

Studies on Heterogeneous Polymeric Systems. I. Influence of Morphology on Mechanical Properties

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Synopsis

Polybutadiene rubbers of well-defined and varying molecular weight were prepared by anionic polymerization and used in the preparation of mass-polymerized polystyrene blends. The particle size of the dispersed rubber phase was varied by (1) controlling the relative viscosity, at phase inversion, of the two liquid phases composed of polystyrene and polybutadiene in styrene monomer; (2) by varying the intensity of mixing, and (3) by adding preformed polystyrene to the prepolymer, prior to phase inversion. The mechanical and dynamic properties of the resulting blends are found to be determined mainly by the particle size of the dispersed rubber phase, independently from the method used to obtain such size. The weight fraction of rubber phase, rather than the weight fraction of rubber charged, is found to correlate with the blend modulus and may also affect its level of toughness. Low molecular weight rubbers are found capable of efficient blend reinforcement, if the excessively small rubber particle size obtained by conventional processes is enlarged by incorporation of preformed polystyrene prior to phase inversion.

INTRODUCTION

Most of the studies conducted on polyblends involve rubbers prepared by emulsion polymerization. The particle size of the dispersed rubber phase in the resulting blends is normally too small (smaller than 1 micron) for good resolution in a phase microscope. The rubber particles in these blends do not generally preserve the size possessed in the original rubber latex but appear to cluster or agglomerate, their final size being influenced by the time-temperature history of processing.¹

On the other end, blends prepared by mass polymerization in the presence of a dissolved rubber normally lead to a rubber phase dispersion which is better defined in shape and size. These blends were, therefore, chosen to study the influence of morphology on blend properties.

EXPERIMENTAL

Preparation of Rubbers

The polybutadiene (PBD) rubbers were prepared by conventional anionic homogeneous polymerizations in hexane by butyllithium (BuLi) initiation. The very stringent purity conditions adopted resulted in excellent

TABLE I
Comparison of Actual and Theoretical Molecular Weight for PBD

Intrinsic viscosity in toluene at 25°C	Actual $\bar{M}_n \times 10^{-5}$ (osmotic)	$\bar{M}_{nk} \times 10^{-5}$
2.55	2.06	2.20
2.12	1.62	1.60
2.12	1.62 ^a	1.60
1.32	0.89	1.00
1.40	0.98 ^a	1.00
0.98	0.65	0.60
0.91	0.61 ^a	0.60
1.27	0.90 ^a	0.90
1.29	0.91 ^a	0.90
1.73	1.26 ^a	1.20
1.72	1.25 ^a	1.20

^a Values obtained indirectly from $[\eta]-\bar{M}_n$ line.

duplication and control of molecular weight, as shown (Table I) by osmotic \bar{M}_n values corresponding to the kinetic number-average molecular weight \bar{M}_{nk} , where $\bar{M}_{nk} = \text{g BD/moles BuLi}$.

A typical charge would consist of 330 g hexane, 45–50 g BD, and 0.18–0.45 ml of a 15.1% BuLi solution in hexane. The polymerization cycle used consisted of 18 hr at 35–36°C, followed by 8 hr at 50°C. At the end of this cycle, the live anions were destroyed by charging deoxygenated isopropanol.

The osmotic \bar{M}_n values were found to fit the following relations:

$$[\eta] = 1.14 \times 10^{-4} [M_n]^{0.82}.$$

The above relation (Fig. 1) is compared with others given in the literature.^{2,3}

The rubbers obtained, protected with an antioxidant prior to exposure to the air, were gel free. They duplicated the microstructure assigned in the literature to polybutadienes prepared by this type of catalysis: about 46% *cis*-1,4; 44% *trans*-1,4; and 10% 1,2 isomer.

Preparation of Styrene Blends

Styrene monomer (93.5 parts) was polymerized at 110°C in the presence of polybutadiene (6.5 parts), 0.1 parts of di-*tert*-butyl peroxide, and 0.07 parts of *tert*-dodecyl mercaptan. Polymerization was conducted past phase inversion^{4–6} which occurred at 15% to 20% conversion, to about 30% conversion. The resulting syrup was then added to water and suspension polymerized⁷ at 140°C in a pressure reactor. The resulting suspension beads were washed, dried, and blended with small amounts of antioxidants and lubricants.

Processing and Testing

The suspension beads were extruded at 220°C into flat ribbons which were compression molded into a sheet. Strips cut from the sheet were

placed in a multiple-cavity flash mold die. Tensile and tensile impact test specimens were obtained by compression molding.

The grip-separation method was used for tensile property determinations. Due to the geometry of the test specimens, this always results in excessively large elongation at yield values and in excessively low Young's modulus values. A correction factor of about 2 is obtained by using a strain-gauge extensometer.

However, because of the fixed geometry of the test specimens and the careful duplication of grip separation in the test procedures, good duplication of test results is achieved and comparisons of mechanical properties are meaningful.

The L-shaped tensile-impact specimens were shaped according to ASTM specifications (D-1822).

Analytic Procedures

The degree of grafting (D.G.) of a rubber is defined as the number of parts of grafted polymer chemically attached to 100 parts of rubber backbone.

The D.G. is obtained by dispersing the blend in dimethylformamide (DMF), which is a solvent for the ungrafted matrix but a nonsolvent for the rubber and grafted rubber. A weighed sample (around 1.0 g) is placed in a centrifuge tube with 30–40 cc of solvent containing a small amount of

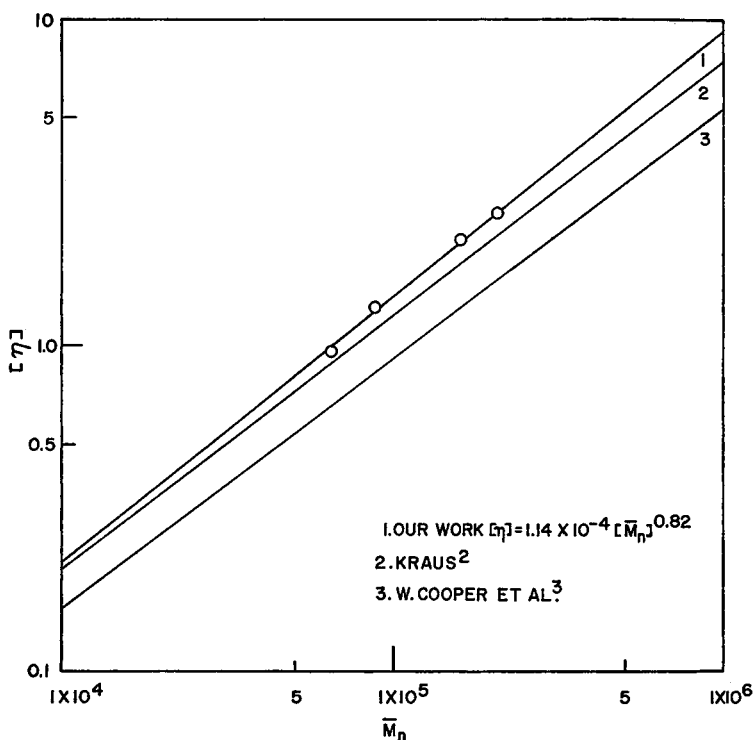


Fig. 1. Intrinsic viscosity- \bar{M}_n relationship for PBD prepared by BuLi initiation.

antioxidant. The polymer is placed on a Syntron vibrator for about 24 hr to insure complete dispersion and dissolution. The supernatant liquid layer is syringed off after 2-3 hr of centrifugation at 17,000 rpm (about 37,000 G's), and the residue is again reextracted in fresh solvent by exactly the same dispersing and centrifugation procedures previously described. Normally 3 or 4 centrifugation cycles are required to completely extract all soluble polymer, as shown by absence of clouding on addition of the supernatant liquid to methanol acidified with hydrochloric acid. Methanol is added to the residue in the tube in order to facilitate the removal of residual DMF, and the supernatant layer is again syringed off after a short centrifugation cycle. Residual solvents are removed under a good vacuum until a constant weight is obtained.

The weight of the residue minus the calculated weight of rubber in the original sample, divided by the calculated weight of rubber in the original sample, gives the D.G. value.

Per Cent Gel in Grafted Rubber

The dry residue obtained above is subjected to the same cycles of dispersion followed by high-speed centrifugation in toluene (containing a small amount of antioxidant) which dissolves any soluble rubber or rubber graft, while leaving behind any crosslinked rubber and rubber graft. The weight of this insoluble residue, after toluene removal, divided by the weight of the residue prior to toluene extraction, gives the % gel. Polystyrene occlusions as later discussed, are not extracted by this procedure.

Blend Morphology

The internal structure of the blends was determined by dark-phase contrast microscopy. Phase morphology was followed during the course of prepolymerization in order to establish the time of phase inversion and the structure and size of the dispersed rubber phase. This was accomplished by placing a very small amount of syrup between two glass slides. The blends obtained after processing were examined by using conventional microtoming techniques. The rubber, being of lower refractive index, appears in the photos as light in color, while the matrix of higher refractive index appears as the dark phase.

DISCUSSION

The polybutadiene (PBD) rubbers used in our work were prepared by anionic polymerization and had sharp and well-defined molecular weight (Table I) and microstructure.

The blends were obtained by mass-polymerizing styrene monomer in the presence of dissolved PBD. Initially one has a homogeneous solution of rubber in styrene monomer. As polymerization of styrene reaches a low degree of conversion, two immiscible liquid phases are obtained (Dobry effect) of PBD dissolved in styrene monomer (PBD-S) and polystyrene (PS)

dissolved in styrene monomer (PS-S). Initially, the PBD-S phase is the continuous phase and the PS-S is the dispersed phase. As polymerization progresses to about 15% to 20% polystyrene conversion, phase inversion takes place, with the rubber in styrene monomer solution becoming the dispersed phase (Fig. 2).

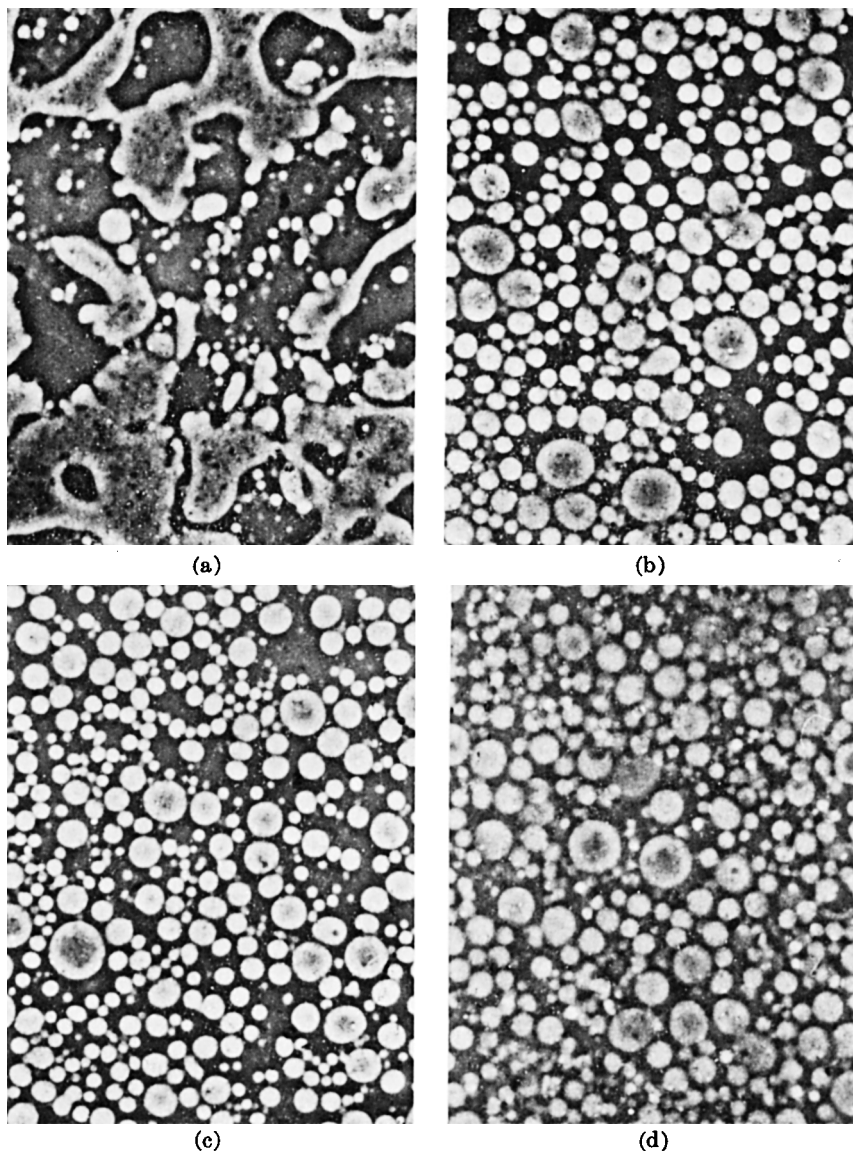


Fig. 2. Morphologic change with conversion for blends prepared by mass polymerization of styrene in the presence of PBD (640 \times): light phase = PBD; dark phase = PS): (a) at phase inversion; (b) $1/2$ hr after phase inversion; (c) 3 hr after phase inversion; (d) following blend extrusion and molding.

The occurrence of phase inversion during mass polymerization of styrene in the presence of rubber was first described in the patent literature by Nemphos, Paradis, and Walter.⁴ Later, Bender⁵ and Molau⁶ described in detail the effect of agitation on phase inversion and the function of the rubber graft as a dispersant and stabilizer for the rubber dispersion. A detailed description of the mechanism of formation of rubber particles and of the type of occlusions formed in the rubber dispersion was given by Molau and Keskkula.⁸

The particle size of the rubber dispersion, at a given rate of mixing, is found, as one could predict from the work of Rumscheidt and Mason,⁹ to depend on the ratio of the viscosity of the PS-S phase over the viscosity of the PBD-S phase at phase inversion or shortly thereafter. Bender⁵ had also indicated that the particle size of the rubber dispersion was related to the viscosity of the initial rubber solution in styrene.

The larger this ratio of PS-S/PBD-S viscosities, the smaller is the rubber-phase particle size. This ratio and, therefore, the rubber size can be controlled by (1) varying the molecular weight of the rubber while keeping the PS molecular weight constant, or (2) by varying the molecular weight of PS during the initial stage of polymerization leading to phase inversion while using the same rubber.

The first alternative is to be preferred and was adopted in our work. For the second alternative, variations of PS molecular weight require adjusting the polymerization temperature or the concentration of chain-transfer agent which would make the results ambiguous by affecting particle size through changes in interfacial tension in addition to changes in PS phase viscosity. Chain-transfer agents were, in fact, found to influence the efficiency and rate of formation of the PS-PBD graft copolymers which reduce rubber phase particle size, presumably by reducing interfacial tension.

For the polymerization blends here described, the extent of rubber grafting at the critical phase inversion region was found to be fairly constant, with approximately 25 to 30 parts of PS being grafted upon 100 parts of rubber.

Blend Properties

To study the response of polyblend properties to varying \bar{M}_n of PBD, every effort was made to maintain all variables constant (i.e., initiator and chain-transfer agent concentration, polymerization conditions, temperature, and cycle).

All blends were processed by the same extrusion conditions and, to avoid orientation, all test specimens were formed by compression molding.

Good correlation was found between the molecular weight of the PBD used and the particle size of the rubber phase dispersion in the resulting blend (Fig. 3). The mechanical properties of the blends are intimately related to the particle size of the rubber phase dispersion in the final blend (Figs. 4-6).

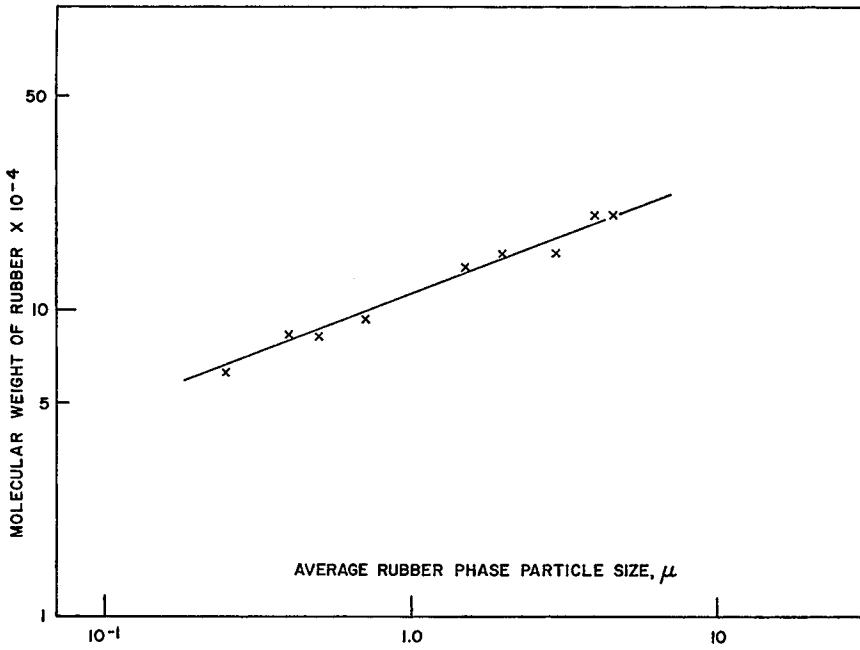


Fig. 3. Molecular weight of PBD vs. particle size of rubber phase.

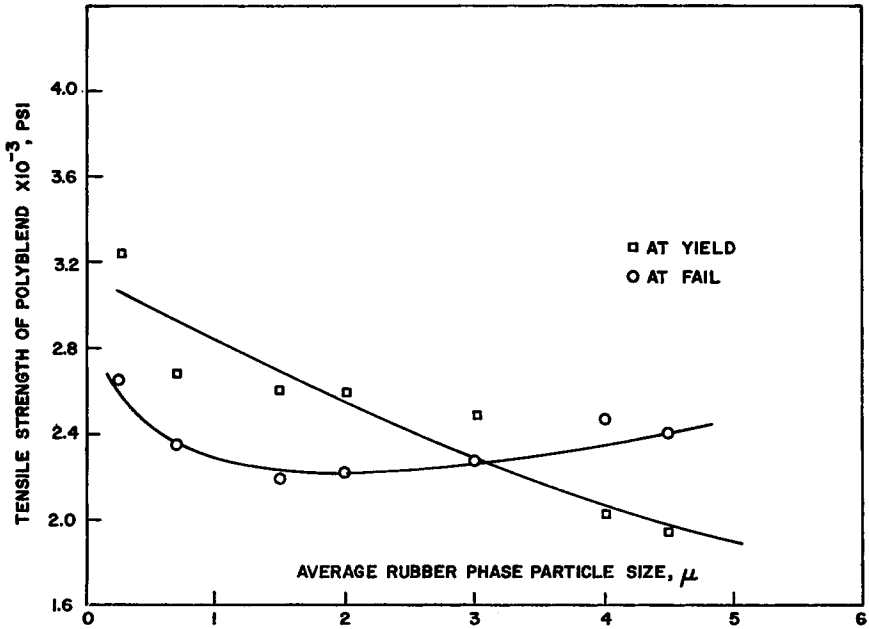


Fig. 4. Tensile properties of blends vs. rubber phase particle size.

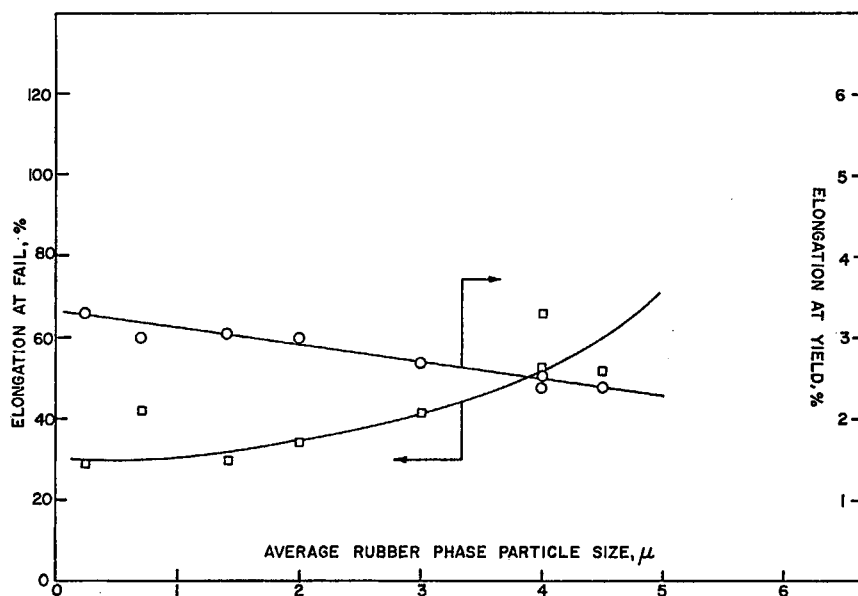


Fig. 5. Elongation of blends vs. rubber-phase particle size.

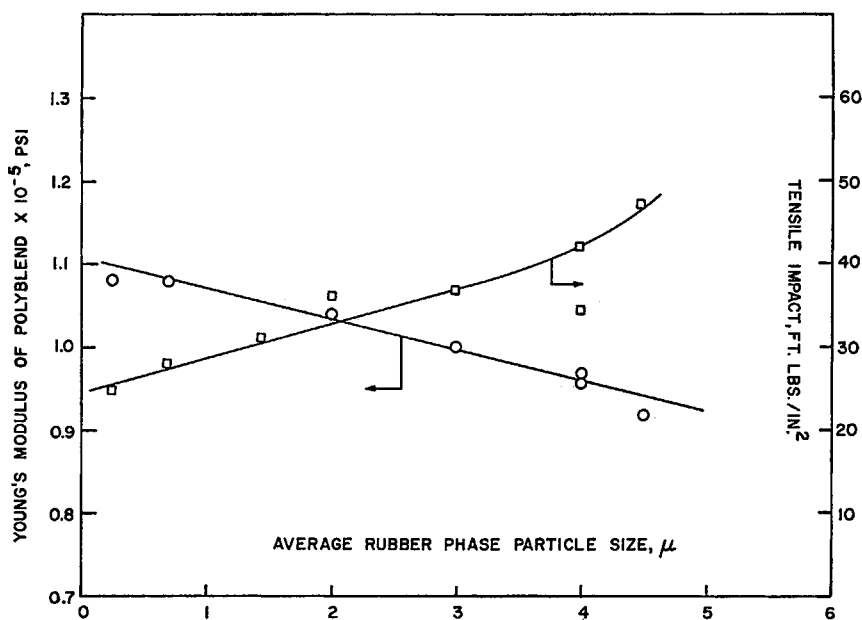


Fig. 6. Young's modulus and tensile impact strength of blends vs. rubber-phase particle size.

With decreasing molecular weight of the rubber, the following trends are observed: (1) a marked decrease in the particle size of the dispersed rubber phase, a linear relationship being obtained in a logarithmic plot; (2) a

steady decrease in toughness (tensile-impact strength); (3) a steady decrease in elongation at fail and increase in elongation at yield; (4) an increase in tensile strength at yield; (5) a steady increase in Young's modulus.

The fact that the mechanical properties of the blends could be equally related to the molecular weight of the rubber and to the particle size of the dispersed rubber phase raised the question of which one was the controlling factor. In order to separate the two effects, blends of varying rubber-phase particle size were produced by subdividing a common syrup, which was well past phase inversion, into three separate parts. One part was used as such. The other two parts were exposed separately to high mixing intensity, under nitrogen, in an Eppenbach homogenizer (for 5 and 10 min, respectively), with resulting marked reduction in rubber-phase particle size. All three syrups were then polymerized to completion by normal polymerization cycles.

The results of Table II show that the rubber-phase particle size influences the blend properties in the same manner as previously described. The mechanical properties of the blends obtained by high-intensity mixing are similar to those of comparable particle size obtained by varying the molecular weight of the rubber at constant rate of mixing. It can, therefore, be concluded that the particle size of the rubber phase, rather than the molecular weight of the rubber, is responsible for the properties of the blends.

TABLE II
Effect of Intensity of Mixing on Rubber-Phase Particle Size and Polyblend Properties^a

Time of mixing, min	Range of Rubber-particle size, μ	Average rubber-particle size, μ	Tensile stress, psi		Elongation, %		Tensile impact, ft lb/in. ²
			Yield	Fail	Yield	Fail	
0	2-10	4	2100	2250	2.9	35	40
5	1-3	1.5	2770	2220	3.4	18	28
10	0.5-1	0.7	2860	2260	3.5	8	20

^a Rubber content in blends 6.5%.

Polyblends Prepared by Polystyrene "Premixing Technique"

Use of low molecular weight rubbers (about 60,000 \bar{M}_n), under the experimental conditions used in our work, resulted in mass-polymerization blends of submicron rubber-phase particle size (Fig. 7d) and, consequently, of very poor toughness. It was of interest to answer the question of whether the poor blend properties were exclusively the result of small rubber-phase particle size or of the inherent inability of a low molecular weight rubber to impart toughness to a blend.

To this end, normal prepolymerization procedures were modified by mechanically mixing a solution of PS (220,000 \bar{M}_n) in styrene with the rubber in styrene solution prior to initiating prepolymerization.¹⁰ The amount of PS premixed in the charge corresponded to a level of 15-20%

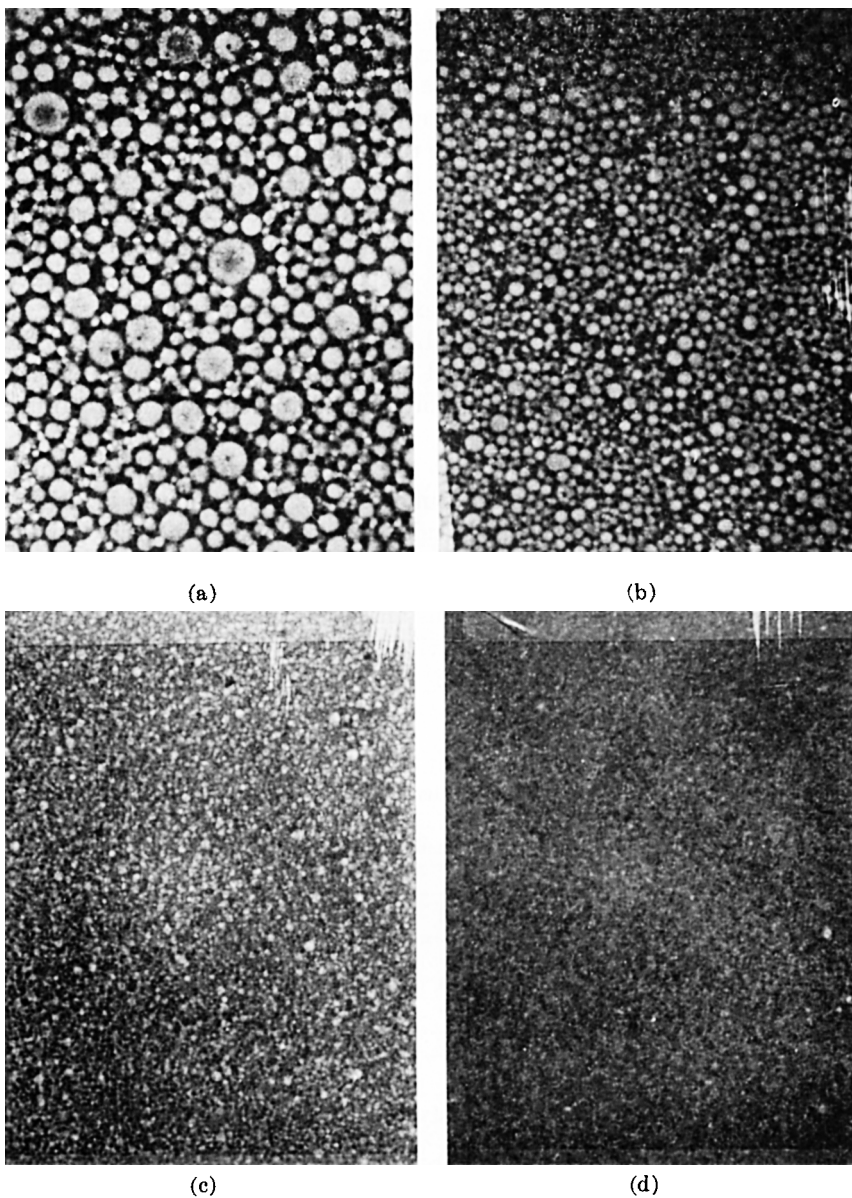


Fig. 7. Effect of rubber molecular weight on rubber-phase particle size ($640\times$): light phase = rubber; dark phase = polystyrene; (a) $\bar{M}_n = 207,000$; (b) $\bar{M}_n = 151,000$; (c) $\bar{M}_n = 93,000$; (d) $\bar{M}_n = 63,000$.

styrene conversion, which normally coincides with the incipient phase-inversion point. Prepolymerization was then continued to about 30–32% conversion (it includes the PS used in premixing), and polymerization was completed by suspension polymerization. This procedure leads to blends in which the resulting rubber-phase particles are considerably larger than

those obtainable in the absence of premixed PS (Table III). This is apparent when comparing the morphology of blends prepared with the same rubber, with and without PS premixing (compare Fig. 8a with Fig. 7d and Fig. 8b with Fig. 7c).

Blends obtained by using low molecular weight rubbers in conjunction with the "premixing technique" are found (Table III) to give blends of mechanical properties comparable to those of equivalent particle size ob-

TABLE III
Comparison of Rubber-Phase Particle Size as Obtained by Normal Mass Polymerization and by "Premixing Technique"

Molecular weight of rubber (\bar{M}_n)	Rubber-phase particle size diameter, μ		Properties of blends obtained by PS premixing	
	Normal prepolymerization	Premixing technique ^a	Tensile @ fail, psi	Elongation @ fail, %
63,000	0.2-0.4 (av. 0.3)	0.5-5 (av. 2) ^b	2180	27
83,000	0.4-1.0 (av. 0.6)	2-8 (av. 4) ^b	2090	40
93,000	0.5-1.0 (av. 0.7)	1-4 (av. 3) ^c	2140	39
155,000	2-5 (av. 3.5)	2-12 (av. 5.5) ^c	2230	51

^a The PS used in premixing had a \bar{M}_v of 220,000.

^b The amount of PS premixed is equivalent to a styrene conversion of 19.6%.

^c The amount of PS premixed is equivalent to a styrene conversion of 15%.

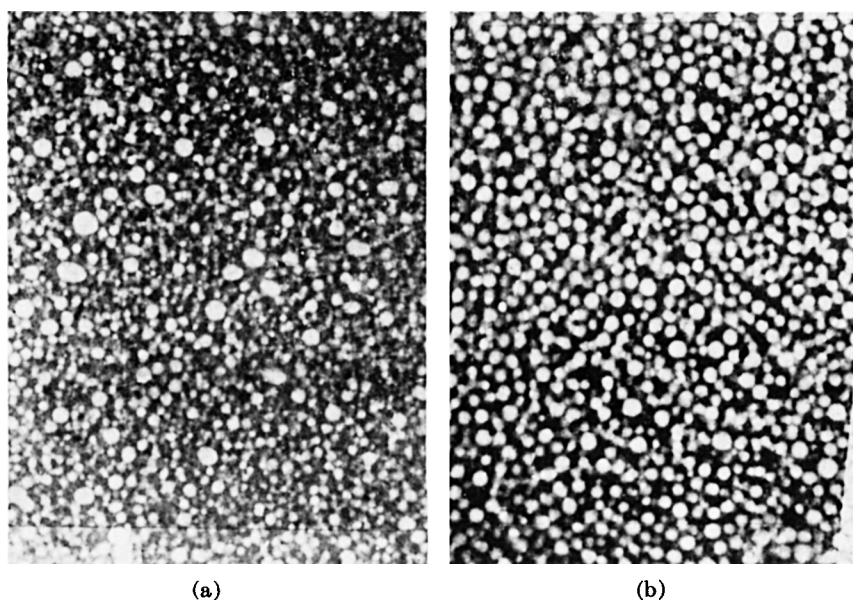


Fig. 8. Effect of premixing PS ($\bar{M}_v = 220,000$), prior to phase inversion, on rubber-phase particle size ($640\times$): (a) PDB = 63,000 \bar{M}_n ; (b) PDB = 93,000 \bar{M}_n .

tained by normal prepolymerization procedures. Thus, rubbers of low molecular weight are capable of full blend reinforcement, if particle size is controlled.

It can be concluded that the mechanical properties of the blends are mainly determined by the particle size of the dispersed rubber phase, independently from the method used to obtain such size, i.e., by control of relative viscosity of phases, or by varying the intensity of mixing, or by the premixing technique.

Phase inversion takes place at about the same concentration of PS in the system, independently from whether the PS is formed in situ during prepolymerization or by dissolving preformed polymer. However, only in the case of in situ prepolymerization considerable grafting can take place by the time-phase inversion is reached because of sufficient exposure time of the rubber to styrene polymerization. Thus, the larger rubber-phase particle size obtained by the "premixing technique" probably derives from the higher interfacial tension between the two liquid phases at phase inversion due to the lower concentration of surface-active graft. Some grafting, however, was found necessary prior to phase inversion to stabilize the dispersion and prevent some phase reinversion in the later stages of polymerization.

Morphology of Blends

The morphology of the blends was followed by phase-contrast microscopy throughout polymerization and also after extrusion and molding. The particle size of the dispersed rubber phase is set shortly after phase inversion and remains essentially unchanged (Fig. 2) throughout polymerization and subsequent processing and molding.

The effect of using rubbers of varying molecular weight on rubber-phase particle size in a final blend is shown in Figure 7.

Degree of Grafting and Per Cent Gel in the Blends

The degree of grafting was obtained by dispersing the blend in dimethylformamide (DMF), which is a solvent for PS but a nonsolvent for the rubber and rubber graft, and by separation of the supernatant layer by repeated high-speed centrifugation. The residue was then extracted by repeated centrifugation with toluene, which greatly swells the residue and dissolves any soluble rubber or rubber graft, or trapped polystyrene. From Table IV it can be seen that essentially all the residue from DMF extraction is insoluble in toluene and that PS occlusions of type I or II by Molau and Keskkula⁸ are either unextracted or chemically bound to the crosslinked rubber network. (Type I are occlusions formed by entrapment of the PS-S solution at phase inversion, while type II are occlusions resulting from phase separation of PS polymerized within the rubber phase following phase inversion.)

The % gel in the blends, containing an equivalent amount of PBD rubber, is found to increase with increasing rubber-phase particle size. The higher gel content in the larger rubber particles may result from two possi-

TABLE IV
Extent of Rubber Grafting and Crosslinking in Final Blends^a

\bar{M}_v of rubber used	Rubber-phase average size, μ	Parts PS grafted per parts 100 rubber (DMF-insoluble)	Rubber graft insoluble in toluene, %	Gel ^b in final blend, %
63,000	0.3	175; 169	97	17.2
151,000	3.0	207; 207	98.4; 98.0	19.6
175,000	4.0	221	97	20.2
207,000	4.5	232; 230	97.9; 96.7	20.9

^a Blends contain 6.5% PBD.

^b Per cent of original blend unextracted by successive DMF and toluene extractions.

ble mechanisms: (1) the PS occlusions formed during phase inversion (type I) have a smaller probability of escaping from a larger rubber particle into the continuous phase (this is simply the result of fewer occlusions being near the interface in the larger rubber particles), or (2) the size of the particles, as previously discussed, increases with increasing \bar{M}_v and viscosity of the rubber solution. The higher viscosity of the rubber phase in the larger particles could be responsible for longer graft chain length because of reduced rate of termination (gel effect) and/or to a more difficult escape of occluded PS from the particles.

Our results are in agreement with those of Cigna¹¹ who showed that the shear modulus of the blends correlates with the rubber-phase amount (i.e., rubber graft and occlusions) and not with the amount of rubber charged. Table V shows that the amount of rubber phase in our blends correlates with Young's modulus and the shear modulus. The excessively low Young's modulus values of Table V results, as indicated in the experimental section, from the grip-separation test method used in our work.

TABLE V
Effect of Rubber-Phase Content on Blend Modulus^a

Rubber-phase av. diam., μ	Gel in blend, %	Young's modulus, psi $\times 10^{-5}$	Shear modulus, psi $\times 10^{-5}$
0.3	17.2	1.1	1.25
3.0	19.6	1.0	1.0
4.0	20.2	0.97	—
4.5	20.9	0.92	0.80

^a All blends contain 6.5% PBD.

The important conclusion from these results is that the polystyrene occlusions in the rubber increase the effective volume of the rubber phase (i.e., rubber and occlusions). This leads to lower modulus values and higher impact strength values than expected from the amount of rubber charged to the blend.

Dynamic Mechanical Properties

A few polyblends were selected for dynamic testing on the basis of their large diversity of rubber-phase particle size and mechanical properties. All blends had been prepared from PBD rubbers under identical polymerization conditions, and they all contained 6.5% rubber. The dynamic properties are found in Figure 9.

The height of the damping peak of the rubber transition was found to correlate well with blend toughness, as measured by energy absorbed in a tensile-impact test. The area of the damping curve, in the region of the rubber transition, apparently reflects the amount of energy which can be dissipated by the rubber phase in the blend¹² and does not depend on the amount of rubber present in the blend. No correlation, however, can be

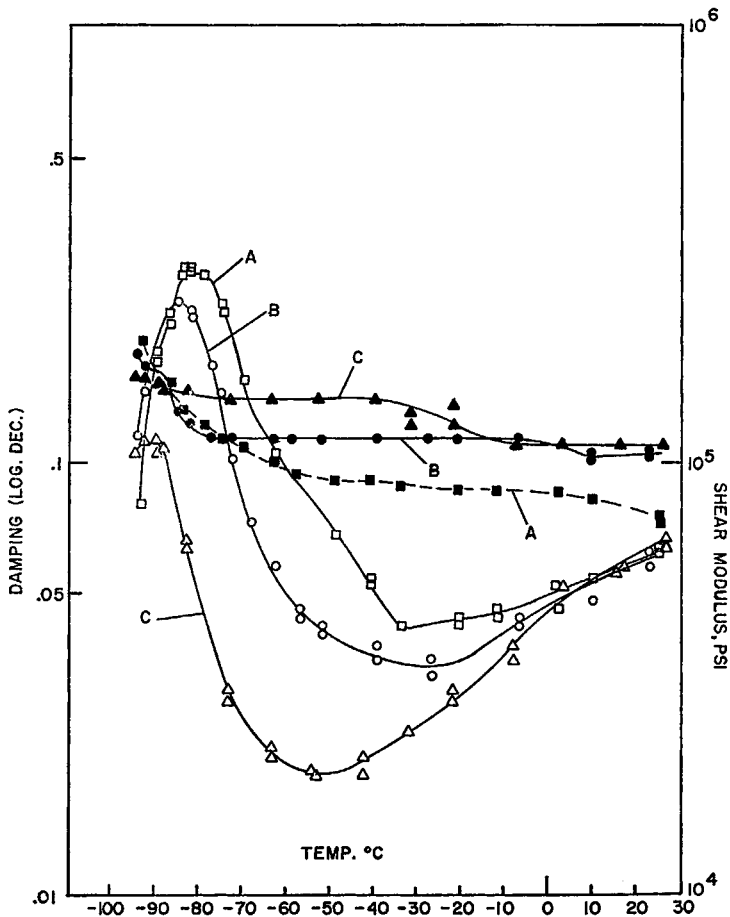


Fig. 9. Effect of rubber-phase particle size on the dynamic properties of PS polyblends: A = 4.5 μ (\bar{M}_n of PBD = 207,000); B = 3.0 μ (\bar{M}_n of PBD = 151,000); C = ~ 0.4 μ (\bar{M}_n of PBD = 84,000); open symbols = damping; closed symbols = shear modulus.

found between room-temperature damping values and room-temperature toughness.

The blends used in the dynamic measurements of Figure 9 range from 17% to 21% in rubber-phase content (% gel in the blend), as shown in Table IV. Such small variations in rubber-phase content are not sufficient to explain the very large differences in the corresponding damping maxima.

The observed large variations in rubber-transition damping area and corresponding blend toughness must, therefore, be mainly attributed to the effect of rubber-phase particle size.

The rubber-transition temperature appears to increase with increasing particle size. While the shift is small, it may be significant. It may reflect the more extensive grafting observed with the blends of larger rubber-particle size since simple PS occlusions in a rubber continuum would not be expected to shift the T_g of the rubber.

The shear modulus of the blends follows the previously discussed trend of increased modulus with decreasing rubber-phase particle size.

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