Registry No. Homopolystyrene, 9003-53-6; butadiene–styrene copolymer, 9003-55-8.

References and Notes

(1) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(2) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.
(3) Fujimura, M.; Hashimoto, H.; Kurashashi, K.; Hashimoto, T.; Kawai, H. *Macromolecules* **1981**, *14*, 1196.
(4) Hashimoto, H.; Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1981**, *15*, 844.
(5) Hashimoto, T.; Shibayama, M.; Kawai, H. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23* (1), 21.
(6) Hashimoto, T.; Todo, A.; Itoi, H.; Kawai, H. *Macromolecules* **1977**, *10* (2), 377.
(7) Helfand, E.; Wasserman, Z. *Macromolecules* **1978**, *11*, 960.
(8) Bates, F. S.; Berney, C. V.; Cohen, R. E.; Wignall, G. D. *Polymer* **1983**, *24*, 519.
(9) Bates, F. S. Sc.D. Thesis, Massachusetts Institute of Technology, 1982.
(10) Eppley, R. L.; Dixon, J. A. *J. Organomet. Chem.* **1967**, *8*, 176.
(11) Geerts, J.; Van Beylen, M.; Smets, G. *J. Polym. Sci., Part A-1* **1969**, *7*, 2805.
(12) Bates, F. S.; Cohen, R. E. *Macromolecules* **1981**, *14*, 881.
(13) Ramos, A. R.; Cohen, R. E. *Polym. Eng. Sci.* **1977**, *17*, 639.
(14) Kato, K. *Polym. Lett.* **1966**, *4*, 35.
(15) Koehler, W. C.; Hendricks, R. W.; Childs, H. R.; King, S. P.; Lin, S. S.; Wignal, G. D. "Scattering Techniques Applied to Supramolecular Systems"; Chen, S., Chu, B., Nossal, R., Eds.; Plenum Press: New York, 1981.
(16) Berney, C. V.; Bates, F. S.; Cohen, R. E. *Polymer* **1982**, *23*, 1222.
(17) Koberstein, J. T.; Morra, B.; Stein, R. S. *J. Appl. Crystallogr.* **1980**, *13*, 34.
(18) Ruland, W. *J. Appl. Crystallogr.* **1971**, *4*, 70.
(19) Helfand, E.; Wasserman, Z. R. "Developments in Block Copolymers"; Goodman, I., Ed.; Applied Science Publishers, Ltd., London, 1982; Chapter 4.
(20) Vonk, E. G. *J. Appl. Cryst.* **1973**, *6*, 81.
(21) Ruland, W. *Colloid Polym. Sci.* **1977**, *255* (5), 417.
(22) Wignall, G. D., personal communication.
(23) Guinier, A.; Fournet, G. "Small-Angle Scattering of X-Rays"; Wiley: New York, 1955.
(24) Hosemann, R.; Bagchi, S. N. "Direct Analysis of Diffraction by Matter"; North Holland Publishing Co.: Amsterdam, 1962.
(25) Cohen, J. B. "Diffraction Methods in Material Science"; Macmillan: New York, 1966.
(26) Bates, F. S.; Cohen, R. E.; Berney, C. V. *Macromolecules* **1982**, *15*, 589.
(27) Warren, B. E. *J. Appl. Crystallogr.* **1978**, *11*, 695.
(28) Schelten, J.; Schmatz, W. *J. Appl. Crystallogr.* **1980**, *13*, 385.
(29) Leary, D. F.; Williams, M. C. *Polym. Lett.* **1970**, *8*, 335.
(30) Leary, D. F.; Williams, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 345.
(31) Leary, D. F.; Williams, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 265.
(32) Helfand, E.; Tagami, Y. *Polym. Lett.* **1971**, *9*, 741.
(33) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1971**, *56*, 3592.
(34) Helfand, E.; Sapse, A. M. *J. Chem. Phys.* **1975**, *62*, 1327.
(35) Roe, R.-J.; Zin, W.-C. *Macromolecules* **1980**, *13*, 1221.
(36) Meier, D. J. *Polym. Prepn., Am. Chem. Soc., Div. Polym. Chem.* **1974**, *15*, 171.
(37) Rounds, N. A. Doctoral Dissertation, University of Akron, 1971.
(38) Cohen, R. E.; Wilfong, D. E., *Macromolecules* **1982**, *15*, 370.
(39) Stribeck, N. Ph.D. Dissertation, Phillips-Universität, Marburg/Lahn, 1980.
(40) Pico, E. R.; Williams, M. C. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1585.
(41) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

Dynamic Mechanical Properties of Polystyrene Containing Microspherical Inclusions of Polybutadiene: Influence of Domain Boundaries and Rubber Molecular Weight

Frank S. Bates,† R. E. Cohen,* and A. S. Argon

Department of Chemical Engineering and Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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ABSTRACT: A model set of well-characterized anionically polymerized diblock copolymer–homopolymer blends was prepared from styrene and butadiene. These materials contain microspherical polybutadiene domains whose phase boundary thickness, size, size distribution, and spatial packing are all known from previous electron microscopy and small-angle neutron scattering studies of the same set of samples. Dynamic mechanical properties were determined in a tensile mode at 3.5 Hz between −140 and +110 °C. Increasing the volume fraction of interfacial material in these composites produces no change in the storage modulus and a small increase in the level of viscoelastic loss in the region between the pure-component glass transition temperatures. Inclusion of polybutadiene in a glassy polystyrene matrix results in a significant lowering of the rubber glass transition temperature, T_g^B, which can be explained on the basis of negative pressure resulting from differential contraction. Composites containing lower molecular weight polybutadienes exhibit smaller T_g^B depressions, suggesting the possibility of cavitation in the rubber in these materials.

Introduction

Although the dynamic mechanical behavior of block copolymers and polymer blends comprised of polystyrene and polybutadiene has been widely investigated, clear interpretation of the mechanical results has often been impossible owing to the lack of extensive molecular, interfacial, and morphological characterization data on the full set of samples under investigation. Conflicting conclusions have been reported on the influence of various structural features of these materials on the dynamic mechanical behavior. This is particular true for the role of the interfacial zone, the structural feature that is most difficult to quantify and therefore most open to speculation in terms of its effect on mechanical properties.

A series of microheterogenous composites based on block copolymers and homopolymers of polystyrene and polybutadiene has been under investigation in our laboratories. Primary focus has been on structural characterization via neutron scattering and electron microscopy (see paper

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† Present address: Bell Laboratories, Murray Hill, NJ 07974.

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immediately preceding this one and ref 1 and 2) and on the contribution of these structural features to mechanisms of large-strain mechanical response leading to fracture in these materials. As a complement to studies on such terminal behavior it is, however, also essential to probe the small-strain dynamic response of these heterogeneous polymers, as that is usually an important component for the understanding of large-strain nonlinear behavior. The following is a report of such an investigation.

From both a mechanical and structural viewpoint a composite made up of spherical particles readily lends itself to analysis. Macroscopic anisotropy, which generally complicates the behavior of block copolymers in which lamellar and cylindrical morphologies exist, is not present in films having a spherical microstructure. Thus, the spherical morphology eliminates ambiguities in the viscoelastic characterization which may arise from poorly defined alignment of an oriented specimen. Also, the scattering experiments used to characterize domain boundary structure require no special considerations of orientation when spherical domains are dealt with, while lamellar and cylindrical morphologies must be highly ordered and aligned with respect to the radiation beam.

For the above reasons the present study has focused on a spherical morphology. Disadvantages of the spherical morphology arise mainly from the fact that nonequilibrium sphere sizes are generally obtained in solvent-cast samples (see preceding paper). This means that it is not always possible to anticipate in advance the sphere size of a given material of known molecular characteristics. However, as will be shown below, the fact that one sample might exhibit a sphere size closer to equilibrium sphere size than another did not, of itself, have a noticeable influence on the dynamic mechanical properties.

This investigation also focuses on glassy-continuous microheterogeneous composites rather than on the rubbery-continuous analogues that have received a major proportion of the attention in the literature. The past emphasis on rubbery-continuous materials is an indication of the interest generated by polystyrene/polybutadiene block copolymer thermoplastic elastomers such as those marketed by Shell Chemical Co. and Phillips Petroleum Co. under the trade names Kraton and Solprene, respectively. On the other hand, owing to the relatively large degree of control over the microheterogeneous structure, studies of glassy-continuous materials might lead to better understanding of the deformation behavior of commercially important macroheterogeneous composites such as high-impact polystyrene and ABS resins. Also, glassy-continuous microheterogeneous composites appear to be interesting and useful materials in their own right as evidenced by the successful introduction by Phillips Petroleum Co. of the series of polystyrene-rich block copolymers known as K-Resins.

Experimental Section

Polymer Synthesis and Molecular Characterization. Polymers used in this study were synthesized via techniques of homogeneous anionic polymerization, the details of which have been reported in the preceding paper and elsewhere.[3] Diblock copolymers of polystyrene and polybutadiene, diblocks of polystyrene and perdeuterated polybutadiene, homopolystyrenes, and homopolybutadienes were prepared. Methods of molecular characterization included NMR spectroscopy, osmometry, UV absorption spectroscopy, and high-performance size exclusion chromatography. Information on the composition and molecular weight of each polymer is summarized in Table I of the preceding paper.

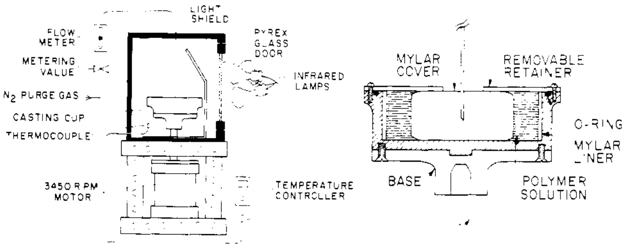

Figure 1. Solvent spin-casting apparatus.

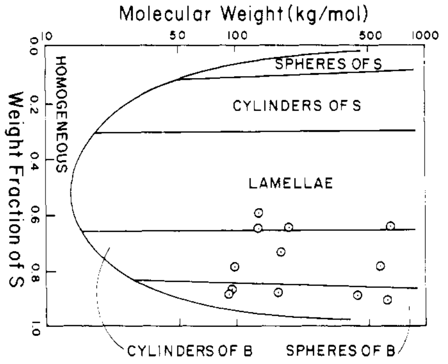

Figure 2. Phase diagram at 90 °C for SB diblock copolymers.[5] Locations of the various samples used in this investigation are indicated by the circles.

Table I
Solvent-Casting Parameters

	δ, (cal/cm^3)$^{1/2\,a}$	bp, °C	casting temp,^{b} °C
methylcyclohexane (30%)^c +	7.8	100	60 → 80
benzene (70%)	9.2	80	
toluene	8.9	110	80
benzene	9.2	80	60 → 80
tetrahydrofuran (70%) +	9.1	67	50 → 80
methyl ethyl ketone (30%)^d	9.3	80	
polystyrene	9.1		
polybutadiene	8.5		

[a] Obtained from ref 14 neglecting hydrogen-bonding effects. [b] 60 → 80 indicates temperature was increased from 60 to 80 °C during casting. [c] Poor solvent for polystyrene. [d] Poor solvent for polybutadiene.

Preparation of Film Samples. Films for mechanical testing were prepared by a solvent spin-casting technique.[3,4] Polymers were dissolved in an organic solvent at a concentration of 2–5 wt % and injected into the spinning caster. The injection is accomplished with a filtration unit (Millipore Corp.) containing a 10-μm filter. The spin-casting unit is illustrated in Figure 1.

Optimal film quality (smooth surface and uniform thickness) was achieved by using elevated casting temperatures and periods of time covering 2–4 days. Table I lists the solvents utilized in preparing samples along with casting temperatures. Film thickness, determined by the quantity of polymer (2–5 g) charged to the caster, ranged from 0.20 to 0.50 mm. At the completion of solvent removal, polymer films were dried and annealed at 120 °C in a vacuum oven for 24 h, cooled (20 °C/h), and stored under vacuum in the absence of light.

Figure 2 illustrates the equilibrium morphologies for the diblock copolymers studied here. Those falling in the lamellar and cylindrical category were modified by the addition of homopolystyrene as reported in the preceding paper. On the basis of composition, all blended samples would then be expected to exhibit a spherical morphology. In practice, this was not found to be the case, as demonstrated by the selected micrographs shown in Figures 3 and 4. Sample SB6/S2, cast from toluene, consists of cylinders of polybutadiene while sample SB4, also cast from toluene, contains polybutadiene spheres. It was possible to cast sample SB6/S2 into a spherical morphology (Figure 3) by using a mixed solvent of 70% THF and 30% MEK. Since the vapor pressure of THF exceeds that of MEK, the solvent becomes a continually poorer one for polybutadiene (Table I) during the

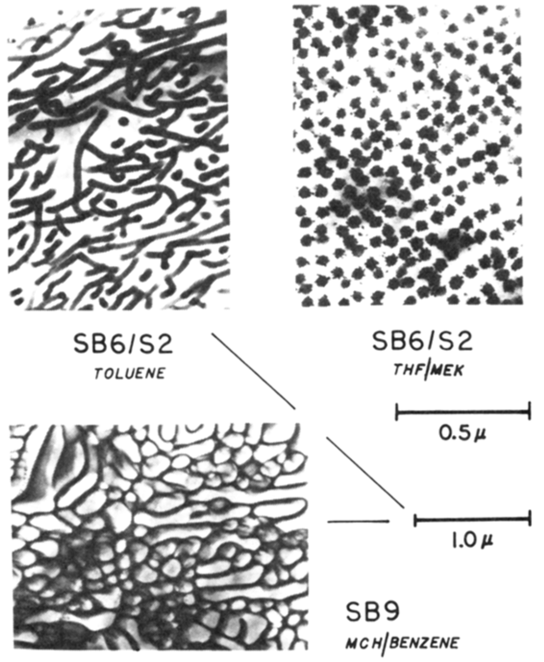

Figure 3. Effect of casting solvent on morphology. Dark regions are osmium tetraoxide stained polybutadiene.

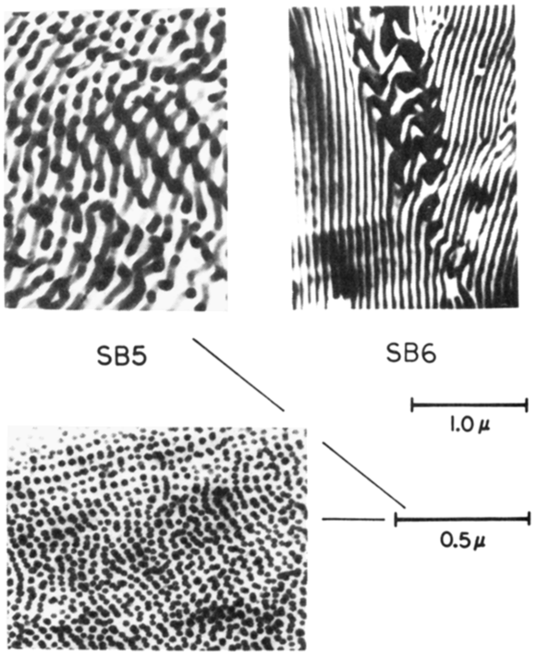

Figure 4. Electron micrographs of selected samples cast from toluene at 80 °C.

course of spin casting. This leads to a relative "swelling" of the polystyrene–solvent phase and subsequently to a spherical morphology of the polybutadiene phase. All but one of the blends examined here were cast in this fashion and all contained spherical polybutadiene domains in the polystyrene continuous phase. In order to obtain one sample in which polybutadiene comprised the continuous phase, sample SB9 was cast from a mixture of methylcyclohexane and benzene (Table I). The morphology of this sample is shown in Figure 3. As discussed later in the paper, this sample was used for diagnostic purposes to clarify the rubbery-phase behavior of the set of materials under examination here.

Electron micrographs of six samples appear in Figure 1 of the preceding paper. All samples consisting of only diblock copolymer or diblock plus polystyrene homopolymer exhibit a very narrow distribution of sphere sizes. Sample $SB_d3/S2/B1$, which contains polybutadiene homopolymer, exhibited a much broader sphere size distribution. Quantitative information on domain dimensions and interfacial thickness was discussed in detail in the preceding paper. Based on that work, it is possible to conclude that all samples in the present study have an interfacial thickness (ΔR as defined in the previous paper) of 22 ± 2 Å regardless of the solvent-casting conditions employed.

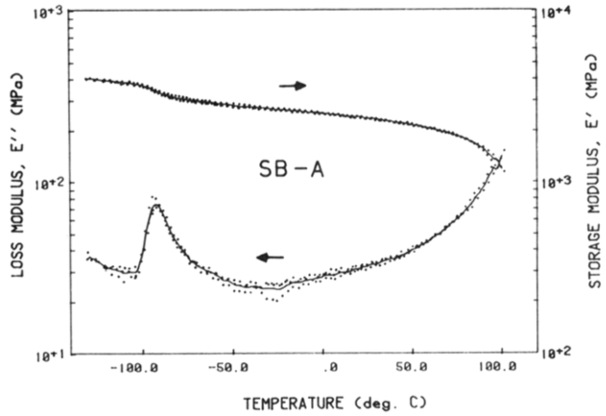

Figure 5. Dynamic mechanical properties of samples in category SB-A. Best-fit curve through the array of points will be used in later figures to represent the average properties of these materials.

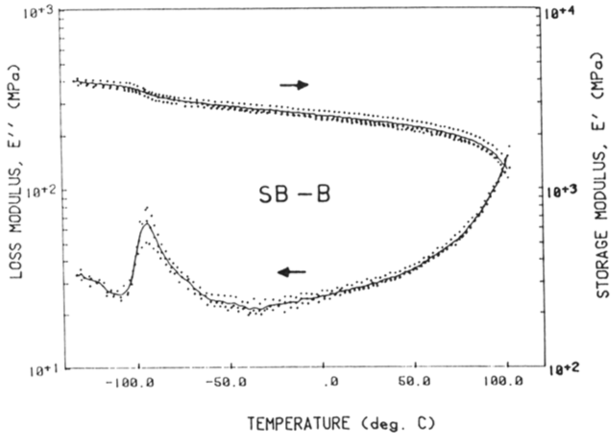

Figure 6. Dynamic mechanical properties of samples in category SB-B.

Dynamic Mechanical Testing. Dynamic mechanical properties of the various samples were determined with a direct-reading dynamic viscoelastometer, Rheovibron Model DVV-II-C (Toyo Baldwin Co., Ltd., Tokyo, Japan). This instrument was fitted with a low-temperature chamber (IMASS, Inc., Accord, MA), thereby extending the range of operation down to −150 °C. During operation, this chamber is kept under nitrogen in order to avoid moisture condensation.

Measurements were conducted at 3.5 Hz between −140 and +110 °C. The instrument was cooled from room temperature to −150 °C and subsequently slowly heated at a rate of less than 1 °C/min. Sample temperature was monitored by means of a copper–constantan thermocouple placed in close proximity to the sample. Various correction factors were applied to the data to account for clamping problems and apparatus compliance.[6-12]

Results

In order to facilitate later discussion, we have reduced a large proportion of the dynamic mechanical data into the following four categories (see Tables I and II of the preceding paper and ref 3).

category	samples
SB-A	SB1, SB_d1
SB-B	SB2/S2, SB4
SB-C	SB3/S2, SB5/S2, SB_d3, SB6/S2
SB-D	SB8/S2, SB9/S2

Hybrid curves for SB-A, SB-B, SB-C, and SB-D are shown in Figures 5–8. These curves were obtained by interpolation of data[3] obtained on the various samples in

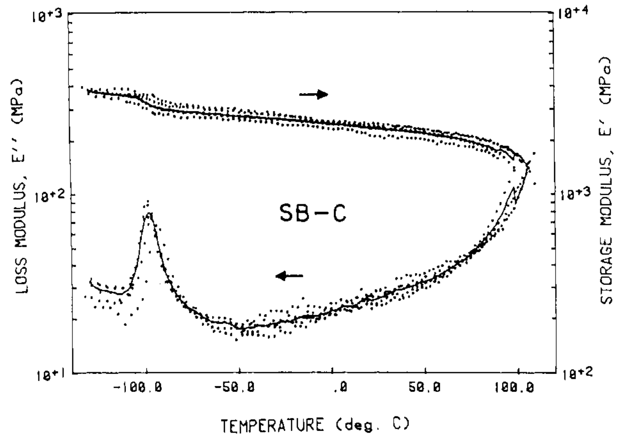

Figure 7. Dynamic mechanical properties of samples in category SB-C. Data for sample SB-7 are also included in this figure.

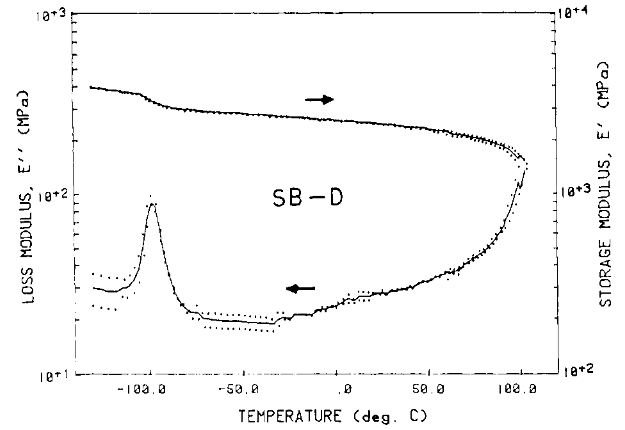

Figure 8. Dynamic mechanical properties of samples in category SB-D.

each category, often including repeat runs using different specimens of the same sample. Figures 5–8 show that scatter of the data around these curves is generally smaller for the storage modulus and in all cases is less apparent in the vicinity of the two main viscoelastic transitions, i.e., below about −50 °C and above about +50°C.

In Figure 9 loss tangent curves for three samples are presented: polybutadiene homopolymer B2, rubbery-continuous diblock SB9 cast from methylcyclohexane/benzene (Figure 3), and blend SB9-S2, which contains exactly the same polybutadiene as the previous SB9 sample but in this case the rubber is organized in a microspherical morphology. The rubber-continuous composite material SB9 exhibits a maximum in tan δ at the same location, −80 °C, as the polybutadiene homopolymer; the T_g of the polybutadiene in the microspherical composite is shifted downward in temperature by 19 °C, far beyond the range of experimental error. The nature of this T_g shift will be addressed in detail in the Discussion.

While the present study does not focus on the phenomenon of aging,[13] any investigation of glassy polymers must take sample thermal history into account. The effects of aging were minimized by annealing and cooling all specimens under the same conditions and examining them within 14 days. In order to assess the validity of this approach, specimens of SB_d1 and SB9/S2, each cast from THF/MEK, were examined within 24 h of annealing and again after 100 days at room temperature. A small change was found for both samples. As seen in Figure 10, each curve has shifted to higher temperatures following aging while essentially maintaining the same shape. There is also a difference in the location of the tan δ peak for the two samples SB_d1 and SB9/S2 when compared at similar aging conditions. These sample-to-sample T_g shifts will be discussed in more detail below.

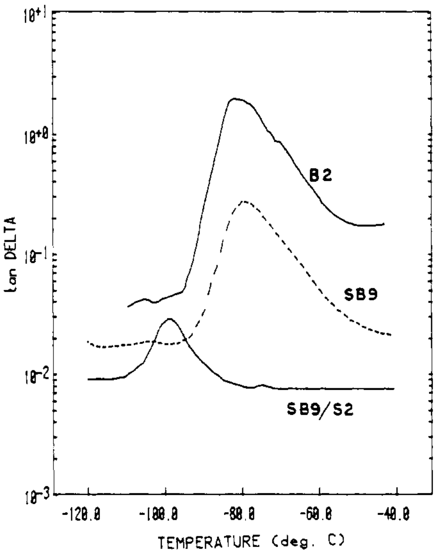

Figure 9. Determination of the glass transition in polybutadiene homopolymer B2 (−80 °C), polybutadiene microspheres of blend SB9/S2 (−99 °C), and the polybutadiene continuous phase of diblock SB9 (−80 °C).

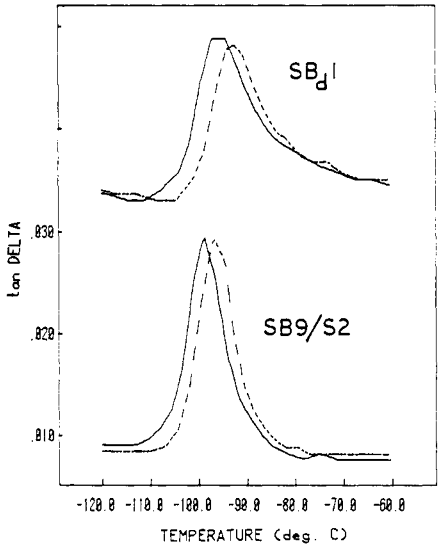

Figure 10. Effect of aging on the polybutadiene glass transition. Solid curves are from freshly annealed specimens and dashed curves are from the same specimens after aging 100 days at room temperature. SB_d1 curves have been shifted vertically 0.025 unit in tan δ.

Discussion

Analysis of the morphological features of these samples has shown that regardless of the molecular weight, composition, aging, or processing history, the interfacial thickness remains essentially constant. On the other hand, domain size and interdomain separations were dependent on some of the above-mentioned variables. The predicted equilibrium domain sizes were obtained for only a few cases—pure block copolymers of low molecular weight for which a low solvent content was present at the point of phase separation. The presence of homopolymers or the appearance of phase separation at high solvent concentrations (high molecular weight copolymers) always led to smaller than expected spherical domains and a loss of paracrystalline order among the spheres.

With these various structural features well described, we found that two important material characteristics could

Table II
Averaged Structural and Molecular Characteristics of Samples[a]

	$10^{-3}M_n^B$ [b]		$\bar{R}$, Å	v_S [c]	v_B [c]	$v_{\Delta R}$ [d]	T_g^B, °C
SB-A	12		120	0.820	0.102	0.078	−92
SB-B	20		155	0.838	0.106	0.056	−94
SB-C	50		223	0.851	0.111	0.038	−98
SB-D	177		326	0.853	0.120	0.027	−98
$SB_d3/S2/B1$	16	(27)[e]	267	0.865	0.105	0.030	−93
B2	22	(44)[e]			1.000		−80

[a] Taking $\rho_B = 0.895$, $\rho_{B_d} = 0.99$, and $\rho_S = 1.05$ g/cm³.[14] [b] Polybutadiene molecular weight per free chain end. [c] Volume fraction of pure component. [d] Interfacial volume fraction based on $\Delta R = 22$ Å. [e] Molecular weight per chain.

be analyzed with the present body of dynamic mechanical data; these are the mechanical behavior of the domain boundary and the properties of the glass-entrapped rubber. The latter of these will be considered first.

In Table II, the temperature of the peak in the loss tangent curve for each of the four sample categories of Figures 5–8 is shown along with data for the polybutadiene homopolymer and sample $SB_d3/S2/B1$. From these results it is clear that the polybutadiene glass transition temperature, T_g^B, in all glassy-continuous samples is shifted down in temperature relative to that of the polybutadiene homopolymer. We recall, however, that in Figure 9 the rubbery-continuous version of SB-9 exhibited a value of T_g^B that was essentially identical with that of the homopolymer. We believe that these observations can be explained on the basis of thermal stresses that influence the polybutadiene behavior in the glassy-continuous materials. The mismatch between the thermal expansion coefficients of polystyrene ($\alpha_S = 2.0 \times 10^{-4}$ K^{-1}) and polybutadiene ($\alpha_B = 7.5 \times 10^{-4}$ K^{-1})[14] places the included rubber particles in a state of negative pressure upon cooling from the liquid state. This dilation of a polymer should, in principle, lower T_g.[15] This has been noted by several authors investigating ABS and HIPS,[16,17] although the magnitude of the T_g shift was not as great as is presently reported.

The thermal stresses developed within a spherical rubber particle can be readily determined from the relation[18]

$$\sigma_B = \sigma_{rr} = \frac{2(\alpha_B - \alpha_M)E_B E_M \Delta T}{6(1 - 2\mu_B)E_M + 3E_B(1 - \mu_M)} \tag{1}$$

where μ is Poisson's ratio, E is the tensile modulus, and the subscripts M and B refer to the matrix and polybutadiene, respectively. Here, the matrix is defined as the composite material external to a spherical rubber particle.

Pure-component tensile properties were taken from experimental data at −50 °C, which is above the glass transition range of polybutadiene but sufficiently low in temperature to represent the properties near T_g^B. Poisson's ratio for polystyrene was taken from ref 14, and for polybutadiene it was calculated by using the experimental tensile modulus and a literature value[14] for the bulk modulus (2.3×10^3 MPa, based upon polyisoprene and corrected for temperature and pressure). In order to estimate the necessary matrix parameters in eq 1, one must account for the effects of the filler (polybutadiene domains) on the polystyrene. Chow[19,20] has derived general equations for calculating the modulus and thermal expansion coefficient from pure-component properties for a system composed of elliptical filler particles. The following results were obtained:

	E, MPa	μ	α, K^{-1}
B	3.0	0.49778	7.5×10^{-4}
S	3.6×10^3	0.33	2.0×10^{-4}
M(calcd)	3.0×10^3	0.35	2.5×10^{-4}
M(exptl)	2.8×10^3	-	-

Assuming eq 1 is valid between +90 and −90 °C, the level of negative pressure within a domain near the polybutadiene T_g is calculated to be $\sigma_B = -78$ MPa. Since the shift of the glass transition temperature with pressure for polybutadiene was not known, the reported value for polyisoprene, $dT_g/dP = 0.24$ °C MPa^{-1}, has been used.[21] This results in a value of $\Delta T_g^B = 18.7$ °C, which falls at the upper limit of the range exhibited by the data ($19 > \Delta T_g^B > 12$ °C). The effects of aging, as evidenced by Figure 10 can also be readily explained by the thermal stress concept. Aging corresponds to the densification, or loss of free volume, in a glass. This process would tend to reduce the hydrostatic tension on the polybutadiene following annealing, which translates into a decrease in the magnitude of ΔT_g^B, as observed.

Because the magnitude of the stress that is induced by the thermal expansion mismatch does not depend on sphere radius (eq 1), the general explanation given above for the T_g^B depression cannot also explain the differences in T_g^B exhibited by the various samples (Table II). Several possibilities for the source of the ΔT_g^B variation have been considered and discussed in detail elsewhere.[3] Of these, the most plausible explanations fall into two categories: one that focuses on the molecular weight of the polybutadiene, and the other on the dimensions of the rubbery domains. For the case of block copolymers, these two parameters are inextricably coupled; domain size increases in direct proportion to molecular weight (see preceding paper). However, by appropriate blending procedures, a material can be obtained that contains large domains consisting of low molecular weight polybutadiene. Sample $SB_d3/S2/B1$ was prepared with this in mind. As shown in Table II, this sample has a polybutadiene molecular weight similar to that of samples in category SB-B, but it has domain dimensions that are about 75% larger.

In Figure 11, sample $SB_d3/S2/B1$ stands out as a clear indication that it is polybutadiene molecular weight, not domain size, that controls the amount of T_g^B depression in these materials. Samples containing high molecular weight polybutadiene exhibit the maximum T_g^B shift (19 °C); this shift remains essentially constant until the polybutadiene molecular weight decreases to about 50 000. At this point, the amount of T_g shift diminishes smoothly with decreasing polybutadiene molecular weight to a value of about 12 °C at 12 000.

The fact that ΔT_g decreases with decreasing molecular weight is surprising since it is well-known that, in the absence of other factors, polymers of low molecular weight exhibit lower T_g's than their high molecular weight counterparts. Evidently some aspect of the thermal stress mechanism which acts to lower T_g^B significantly in these composite materials is influenced by molecular weight. Of the various possibilities considered, [3] the most appealing is the concept of rubber failure within the domains containing lower molecular weight polybutadienes. Samples of high molecular weight, which apparently do not cavitate, exhibit the maximum amount of T_g lowering. Cavitation

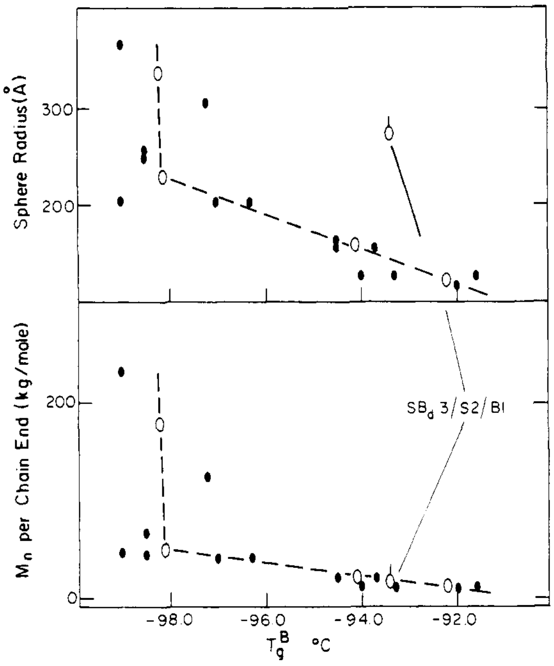

Figure 11. Polybutadiene domain size and rubber molecular weight as a function of glass transition temperature. Solid points correspond to individual data and open circles were taken from hybrid curves. T_g of the pure polybutadiene samples was -80 °C in these experiments.

in the domains containing lower molecular weight rubber tends to relieve some of the thermal stress, thus reducing the magnitude of the T_g depression. Whether the proposed failure mechanism has practical implications for the utilization of these materials is open to speculation. Domain cavitation prior to crazing has been observed in similar microheterogeneous materials by Argon et al.,[22] and Donald and Kramer [23] have pointed out that cavitation in the large rubber particles of ABS is important for craze initiation in that rubber-modified material. Further investigation of potential interrelations between the observed T_g shift and macroscopic fracture properties of the present set of microheterogeneous composites is now under way.

We now turn our attention to the effect of the interfacial zones of these materials on the dynamic mechanical behavior. Many previous studies have touched on this topic in various ways.[24-33] We believe that the unusually well-characterized (at various molecular and morphological levels) set of materials used in this study enables us to clarify some of the contradictory findings that have appeared. First, we note that all of the storage modulus curves obtained for the full range of glassy-continuous samples studied here were nearly identical. Pure parallel coupling between polystyrene and polybutadiene would result in a 13% decrease of E' in the region of the glass transition of polybutadiene; a maximum drop of 22% was actually observed. Based on these facts, it is clear that the presently available variations in interfacial volume fraction (Table II) will have little or no noticeable influence on the shape of the E' curve. However, the loss modulus behavior is much more sensitive to the interfacial zone, as shown in Figures 12 and 13. In Figure 12, it is clear that the entire level of loss between the two major viscoelastic transitions increases as the interfacial volume fraction increases. This is similar to the finding of Kraus and Rollman, [32] who worked on a well-characterized set of lamellar triblock copolymers of styrene and butadiene. It is also noteworthy that the fourth hybrid loss curve, not shown in Figure 12, for samples in category SB-D (containing the *lowest* amount of interfacial material) was similar in level to that of SB-C but exhibited a broad loss peak centered in the region 10–20 °C; because a similar feature was apparent in the loss modulus data obtained on polystyrene homopolymer,[3] we concluded that this broad secondary maximum in SB-D samples is related to the polystyrene phase and is masked by the increased level of loss associated with the interface in the other three categories of materials.

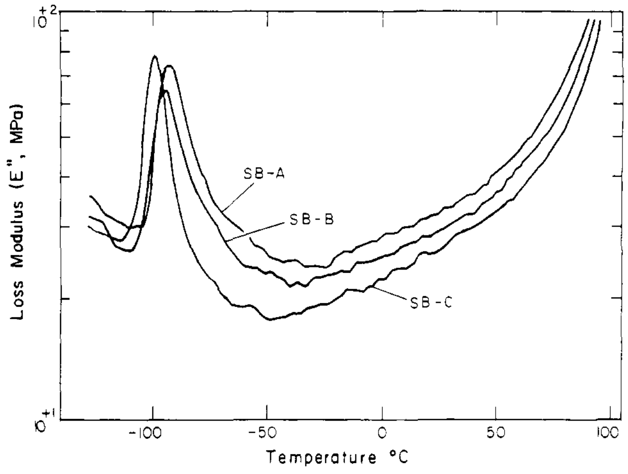

Figure 12. Loss modulus curves for sample categories SB-A, SB-B, and SB-C.

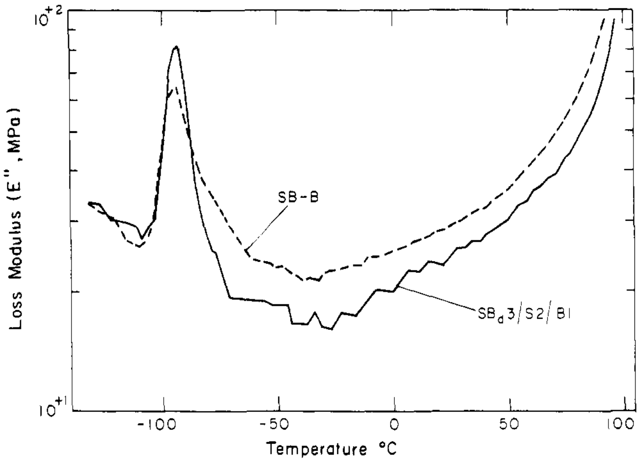

Figure 13. Comparison of loss modulus curves for sample SB-B ($v_{\Delta R}$ = 0.55) and $SB_d3/S2/B1$ ($v_{\Delta R}$ = 0.029).

The concept of an increased intertransitional loss modulus in materials of larger interfacial volume fraction is supported further by the evidence presented in Figure 13. Referring to Table II, we note that SB-B and SB_d3–S2/B1 differ by nearly a factor of 2 in interfacial volume fraction but are closely similar in other respects. The significant variation in the intertransitional loss modulus seen in Figure 13 is thus readily associated with the interfacial zone.

We have chosen not to carry the analysis to the further stage of "subdividing" the interfacial zone[24,31] for the purpose of developing mathematical models of the viscoelastic response of the interface in these materials. Even though we had direct measurement of interfacial thicknesses in our materials and clear evidence that all samples consisted of well-separated polybutadiene microspheres in a polystyrene matrix, we still considered this to be insufficient information to warrant making judgements on the detailed composition profile of the interfacial zone. In fact, symmetrical composition profiles had to be assumed in order to make calculations of interfacial thickness from our scattering data (see preceding paper).

Diamant et al.[24,31] have taken the opposite approach. They modified the two-phase Nielsen model[34] into a multiphase model in which the domain boundaries of a set of SBS triblock copolymers were treated as 70 discrete phases. All coupling constants were statistically averaged to a single fitting parameter $\Phi_{\max}$, and a polystyrene continuous matrix was assumed. The authors contend that the interfacial volume fraction, $\upsilon_{\Delta R}$, and the interfacial composition profile, $\rho_B(r)$, can be determined by fitting $G''(T)$ torsion pendulum data with this model. The parameter $\varphi_{\max}$ is independently fit to G' data, which they claim is insensitive to $\rho_B(r)$ and $\upsilon_{\Delta R}$. The latter point is consistent with the findings of this study. While the loss modulus trends predicted by their model are in general agreement with this work, Diamant et al. arrive at several conclusions, based on fitting of G'' data, that conflict with the present findings. First, they conclude that varying casting solvent brings about as much as a fourfold variation in $\upsilon_{\Delta R}$. Second, they report, based on fits to dynamic mechanical data, that $\upsilon_{\Delta R} = 0.04$ for 7000–36 000–6000 SBS and $\upsilon_{\Delta R} = 0.10$ for 16 000–78 000–16 000 SBS, both cast from the same solvent. The first point conflicts with the concept that local interactions dictate interfacial composition (see preceding paper). The second is directly opposed to the results presented in Table II of this paper. Unfortunately, Diamant et al. included neither EM nor small-angle scattering data to exclude the likely possibility of morphological changes from sample to sample beyond the level of structure of the interfacial zone. Kotaka et al.[35] have established a strong correlation between solvent-induced structure and dynamic mechanical properties in SBS triblock copolymers similar to those studied by Diamant et al.

Conclusions

Owing to the control over and knowledge of molecular and morphological characteristics of the set of samples examined here, several clear structure/property relations have been established. In microheterogeneous composites comprised of a glassy polystyrene continuum and spherical inclusions of rubbery polybutadiene, the glass transition temperature of the rubbery phase is substantially lower than that of the corresponding rubbery homopolymer. If the rubber molecular weight is large enough ($> \sim 50\,000$), this T_g depression can be predicted quantitatively from the knowledge of the differential thermal contraction induced negative pressures in the rubbery domains, which are set up in the material during cooling from the melt state. At lower molecular weights, earlier cavitation of the polybutadiene domains appears to be occurring as a result of the higher free volume.[3] The cavitation of the rubber relieves the thermal stress, thereby reducing the T_g depression. This also explains why in composite samples with rubbery-continuous morphologies the polybutadiene glass transition is in the same location as in the homopolymer.

Because of the very small domain dimensions in these microheterogeneous materials, surface-to-volume ratios are relatively large, and thus a significant proportion of the material resides in the interfacial zone (Table II). Because interfacial thickness is essentially independent of molecular weight and processing conditions, interfacial volume fraction depends only on domain dimensions. Thus, appropriate comparisons of dynamic mechanical properties led to the following conclusions. The storage modulus is essentially unaffected by variations in interfacial volume fraction. The loss modulus is influenced to a significant extent by the interfacial zone. An increase in interfacial volume fraction leads to a general increase in the level of loss between the two main transitions and an inward broadening of these two loss peaks. No evidence for the appearance of a separate transition (loss modulus peak or storage modulus inflection) with increasing interfacial volume fraction was seen in the dynamic mechanical spectrum.

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Registry No. Butadiene–styrene copolymer, 9003-55-8.

References and Notes

(1) Bates, F. S.; Cohen, R. E.; Berney, C. V. *Macromolecules* **1982**, *15*, 589.
(2) Berney, C. V.; Cohen, R. E.; Bates, F. S. *Polymer* **1982**, *23*, 1222.
(3) Bates, F. S. Sc. D. Thesis, Massachusetts Institute of Technology, 1982.
(4) Kaelble, D. *J. Appl. Polym. Sci.* **1965**, *9*, 1209.
(5) Helfand, E.; Wasserman, Z. R. "Developments in Block Copolymers"; Goodman, I., Ed.; Applied Science Publishers, Ltd., London, 1982; Chapter 4.
(6) Massa, D. J. *J. Appl. Phys.* **1973**, *44*, 2595 (1973).
(7) Ramos, A. R. Sc. D. Thesis, Massachusetts Institute of Technology, 1977.
(8) Ramos, A. R.; Bates, F. S.; Cohen, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 753.
(9) Voet, A. Morawski, J. C. *Rubber Chem. Technol.* **1974**, *47*, 758.
(10) Ramos, A. R.; Cohen, R. E. *Polym. Eng. Sci.* **1977**, *17*, 639.
(11) Cohen, R. E.; Ramos, A. R. *Macromolecules* **1979**, *12*, 131.
(12) Wedgewood, A. R.; Seferis, J. E. *Polymer* **1981**, *22*, 966.
(13) Struik, L. C. E. "Physical Aging in Amorphous Polymers and Other Materials"; Elsevier: New York, 1978.
(14) Brandrup, J.; Immergut, E. H., Eds.; "Polymer Handbook", 2nd ed.; Wiley: New York, 1975.
(15) Ferry, J. D. "Viscoelestic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(16) Bohn, L. *Angew. Makromol. Chem.* **1971**, *20*, 129.
(17) Marbitzer, L.; Ott, K.; Schuster, M. Kranz, D. *Angew. Makromol. Chem.* **1972**, *7*, 57.
(18) Beck, R. S.; Gratch, S.; Newman, S.; Rusch, K. C. *Polym. Lett.* **1968**, 707.
(19) Chow, T. S. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 959.
(20) Chow, T. S. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 967.
(21) O'Reilly, J. M. *J. Polym. Sci.* **1962**, *57*, 429.
(22) Argon, A. S.; Cohen, R. E.; Jang, B. Z.; VanderSande, J. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 253.
(23) Donald, A. M.; Kramer, E. J. *J. Mater. Sci.* **1982**, *17*, 2351.
(24) Diamant, J.; Soong, D. S.; Williams M. C. *Contemp. Top. Polym. Sci.* **1981**, 4.
(25) Fesko, D. G.; Tschoegl, N. W. *Int. J. Polym. Mater.* **1974**, *3*, 51.
(26) Kaelble, D. H. *Trans. Soc. Rheol.* **1971**, *15*, 235.
(27) Beecher, J. F.; Marker, L.; Bradford, R. O.; Aggarwal, S. L. *J. Polym. Sci.* **1969**, *62*, 117.
(28) Shen, M.; Kaelble, D. H. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 149.
(29) Cohen, R. E.; Tschoegl, N. W. *Trans. Soc. Rheol.* **1976**, *20*, 153.
(30) Sawada, Y.; Cohen, R. E. *Trans. Soc. Rheol.* **1977**, *21*, 157.
(31) Diamant, J.; Soong, D. S.; Williams, M. C. *SPE-ANTEC* **1981**, *39*, 414.
(32) Kraus, G.; Rollman, K. W. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1333.
(33) Beamish, A.; Goldberg, R. A.; Harriston, D. J. *Polymer* **1977**, *18*, 49.
(34) Nielsen, L. E. *Rheol Acta*, **1974**, *13*, 86.
(35) Kotaka, T.; Miki, T.; Arai, K. *J. Macromol. Sci., Phys.* **1980**, *B17*, 303.