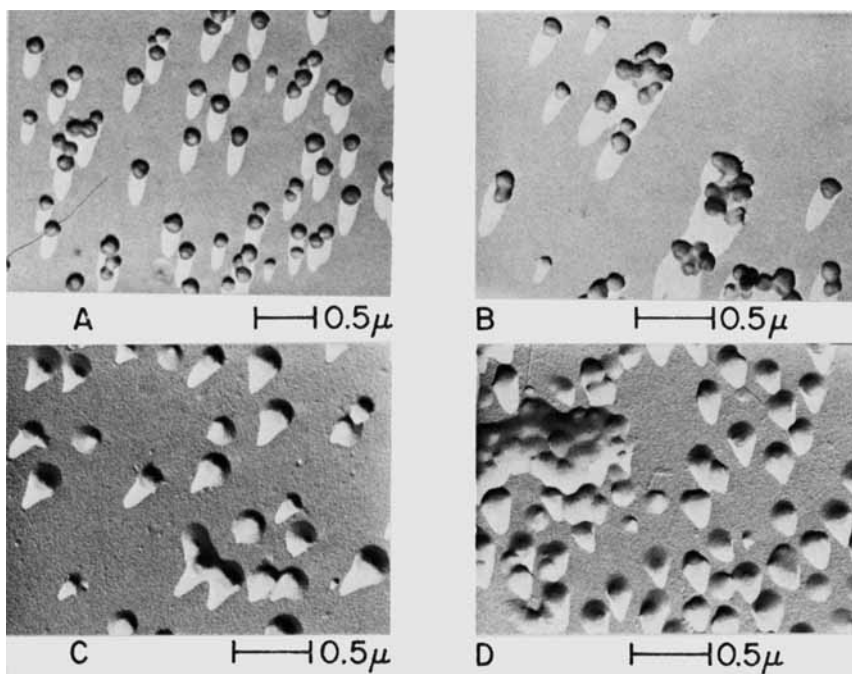


Fig. 5. Shadowed HLP2 latex particles: (A) and (B), 75G/25R; (C) and (D), 25G/75R; (A) and (C), first-stage monomer charge comprises 95 mole-% MMA and 5 mole-% BDMA, whereas second stage monomer is BA; (B) and (D), first-stage monomer is MMA, second-stage monomer charge comprises 95 mole-% BA and 5 mole-% BDMA.

The particles of Figure 5a are essentially indistinguishable from those of Figure 4a (both are 75G/25R). Those of Figure 5c (25G/75R) show a distinct intraparticle phase separation (note particle at center of figure, which apparently consists of a hard core surrounded by a less dimensionally stable material). There is also some interparticle variability, substantially more than observed for the HLP1. There does not appear to be much difference between the HLP2 incorporating a crosslinking comonomer in the first stage and those which include such a comonomer in the second stage.

In view of the microscopically observed particle structures, it is not surprising that HLP2 latexes tend to form continuous films at room temperature, whereas the HLP1 latexes tend not to. There are exceptions: at 75G/25R, HLP2 latexes do not form a continuous film, whereas at 25G/75R, HLP1 latexes do.

Although the results presented are consistent with a simple shell-core latex particle morphology, the possibility of a more complicated structure, as found, for example, by Kato³ for ABS latex particles, cannot be completely discounted for the present acrylic system. In the analysis of mechanical property data discussed in this and the subsequent paper,⁸

however, it has been found that the most satisfactory representation of all of the available data calls for assumption of simple shell-core morphology.

Physical Properties of Molded Specimens

Optical Properties

Compression-molded sheets of HLP1 and HLP2 show a remarkably high degree of clarity over the full range of compositions studied. Physical blends of similar composition and latex particle size are opaque; even blends of HLP1 of different rubber-to-glass ratio are quite hazy. The clarity of the HLP probably results in large measure from the small size of the included particles (the refractive indexes of the component polymers are not equal). The high turbidity of the physical blends is probably due to the presence of aggregates of particles, as suggested microscopically. Severe mechanical working (as by injection molding) of the HLP1 described so far results in a marked increase in haze; this result can also be explained in terms of the formation of particle aggregates, perhaps due to partial disruption of the particle structure.

Particle size effects on turbidity are clearly illustrated by a series of HLP1 of increasing rubber particle size. These materials were based on rubber seed latexes prepared by sequential seeded polymerizations in which rubber particle diameters were built up from about 250 Å to about 2000 Å in five stages. HLP1 of 75G/25R composition were prepared from three of these latexes; the results of transmittance measurements are summarized in Table I. Most of the HLP have first-stage particle sizes between those of samples 1 and 2, and thus are below the critical size for light scattering.

If the haze formation observed upon severe mechanical working is due to aggregate formation, then matching of the refractive indexes of the component phases should suppress the effect.⁷ As indicated in Figure 6, the refractive index of an HLP1 can be made equal to that of PMMA (prepared and molded in the same way) by incorporating about 18 to 20 mole-

TABLE I
Transmittance of Compression-Molded HLP1 Specimens

| Sample | Type | Rubber particle diameter, ^a Å | Transmittance at 24°C | |
|--------|-------------------|--|-----------------------|--------|
| | | | 550 mμ | 460 mμ |
| 1 | HLP1 | 250 | 0.88 | 0.86 |
| 2 | HLP1 | 700 | 0.83 | 0.65 |
| 3 | HLP1 | 2000 | 0.25 | 0.12 |
| 4 | PMMA ^b | | 0.91 | 0.90 |

^a Calculated from apparent diameter and shadow length assuming particles to be spherical caps. Value is number average of 150 to 200 measurements.

^b Rohm and Haas Plexiglas molding powder. Specimens prepared and measurements performed as for samples 1-3.

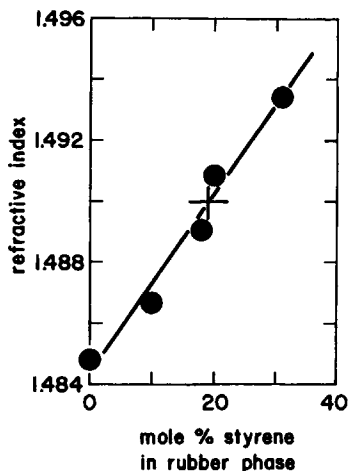


Fig. 6. Refractive index of 75G/25R HLP1 as a function of styrene content of rubber phase. Cross marks point at which HLP1 refractive index matches that of a comparable PMMA specimen.

% styrene in the rubber stage monomer charge. In fact, materials prepared in this way do not exhibit haze formation on mechanical working and can be mechanically blended with PMMA to obtain materials of relatively low haze. It is to be expected that materials of this type will develop haze at temperatures different from that at which the refractive indexes have been made equal as a result of the inequality of the temperature coefficient of refractive index (dn/dt) for glassy and rubbery polymers. Thus, at room temperature for PMMA, $dn/dt = 1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$, while for poly(butyl acrylate), $dn/dt = 3.3 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$. There may, however, be additional factors operative in these materials as there is qualitatively no change in their appearance upon immersion in liquid nitrogen or boiling water.

Tensile Modulus

Tensile modulus is sensitive to changes in phase morphology and structure and is therefore a particularly valuable tool for the study of heterogeneous systems. A detailed analysis of the dynamic Young's modulus of the materials described in this paper will appear subsequently.⁸ The present discussion is limited to an examination of the dependence of elastic modulus on composition and morphology.

Data are presented in Figure 7 for a range of physical blends of HLP1 and HLP2. For the purposes of this figure, volume fraction concentrations have been calculated from the known weight compositions and densities assuming volume additivity. For the HLP1 and HLP2, a correction to account for copolymerization of unreacted first-stage monomer with second-stage monomer is also required. A consideration of monomer reactivity ratios (see, e.g., ref. 9) leads us to conclude that the first-formed

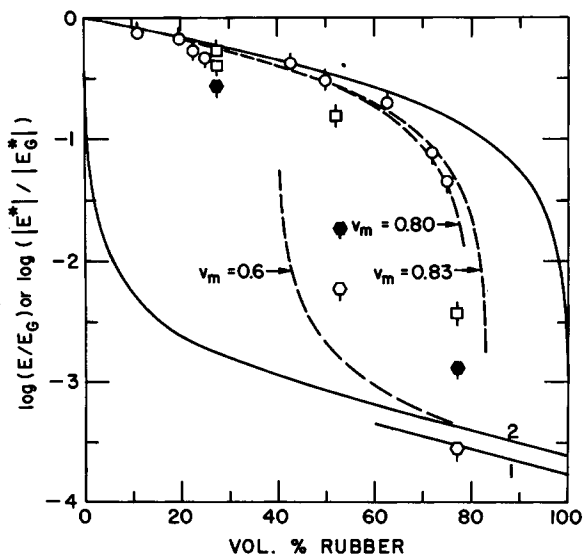


Fig. 7. Dependence of tensile modulus of compression-molded specimens on latex particle composition and type: E_G is Young's modulus of glass-phase polymer; open squares, physical blends; open circles, HLP1; open hexagons, HLP2 with BDMA in first stage; filled hexagons, HLP2 with BDMA in second stage; pip up, E/E_G ; pip down, $|E^*|/|E_G^*|$; solid curves, calculated from Kerner equation; curve 1, based on BA homopolymer data; curve 2, based on BA/BDMA copolymer data; broken curves, calculated from eq. (1) with v_m as noted.

polymer will be relatively rich in MMA. Taking into consideration the incremental addition process used for these polymerizations, it has been assumed that (1) for the HLP1, all of the unreacted first-stage monomer copolymerizes uniformly and randomly with the second-stage monomer; and (2) for the HLP2, the first stage monomer polymerizes completely as the homopolymer. These assumptions result in a correction both to the composition and to the modulus of the matrix for the HLP1. Matrix modulus values for the HLP1 have been estimated from the calculated composition and modulus measurements on random copolymers spanning the appropriate range of composition.

The modulus data are compared with the predictions of an equation derived by Kerner¹⁰ for the modulus of a dispersion of spherical grains in a continuous matrix, and with a modified form of this equation which introduces an interaction parameter in the form of a maximum packing fraction, v_m . The modified equation is

$$\frac{E}{E_m} = \frac{(1 - \psi v)E_m + \beta(\alpha + \psi v)E_i}{(1 + \alpha\psi v)E_m + \alpha\beta(1 - \psi v)E_i} \quad (1)$$

where E is Young's modulus; v is the volume concentration of inclusions; subscript m denotes a matrix property; subscript i denotes an inclusion property; α is a function of v_m , Poisson's ratio of the matrix,

$$\alpha = 2(4 - 5v_m)/(7 - 5v_m), \quad (2)$$

and β is given by

$$\beta = (1 + \nu_m)/(1 + \nu_i). \quad (3)$$

It is assumed that ν , Poisson's ratio of the composite is equal to ν_m . The maximum packing fraction v_m is introduced through the function ψ , which is required to satisfy the conditions

$$\psi v = 0 \text{ at } v = 0$$

$$d(\psi v)/dv = 1 \text{ at } v = 0$$

$$\psi v \simeq 1 \text{ at } v = v_m$$

$$\psi v = v \text{ at } v_m = 1.$$

The first two conditions are required so that eq. (1) reduces to the Einstein equation at small v ; the third, for approximate representation of observed behavior; and the fourth, so that the volume fraction dependence of the original Kerner equation is retained for v_m approaching unity, as in the case of very soft filler particles. One form for ψ which fulfills these requirements is

$$\psi = 1 + v(1 - v_m)/v_m^2. \quad (4)$$

This treatment of modulus in terms of an equation of the Kerner form, modified to include interaction effects, is similar to that proposed by Nielson,¹¹ but retains the symmetry with respect to phase inversion of the original Kerner treatment.

Data on the HLP1 can be quite well represented by assuming (1) that the molded composite comprises simple rubbery inclusions in a glassy matrix, and (2) that $0.8 \leq v_m \leq 0.83$. If the HLP2 are described as simple glassy inclusions in a rubbery matrix, then v_m should be about 0.6 (the value for rigid monodisperse spheres). However, only one point, for a 25G/75R HLP2 based on a crosslinked glassy particle, is nearly in agreement with this prediction. Data on the corresponding 50G/50R HLP2 could be brought into line by assuming $v_m \approx 0.5$; however, the loss tangent behavior of these materials is more consistent with the higher value of v_m and assumption of partial phase inversion.

The relative values of v_m imply that the interaction between soft inclusions in a hard matrix is weaker than that between hard inclusions in a soft matrix; if v_m is interpreted as a maximum packing fraction, then the higher value observed for soft particles may be due to the greater deformability of the inclusions.

The physical blends also go through a phase inversion, but always appear to consist of a continuous glass phase with composite rubbery inclusions. This somewhat curious result may be attributed to the fact that the rubber phase is crosslinked in emulsion giving the rubber particles substantial structural integrity even during molding. Similarly, HLP2 based on a PMMA latex with a crosslinked rubber second stage appear to

phase invert somewhat more readily than HLP2 based on a crosslinked glassy particle. A more detailed analysis of the phase inversion problem is given in reference 8.

Thermal Expansion Coefficient

The thermal expansion coefficient α of particulate composites generally is not as sensitive to changes in phase morphology and structure as tensile modulus; indeed, some of the equations which have been proposed for α are symmetric with respect to the phases. (Linear coefficients of expansion are reported; since the composites discussed are assumed to be isotropic, $\alpha_v = 3\alpha$, where α_v is the volumetric expansion coefficient.) Data obtained on the materials described in this report suggest, however, that there may be significant differences in expansion coefficients for materials of the same composition but different morphology. Figure 8 presents data on α as a function of composition and type of material. The data are compared with a theoretical expression derived by Kerner¹⁰ as a part of his treatment of the elastic and thermoelastic properties of composites. Schapery¹² has obtained the same expression by a different approach. For a two-phase material, Kerner's equation may be written in the form

$$\alpha = \alpha_m(1 - v) + \alpha_i v + (\alpha_m - \alpha_i)v(1 - v) (K_m - K_i) / [(1 - v)K_m + vK_i + (3K_m K_i / 4G_m)] \quad (5)$$

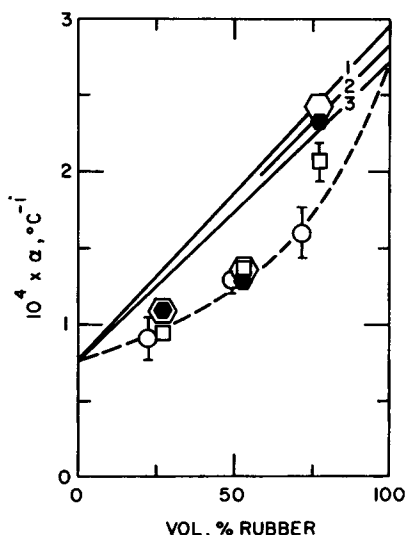


Fig. 8. Dependence of thermal expansion coefficient of compression-molded specimens on latex particle composition and type: open squares, physical blend; open circles, HLP1; open hexagons, HLP2 with BDMA in first stage; filled hexagons, HLP2 with BDMA in second stage; solid curves, rule of mixtures prediction for PMMA and (1) homopolymer BA, (2) BA/BDMA latex copolymer, or (3) cast BA/BDMA copolymer; broken curve calculated from eq. (5) as discussed in text.

where K is bulk modulus, G is shear modulus, and v is volume fraction of inclusions. As previously, subscript m denotes a matrix property, while subscript i denotes an inclusion property. Equation (5) can readily be written in terms of Poisson's ratios and Young's moduli; then it is found that, for simple rubbery inclusions, the calculated values of α are very sensitive to small changes in ν_i as ν_i approaches 0.5. The data on the HLP1 can be well represented by assuming that $\nu_i = 0.4998$, $\nu_m = 0.35$, and $E_m/E_i = .588 \times 10^3$. Values of α calculated for the simple glassy inclusion case differ insignificantly from the rule of mixtures. As might be expected from the tensile modulus behavior, data for the physical blends fall close to the simple rubbery inclusion curve, except at 75R/25G, where the experimental value is intermediate between the two calculated values. Also, the 75R/25G HLP2 data fall on the rule-of-mixtures prediction.

Presumably, the maximum packing fraction concept discussed with reference to modulus could also be introduced in the expression for thermal expansion coefficient; however, the data are not of sufficient accuracy to warrant this refinement.

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