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Time-Temperature Superposition in Styrene/Butadiene/Styrene Block Copolymers

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The dynamic mechanical response of a styrene/butadiene/styrene (SBS) block copolymer with segment molecular weights of 16,000/78,000/16,000 (designated as Shell 16/78/16) was determined at various temperatures between -83 and $+86^{\circ}\text{C}$ at frequencies between 0.1 and 1000 Hz. The data were shifted into a master curve according to a procedure developed for thermorheologically complex materials and utilizing an additive compliance model. Data on two other triblock copolymers, Kraton 102, and an SBS triblock copolymer exhibiting a continuous polystyrene phase (designated NBS 10/30/10), are also presented.

A noteworthy feature of all three triblock copolymers is a long-drawn-out intertransition plateau in which the modulus changes very little for many decades of time. The modulus is high because of the presence of the polystyrene phase and trapped entanglements in the polybutadiene phase. The extent of the plateau, effectively the distance between the two glass transitions, depends on temperature because the transition for the glassy phase shifts much more rapidly with temperature than that for the rubbery phase.

The data on Shell 16/78/16 and Kraton 102 appear to present evidence for an interlayer between the polystyrene and polybutadiene domains. In these materials the polystyrene domains act essentially as inert filler over the polybutadiene transition region and well into the intertransition plateau. NBS 10/30/10, containing about 40% of styrene, is very different from the other two which contain less styrene. It has a continuous polystyrene phase giving rise to a high intertransition modulus much more reflective of glassy behavior. Consequently interlayer effects are suppressed.

INTRODUCTION

Several investigations of the mechanical properties of block copolymers have been reported in recent years, but the interdependence of time and temperature effects in these materials is as yet poorly understood. Most previous

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work has been concerned with isochronal data which give little insight into the time dependence. When isothermal data were obtained, they were simply shifted empirically to yield master curves.¹⁻⁴ Occasionally data have shown poor superposition, indicating that simple shifting along the logarithmic time-axis may not be valid.⁴⁻⁶ Indeed, where more than one relaxing phase is present, each with its own temperature dependence, simple time-temperature superposition can not be generally valid on theoretical grounds. This has been discussed in a previous publication⁷ in which a general treatment was presented for the time-temperature superposition of data obtained on two-phase materials. In such thermorheologically complex materials shift factors depend on time as well as on temperature. For a complete analysis of isothermal data obtained on a thermorheologically complex material, contributions of various mechanisms to the mechanical properties must be isolated by decomposition, and the time-temperature relationship must be determined separately for each contribution. This has been carried out to account for the effect of β -mechanism in polymethacrylates,⁸ slippage in rubbery networks,⁹ and terminal flow viscosity in polystyrene.¹⁰

In this paper we present data on three triblock copolymer elastomers (thermoplastic rubbers) of the polystyrene-1,4-polybutadiene-polystyrene (SBS) type. The purpose of this paper is to describe the general features of such materials in small deformation dynamic experiments. The dynamic mechanical properties of one of the materials, on which the most extensive data have been obtained, have been subjected to a full analysis of the time and temperature dependence using the model procedure outline in the previous publication.⁷

EXPERIMENTAL

Materials

Three styrene/butadiene/styrene copolymers were investigated. The first, designated here as Shell 16/78/16, is a research grade material (Experimental Block Copolymer TR-41-1648) graciously provided by the Shell Chemical Company. It was prepared by sequential addition in which particular care was exercised to produce end blocks of equal lengths. According to the analytical data furnished by the company, the material has block molecular weights of 16,000/78,000/16,000. This is equivalent to a styrene content of 29%. NMR measurements in this laboratory gave 28.4%. The center block is stated to contain 41% cis 1,4-, 49% trans 1,4-, and 10% 1,2-addition as determined by IR spectroscopy. DTA in this laboratory showed a glass transition at -91°C but could not resolve any transition at higher temperatures. The sample contained about 0.2% Ethyl Corporation Antioxidant 330.

The second triblock, referred to here as NBS 10/30/10, was prepared by Dr. L. Fetters at the National Bureau of Standards and supplied to this laboratory by courtesy of Dr. F. N. Kelley of the Air Force Rocket Propulsion Laboratory. The block molecular weights of 10,000/30,000/10,000 were determined stoichiometrically by Dr. Fetters. The styrene content calculated from the molecular weights is 40%. NMR measurements gave 39.4%. DTA showed a polybutadiene glass transition at -93°C , but again gave no indication of a polystyrene transition.

The third triblock was a commercial material, Shell Kraton 102. It has been described in detail in a previous publication.³ We are again indebted to the Shell Company for a generous supply of the material.

Specimen preparation

Samples were prepared by casting on mercury a degassed solution of 17.0 g polymer and 0.04 g N-phenyl-2-naphthylamine antioxidant dissolved in 200 ml benzene. After drying for one week, the sample was carefully detached from the dish, lifted off the mercury, dried in vacuum at room temperature for twenty-three hours, and stored at -18°C . The resultant film was 1.02 mm thick. It revealed no stress patterns under polarized light.

The measurements on the Shell 16/78/16 sample were made in uniaxial compression. Two specimens were used. Each specimen was composed of three laminations, each lamination being cut from the cast film with a razor blade. The laminations were put together by washing the surfaces with methanol, placing them together while still wet, and allowing the laminated sample to dry first at atmospheric pressure and then in vacuum for a few hours. A roughly trapezoidal section was cut out with a razor blade, washed with methanol, and dried for twenty-four hours in vacuum before installation in the rheometer. The lamination process was carried out independently for each specimen. The imposed strain was perpendicular to the laminations. Adhesion between laminations and between the specimens and the rheometer in both the annealed and unannealed specimens was very good; and once the specimens were cut, it was difficult to determine the precise location of the interfaces visually.

The first specimen was 0.308 cm thick with a cross-sectional area of 0.200 cm². The second specimen was 0.404 cm thick and had a cross-sectional area of 0.176 cm². The only difference in preparation between the two specimens was that the second laminated sample was annealed at 100°C for six hours in a small evacuated desiccator before the trapezoidal specimen was cut. Annealing produced up to 30% changes in the specimen dimensions.¹⁶ Differences in the mechanical properties were noticeable only at temperatures above about 50°C . Figure 1a shows a transmission electron micrograph of

the center portion of the annealed sample. The micrograph was obtained on an ultramicrotome section cut perpendicular to the surface of the cast sheet and stained with osmium tetroxide. It reveals a regular morphology and shows discrete polystyrene domains embedded in the polybutadiene matrix.

Measurements on the NBS 10/30/10 sample were made in simple shear. A single specimen 0.55×0.87 cm in lateral dimension and 0.188 cm thick was cut from the film and dried in vacuum at 10^{-5} torr for 27 hours at room temperature. Annealing of this sample did not result in dimensional changes. An electron micrograph of a stained section of the unannealed material (Figure 1b) reveals a definite laminar structure. Microtoming results in some separation of the lamellae by disrupting the polystyrene phase as shown in the lower left-hand corner of the photograph. This delamination was never observed in the unannealed sample of the Shell 16/78/16 material.

Kraton 102 was examined in simple shear and in uniaxial compression. In simple shear the measurements were made on specimens with dimensions of about $0.9 \times 0.6 \times 0.15$ cm, prepared by solvent casting in the same way as the NBS 10/30/10 specimen. One specimen was exhaustively extracted with

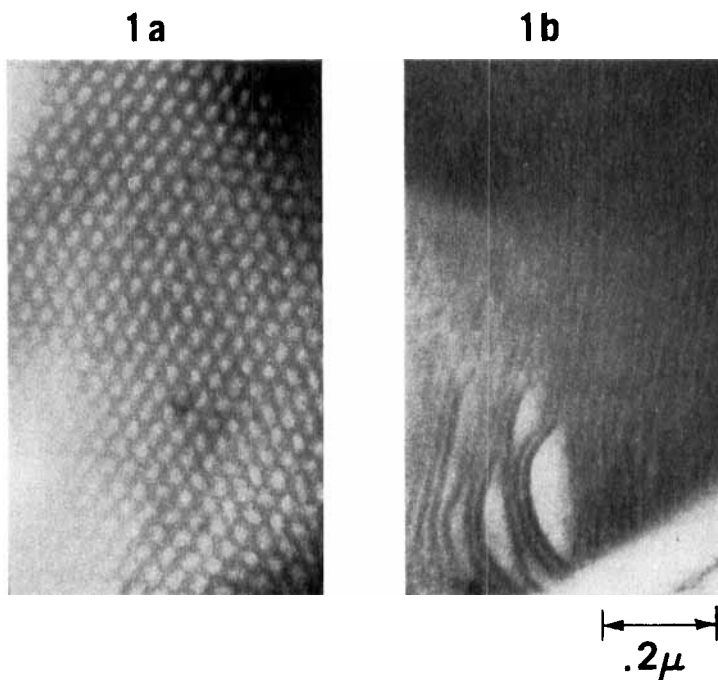


FIGURE 1 Transmission electron micrographs on: (a) Shell 16/78/16, annealed sample; (b) NBS 10/30/10, unannealed sample.

methanol over a period of several months to remove possible traces of the casting solvent. The specimen was kept at -15°C during the exhaustion to minimize oxidation of the polybutadiene. A third specimen was prepared by compression molding in vacuum at minimal pressure to minimize internal stresses. A specially constructed mold was used.⁴ This consisted of a precision bored stainless-steel cylinder which could be closed by a screw-in plug at the bottom and a tight-fitting piston at the top. About two-thirds from the bottom the cylinder bore a side arm through which it could be evacuated. Specimens were molded by placing the cylinder, closed at the bottom and containing an appropriate amount of small pieces of the material, about halfway in an oil bath, with the piston just above the opening of the side arm. The cylinder was then evacuated for about 10 minutes at room temperature. Maintaining a constant vacuum, the temperature of the bath was raised to the molding temperature (about 130°C) and kept there for about 30 minutes. A slight pressure was then applied, released, and reapplied for 10 minutes. After the vacuum was broken, the mold was removed from the bath and cooled. The specimen was then extruded by help of the piston after unscrewing the bottom plug. Specimens prepared in this way were transparent but slightly iridescent when viewed between polarizing filters.

Two specimens of Kraton 102 were studied in uniaxial compression. The first was prepared as described for the Shell 16/78/16 material and was examined with the laminations perpendicular to the direction of compression. The second was cut from the same sample in such a way that, upon installation in the rheometer, the laminations were parallel to the direction of compression.

Kraton 102 specimens were unannealed because the importance of annealing had not been recognized at the time the measurements were made. For this reason data on Kraton 102 above 50°C are suspect and were discarded.

In all cases, shape factors were calculated from sample geometry assuming no distortion of the specimen. In fact, the deformations were never large enough to cause perceptible bulging or buckling of the specimens.

Instrumental

The measurements, both in uniaxial compression and in shear, were made in an extensively modified Melabs Rheometer (Melabs Inc., Palo Alto, California).¹¹ A schematic of the central part of the rheometer is shown in Figure 2. A stack of ceramic disks enclosed in a thin-walled stainless-steel housing (A) acts as a driver. Energy is supplied to the driver from a frequency generator through a power amplifier.

In simple shear the specimen (I) is contained between the driver plate (B) and the monitor plate (C). The force transmitted through the specimen to the monitor plate is picked up by a ceramic transducer (D) in the plate. In this

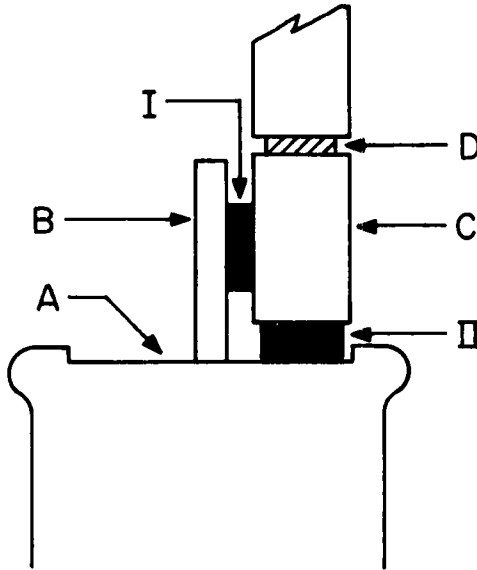


FIGURE 2 Schematic of central part of rheometer: (A) stainless-steel cylinder containing stack of ceramic disks; (B) driver plate; (C) force monitor plate; (D) ceramic transducer; (I) specimen in simple shear; (II) specimen in simple compression.

operating mode small arbitrary vertical shifts were often required to achieve satisfactory superposition because of differences in the bending moment placed on the force transducer. The specimen is contained by forcing the monitor plate against the specimen and the driver plate.

In uniaxial compression the specimen (II) is placed between the driver and the monitor plate. Since the driver had not originally been designed for this application, it was necessary to cut the specimens to a roughly trapezoidal shape to accommodate them in a depression in the top of the driver housing.

The charge generated in the ceramic force transducer is fed to a charge amplifier followed by a preamplifier. The moduli or compliances were obtained from the measured amplitude ratios and phase angles. The phase angles were measured by a method¹² which allows the determination of small phase angles at low frequencies with excellent accuracy.

The apparatus was modified in four major respects. The three spindly legs with which the instrument was supplied were replaced by a 10 kg solid copper block. The temperature control system was completely rebuilt using a more effective heating and lagging system and a proportional-integral controller. Some of the wiring was exchanged for better quality cables. Special electronic circuitry was added to allow measurements of the phase

angles by the method referred to above. The apparatus was then carefully calibrated over the entire frequency and temperature range using stainless-steel rings of known compliance and negligible loss in place of specimen II. Further details have been presented elsewhere.¹³

Measurements were made from about -80°C to about 86°C over a frequency range from about 0.1 to 1000 Hz at most temperatures. The static strain applied to the specimen in containing it between the driver and the monitor plate was estimated to be about 2–3% in shear and about 5% in compression. The sinusoidal applied strain was estimated to be of the order of 0.003%.

After installation of a specimen the apparatus was heated to 50°C for twenty-four hours. This allowed some annealing to take place and resulted in good contact between the specimen and the driver and force monitor plates. A nitrogen blanket was kept over the specimen except at the lowest temperatures. The first data were taken at 50°C followed by the low temperature measurements. The 50°C measurements were then repeated before and after the high temperature series. The 50°C data were reproducible except for the final set for the unannealed specimen of Shell 16/78/16 which had annealed further in the apparatus at the high temperatures.

RESULT

Shell 16/78/16

The tensile storage compliance for the annealed specimen is shown in Figure 3 for nine temperatures. The data are plotted in units of reciprocal bars. One bar equals 10 N/m^2 , or 10^6 dynes/cm^2 , or 14.5 psi. Data at 16 other temperatures, primarily in the $0\text{--}80^{\circ}\text{C}$ range, have not been included in order to simplify the presentation. Compliances appearing below the value of $10^{-3.5}$ in Figure 3 are beyond the calibrated hardness range of the rheometer and the values may not be precise. However, the time-temperature superposition results will not be affected because the apparatus compliance is essentially independent of time or temperature.

The usual temperature⁹ correction T/T_0 was applied to reduce data in the intertransition (rubbery) region. In the transition region of the polybutadiene phase, the correction was allowed to vary systematically between unity and T/T_0 to obtain the best superposition. The often used density correction ρ/ρ_0 was not applied since the rheometer, in confining the specimen to a constant thickness, measures the density reduced compliance.

Figure 4 shows master curves of the storage and loss compliances at 85°C obtained from the data on the annealed specimen by the shifting procedure described in an earlier publication.⁷ The procedure will be discussed in a late

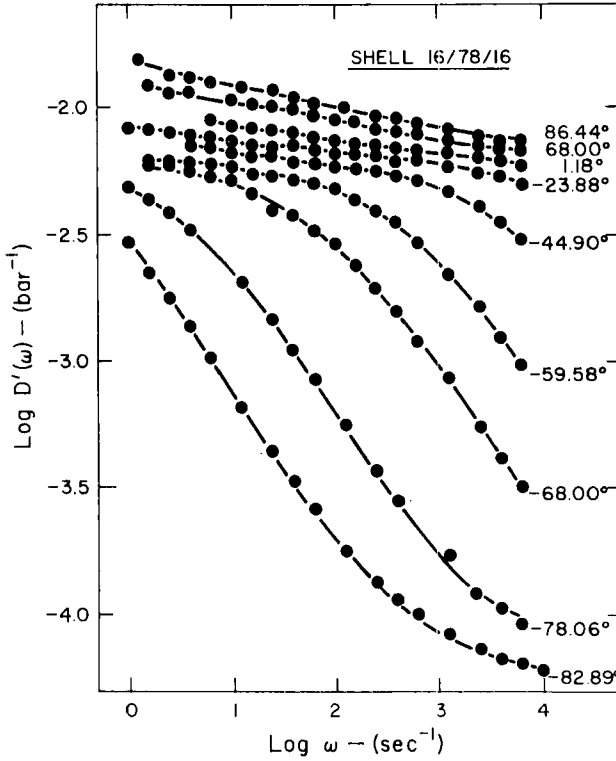


FIGURE 3 Storage compliance of Shell 16/78/16 in simple compression as function of frequency at various temperatures.

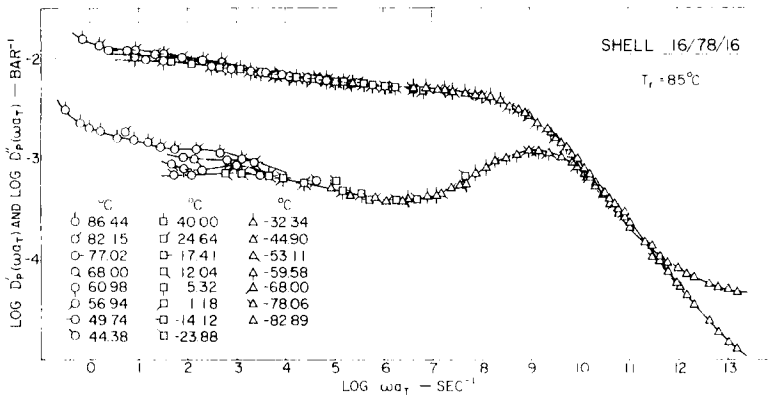


FIGURE 4 Master curves of the storage and loss compliances of Shell 16/78/16 in simple compression as functions of frequency at 85°C.

section. Empirical shifting to the best fit obtainable would have produced a roughly similar master curve for the storage compliance except in the region $0 < \log \omega a_T < 4$, where empirical shifting would tend to draw out the abscissa much further.

As seen in Figure 4, at the higher frequencies the storage and loss data cover the glass-to-rubber transition of the polybutadiene phase in its entirety. Below about $\log \omega a_T = 9$ at this reference temperature, the storage compliance exhibits a broad intertransition plateau, covering roughly eight logarithmic decades of time. Over this wide frequency range the storage compliance changes by less than half of a logarithmic decade. The average value of the logarithm of the storage compliance in this region is about -2.16 corresponding to a tensile modulus of about 175 bars (1.75×10^8 dynes/cm² or 2500 psi) at 25°C. This region represents the rubbery response of the triblock copolymer. The modulus is high because of the presence of the polystyrene domains which act as reinforcing filler particles. The long drawn-out high modulus rubbery plateau is a characteristic and noteworthy feature of triblock copolymer elastomers.

Around $\log \omega a_T = 1$ the ascent into the polystyrene transition begins. This region could not be covered experimentally, however, because of the large compliance and the diminishing sensitivity of the piezo-electric transducers. There is a clear lack of superposition in the region $1 < \log \omega a_T < 4$ at temperatures above about 40°C. It is most marked in the loss compliance data. This lack of superposition, which no amount of horizontal shifting can overcome, is thought to arise from an interlayer at the domain boundaries which will be discussed in the next section. The data below 40°C form a second broad maximum in the loss compliance curve which has recently been ascribed to the slippage of trapped entanglements. As this is fully discussed in another paper by Cohen and Tschoegl¹⁶ it will not be considered further here.

The shift factors obtained on the annealed as well as the unannealed specimen by empirical shifting are shown in Figure 5. The solid line represents the WLF equation determined from a plot of $\Delta T/\log a_T$ vs. ΔT at a reference temperature of -78°C , i.e.

$$\log a_T = \frac{7.76 (T + 78.0)}{51.1 + (T + 78.0)} \quad (1)$$

where T is the temperature in °C. The shift data deviate from the WLF equation at about 0°C for the annealed, and at about -40°C for the unannealed material. Above these temperatures they can be fitted to Arrhenius equations, as described in an earlier publication.³ Thus, the mechanical properties of the two samples show clear differences. The shift characteristics of the polybutadiene transition in each sample, however, are identical. Hence, the

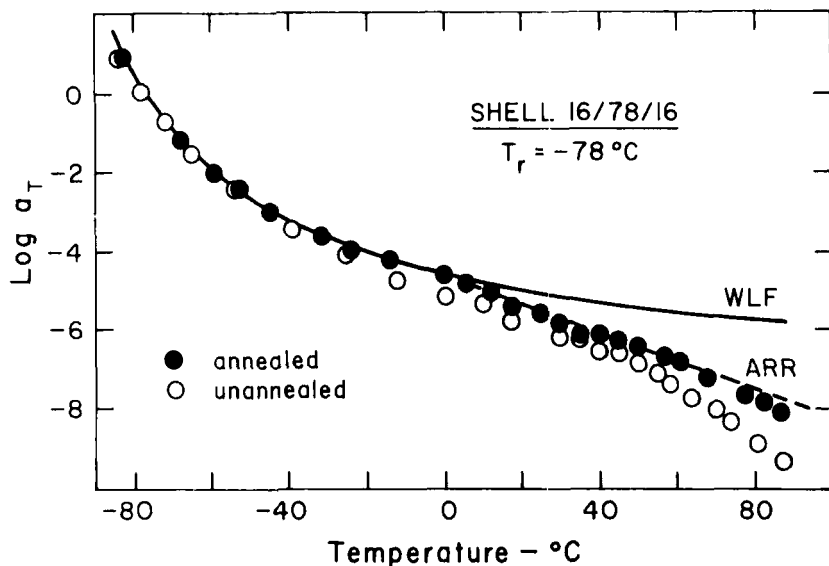


FIGURE 5 Shift factors for Shell 16/78/16 as function of temperature.

shifts are referred to -78°C . The data obtained on the unannealed specimen have been described elsewhere¹³ and will not be considered further here.

NBS 10/30/10

The measurements were made in simple shear at 15 temperatures between -80 and 86°C . The master curves of the storage and loss shear compliances obtained by empirically shifting to a reference temperature of 40°C are shown in Figure 6. The polybutadiene transition at high frequencies is clearly revealed but is much smaller than that in the Shell 16/78/16 material. Interestingly the glass compliance appears to be higher than in the Shell sample. There is again an enormously drawn out intertransition plateau, covering, at the reference temperature, about twelve logarithmic decades of frequency over which the storage compliance rises by less than half of a logarithmic decade. At the lowest frequencies the beginning of the polystyrene transition is more clearly seen than in the Shell sample.

The value of the logarithm of the shear storage compliance in this region is about -2.5 at 40°C , corresponding to a tensile modulus ($E = 3G$) of 970 bars (9.7×10^8 dynes/cm², or 14,000 psi). This is more than five times the corresponding modulus of the Shell 16/78/16 sample. Indeed the film was much stiffer, and was rather similar in feel to the corrugated cardboard used in boxes.

TIME-TEMPERATURE SUPERPOSITION

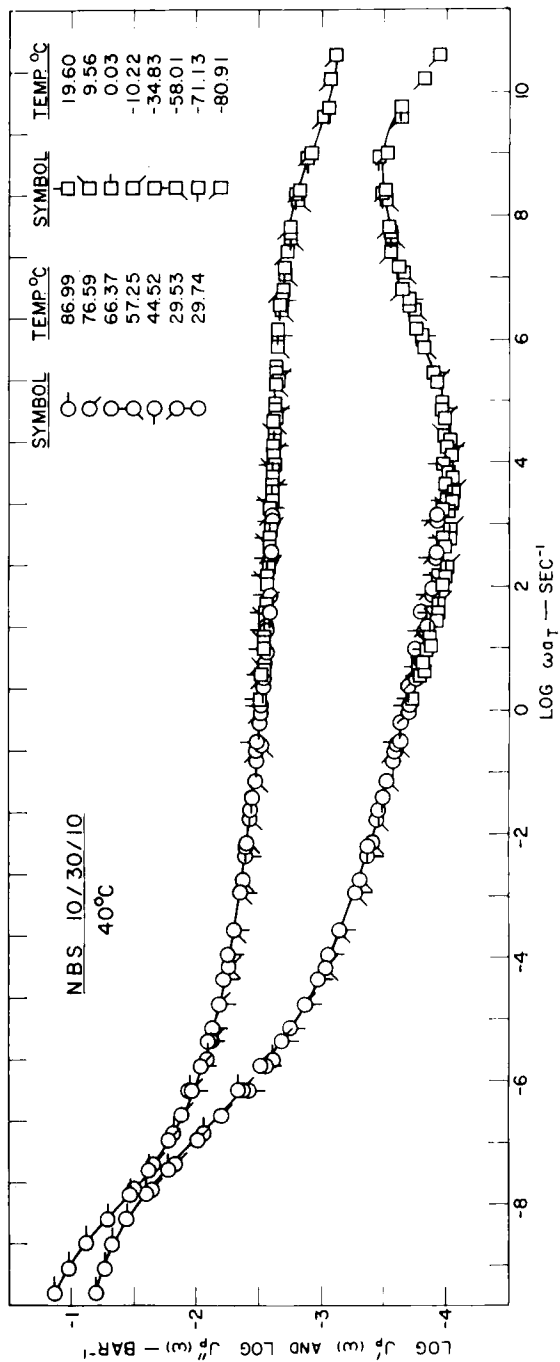


FIGURE 6 Master curves of the storage and loss compliances of NBS 10/30/10 in simple shear as functions of frequency at 40°C.

Electron micrography had revealed a lamellar structure for this polymer (cf. Figure 1b). A plot of force vs. length for a constant strain rate experiment at a crosshead speed of 2 in./min. at room temperature (nominal length of strip specimen was 2.9 inches), shown in Figure 7, revealed a yield point characteristic of a continuous polystyrene phase. Because of the high polybutadiene content, however, it is likely that both phases are continuous and Figure 1b supports this conclusion. Figure 7 also shows the tracing for the second stretch illustrating the typical stress softening of block copolymers^{14,15} resulting from the disruption of the continuous polystyrene phase at the yield point so that the composite thereafter acts as an elastomer. Annealing allowed one to reproduce the yield curve repeatedly. This annealing phenomenon and its relation to morphology has been discussed elsewhere.^{14,17} In view of the very small strains employed in our dynamic measurements the polystyrene phase could not have been disrupted and the measurements thus reflect the particular morphology of this sample.

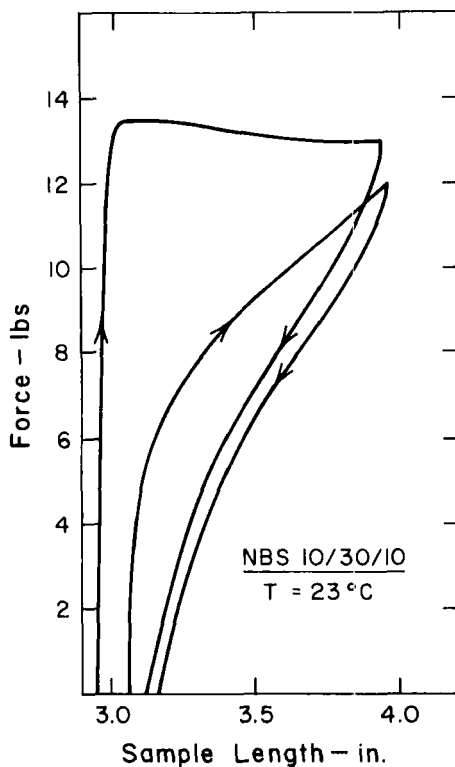


FIGURE 7 Force-extension curve of NBS 10/30/10 at 23°C.

Because of the high modulus of this material, the measurements were very easy to make and the resulting accuracy in both $J'(\omega)$ and $J''(\omega)$ lends considerable confidence to the empirical shifting, despite the small arbitrary vertical shifts (at most 0.2 logarithmic decades) referred to earlier. The subscript p on $J_p'(\omega)$ and $J_p''(\omega)$ here represents reduction involving these vertical shifts as well as the temperature correction factor. Indeed, in this case where the compliance is dominated by the glassy polystyrene, the temperature correction should probably not have been applied. The vertical shifts were arbitrarily made relative to the data at 0°C . The empirically determined shift factors referred to 0°C are shown in Figure 8. The choice of 40°C as the reference temperature for the master curves in Figure 6 will be explained below. Shifting $\log \tan \delta$, in which any vertical shift effect, temperature correction factor, and apparatus error cancels out, resulted in $\log a_T$ values identical to those obtained by shifting $J_p'(\omega)$ and $J_p''(\omega)$.

Kraton 102

Measurements were made in simple shear and in simple compression on unannealed specimens. The tensile compliance master curves obtained by the shifting method described later are shown in Figure 9. The low temperature compliances here are from a specimen, designated A, in which the strain was perpendicular to the laminations within the specimen. The shape factor

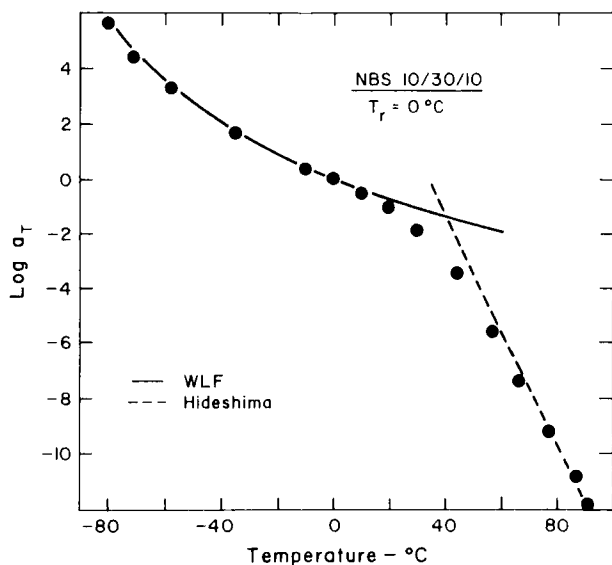


FIGURE 8 Shift factors for NBS 10/30/10 as function of temperature.

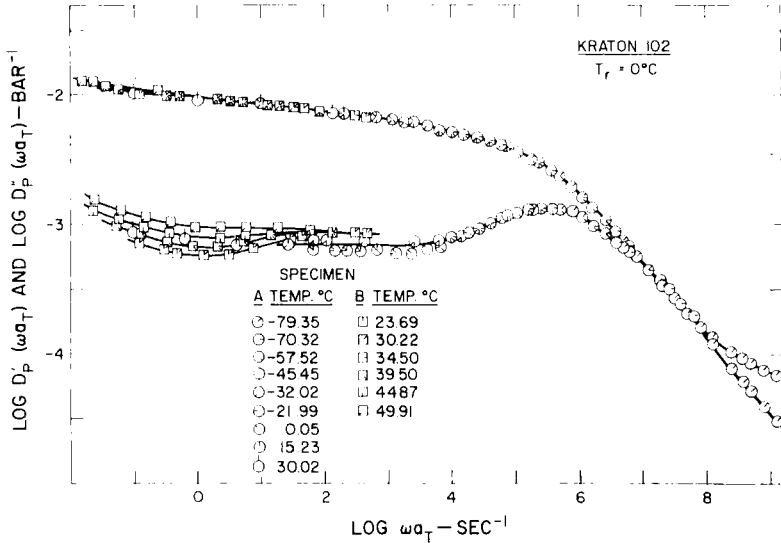


FIGURE 9 Master curves of the storage and loss compliances of Kraton 102 in simple compression as functions of frequency at 0°C .

of this specimen was too high to permit measurements at higher temperatures. Therefore, data from the specimen for which the strain was parallel to the laminations, designated as B, are included. The data agree very well except that the loss data for specimen B appear to be slightly higher than those of specimen A in the region of overlap. If this is due to experimental error, the data for specimen B should be more reliable since the measurements were easier to make on this specimen. The discrepancy may, however, be real, resulting from anisotropy or from differences in the amount of static compression applied to the two specimens.

Qualitatively, the storage and loss compliances in Figure 9 are very similar to those determined on the Shell 16/78/16 research grade material with only a small horizontal shift of about 0.5 decades, which is explained by the difference in T_g 's. However, the loss compliance in the plateau region for Kraton 102 is slightly higher, with a correspondingly steeper slope of the storage compliance; and the lack of superposition, seen primarily in $D''(\omega)$, is more pronounced.

The empirical shift factors are shown in Figure 10 for a reference temperature of -60°C , together with those obtained from the data in shear on a solvent cast, a compression molded, and a solvent cast and methanol extracted specimen. The shift factors are in excellent agreement. They show well-defined WLF behavior at temperatures below about 0°C . The solid line

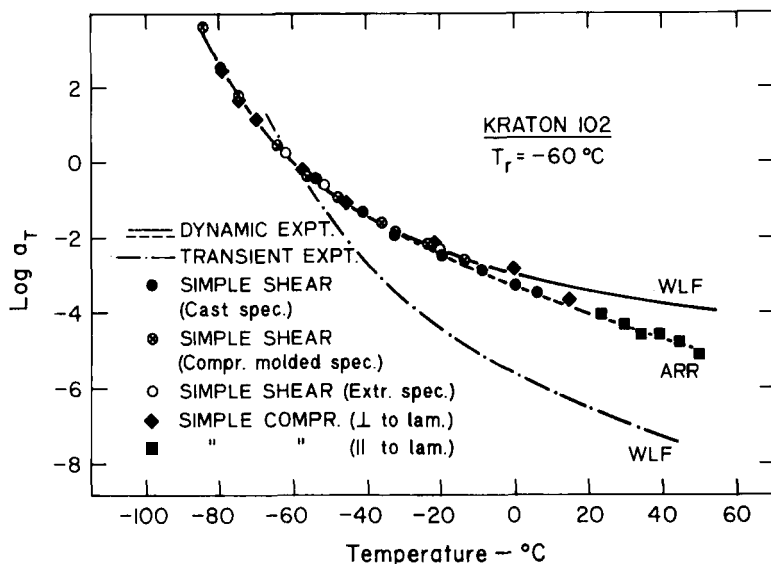


FIGURE 10 Shift factors for Kraton 102 as function of temperature.

represents the WLF equation

$$\log a_T = - \frac{9.14 (T + 60)}{52.4 + (T + 60)} \quad (2)$$

calculated from the shift factors below 0°C. The temperature dependence begins to depart from WLF behavior at about -10°C.

DISCUSSION

Block copolymers are inherently thermorheologically complex because of their two-phase nature. In the previous section we have presented master curves for three block copolymers. The procedures used in constructing these master curves must now be examined.

In a previous publication⁷ we have shown that, for thermorheologically complex materials, the shift distance required to bring a point on a response curve recorded at one temperature into coincidence on the response curve recorded at another temperature becomes a function of time as well as temperature. This means that such shifts can, at best, be carried out point-by-point only.

It follows from the equations presented in our earlier paper that, for the storage compliance, the change in the shift factor with respect to temperature

at constant frequency is given by

$$\left[\frac{\partial \log a'_T(\omega)}{\partial T} \right]_{\omega} = - \left(\frac{\partial D'(T)}{\partial T} \right)_{\omega} \left[\frac{\partial D'[\omega a_T'(\omega)]}{\partial \log \omega a_T'(\omega)} \right]_{T_r}^{-1} \quad (3)$$

i.e. it depends on the change in the compliance with respect to temperature at the constant frequency as well as on the change in the compliance with respect to logarithmic frequency at the reference temperature, T_r .

Similar equations can be written for other monotonically increasing or decreasing viscoelastic response functions such as e.g., the relaxation modulus and the storage modulus.

In our earlier paper⁷ we had tacitly assumed that the same reasoning would apply also to non-monotonic functions such as, e.g., the loss compliance, the loss modulus, the retardation spectrum, and the relaxation spectrum. Such functions, however, may have regions in which a given value of the response function at one temperature has no corresponding value at another temperature. This is shown schematically in Figure 11, which displays a loss compliance master curve such as one might observe on a two-phase material, at two temperatures, T_1 and T_2 . We assume that the contributions of the two phases are additive and that they are individually thermorheologically simple. Generally, the two transitions will shift along the time axis differently. Thus, while the ascending branches at low frequencies, or the descending branches at high frequencies may be shifted onto each other, this is clearly impossible for the minimum between the two peaks which rises and falls with temperature. Furthermore, at the maxima, where the slope of

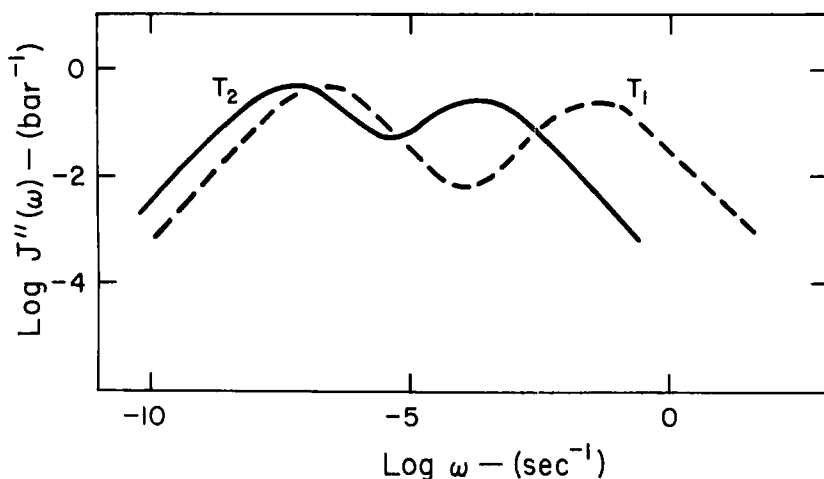


FIGURE 11 Schematic representation of shear loss compliance of a two-phase material at two temperatures.

the curve is zero, the change in the shift distance with temperature is undefined.

Equation (3), although it lends some insight into the complex time-temperature relations in thermorheologically complex materials, cannot readily be applied in practice. In our previous paper we have, therefore, introduced an approach based on a model to describe the combination of the contributions of the individual phases. For Shell 16/78/16, in which the polystyrene domains are embedded in a continuous polybutadiene phase (cf. Figure 1b), a model assuming the additivity of the strains (i.e. the compliances) in the individual phases appears to be adequate. For Kraton 102, whose morphological structure, judging from the evidence presented here, must be very similar, support for the additivity of the compliances was advanced by Lim, Cohen, and Tschoegl³ in an earlier publication.

In our previous paper we used the additive compliance model in conjunction with equations analogous to Eq. (3) to obtain further insight into the time-temperature relations of two-phase materials. Thus, it was shown that in an SBS block copolymer the polybutadiene phase dominates the temperature dependence at low temperatures when the polystyrene domains act largely as inert filler, while, at higher temperatures, the polystyrene phase may be expected to dominate the behavior because then the shift factors for the polybutadiene phase no longer change appreciably with temperature. It was also shown that the time-dependent shift functions derived from different response functions can differ. This results essentially from the fact that the various response functions weigh the spectral functions differently. One may therefore distinguish $\log a_T(t)$ for the creep compliance from $\log a_T'(\omega)$ for the storage compliance and from $\log a_T''(\omega)$ for the loss compliance. Another symbol (such as b_T) could then be used for the corresponding relaxation functions.

The equations derived from the combination of Eq. (3) with the model, although instructive, still cannot be integrated. However, they lead directly to another, more practical, approach. If the storage compliances and their temperature dependences are known for both phases, the shift factors can be derived from the assumption that the compliances are additive. On this assumption one can construct a reference master curve of the storage compliance at the reference temperature. Similar short response curves can also be generated for the temperatures and frequencies at which data are available. Then, by comparing the frequency ω at which a given compliance appears at temperature T to the frequency $\omega a_T'(\omega)$ at which the same compliance value appears on the master curve, and taking the difference, one obtains the shift distance, $\log a_T'(\omega)$, for that temperature and frequency. An appropriate set of shift factors can thus be generated for the superposition of experimental data.

In terms of the weighted combinations of the known shift factors for the

individual phases, the shift factors for the composite may be decomposed according to

$$\log a_T'(\omega) = n_B \log a_{TB} + n_S \log a_{TS} \quad (4)$$

with

$$n_B + n_S = 1 \quad (5)$$

Eq. (5) is not applicable generally but leads to reasonable insight in our case.

Using the relations discussed in our earlier paper⁷ for the storage compliances and their temperature functions one obtains the weighting factors as shown in Figure 12 for Shell 16/78/16. Most of the transition from dominance by the polybutadiene phase to dominance by the polystyrene phase occurs over a relatively small temperature range, the location of which depends on the frequency. Because the weighting coefficients change rapidly when they do change, precise values of the viscoelastic functions of the individual phases are not required; nor is an extremely accurate model necessary. However, one must have truly representative shift data for the individual phases of the composite.

Shell 16/78/16

The storage compliance master curve shown in Figure 4 was obtained using a set of shift factors generated as explained in the preceding section and in our earlier paper.⁷ The data for the storage compliance of the polybutadiene matrix were taken from the polybutadiene transition and plateau regions of the response of Shell 16/78/16 itself. Below 40°C the polystyrene acts essentially

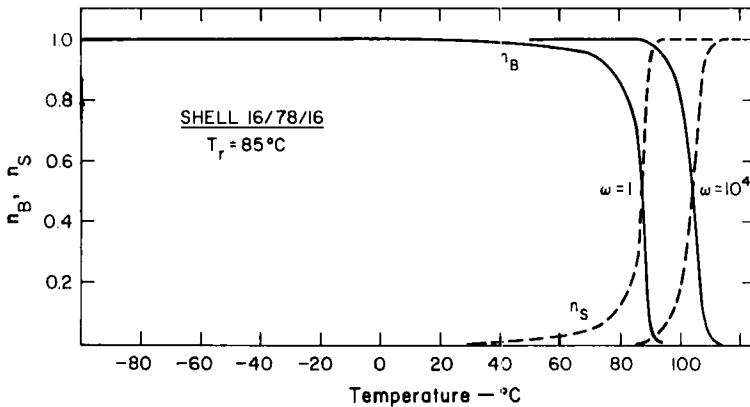


FIGURE 12 Weighting factors for Shell 16/78/16 as function of temperature at two frequencies.

as an inert filler. The storage compliance data thus represent filled, cross-linked polybutadiene. Compliance data for homopolybutadiene were not used because adjustments for the filler effect and effective crosslink density would have to be made and these factors are not well defined. However, the difference, arising from the glass compliance of the polystyrene phase, is very small (it is estimated to be of the order of 1%). Indeed, as discussed above, the change from dominance of one relaxation mechanism to the other occurs rapidly enough for the calculation scheme to be quite insensitive to the values of the assumed compliance data as long as these are smooth.

A WLF equation

$$\log a_{TB}(\text{WLF}) = - \frac{4.45 (T - 0)}{146.3 + (T - 0)} \quad (6)$$

provided an excellent fit to data below 0°C. Above 0°C an Arrhenius term

$$\log a_{TB}(\text{ARR}) = 1760 \left[\frac{1}{273 + T} - \frac{1}{273} \right] \quad T \geq 0^\circ\text{C} \quad (7)$$

was added to account for deviation from WLF behavior. This deviation appears to be linked with the secondary peak in the loss compliance referred to earlier. A rigorous examination of the experimental data would require decomposition of the contributions to the overall compliance. This decomposition has been neglected as the effects are small; further, the accuracy of the data and the assumptions that would have to be made, make this treatment unwarranted. The reasons for the choice of the data describing the polystyrene phase were discussed earlier.⁷

For the loss compliance, the time-temperature shifts are ambiguous for the reasons given above. Therefore, points which were felt to belong to the polystyrene transition were given the polystyrene shifts, and points reflecting the entanglement peak (and all lower temperature data) were given polybutadiene shifts. Data falling in between were discarded. However, data at 86.44°C and 82.15°C, shifted as polystyrene, were retained as they are felt to be sufficiently close to the reference temperature and the total shift is very small. Although this process is subjective, the choice of points to be deleted was guided by the calculated shift factors, generated by loss data of the two homopolymers in the same fashion as for the storage compliance shifts. Those data with shifts differing from either of the shifts for the two homopolymers by more than 0.5 logarithmic decades of time were discarded.

For reasons which will be discussed later, for a reference temperature in the vicinity of 85°C, empirical shifting would have resulted in a master curve very similar to that shown in Figure 4. This is so because the change from dominance

of the shift behavior by the polybutadiene phase to dominance by the polystyrene phase is rapid around this reference temperature as discussed above. The storage compliance data are so flat in the region of this rapid change that the empirical shift is very subjective and deviation from thermorheologically simple behavior is not readily observed. The situation is further clouded by additional temperature effects in the 44° to 82°C temperature range on the overall relaxation. These effects will be discussed below. Thus, the excellent superposition in Figure 4 seen outside the 44° to 82°C temperature range cannot be taken as proof of the validity of the shifting scheme outlined here. Measurements are at present underway in our laboratory on a polystyrene-1,2-polybutadiene-polystyrene triblock copolymer. In this material the two transitions are much closer to each other than in Shell 16/78/16; and thus the lack of superposition upon empirical shifting might be seen more readily. It is hoped that these data will allow us to test our proposed shifting scheme in a more convincing fashion.

The lack of superposition, even after applying our shift procedure, at temperatures above about 40°C in Shell 16/78/16 and in about the same region for the two specimens of Kraton 102 is most noticeable in the loss compliance. In this region the data cannot be superposed by a horizontal shift alone. It does not seem likely that the lack of superposition should arise from the complex time-temperature behavior, as suggested by Figure 11. The (converted) data of Plazek and O'Rourke on homopolystyrene indicate that, in this region, the polystyrene phase would not exhibit a peak and should make a negligible contribution to the total compliance. The low compliance of the NBS 10/30/10 material (cf. Figure 6) further supports this claim. Although the characteristics of the polystyrene phase in Shell 16/78/16 are not truly known, and homopolymer data may not be directly applicable, it is unlikely that the characteristics of the polystyrene in the block copolymer should be drastically different from those of a homopolymer of comparable molecular weight.

We incline to the view that the lack of superposition at temperatures above about 40°C is due to contributions from another added compliance which makes itself felt in this temperature region. We note that the data cannot be superposed by a horizontal shift alone. Vertical shifts, along the compliance axis, also seem necessary to effect superposition. Such vertical shifts would be indicated if the composition of the system was changing to make it more compliant at higher temperatures. We may consider that the boundary between the polystyrene and polybutadiene domains cannot be a sharp one. Rather, one would expect regions of essentially pure polystyrene and pure polybutadiene to be separated by an intermediate layer in which both polystyrene and polybutadiene are present essentially in a molecular mixture; and since the domains are only about 200 Å in diameter, an interlayer of only

a few tens of angstroms would be significant. The presence of such an interlayer has been postulated by Kaelble.¹⁸

An interlayer can be regarded, if somewhat superficially, as a third component which contributes to the overall compliance independently. In a first approximation one may model the interlayer by dividing it into glassy and rubbery portions and a region in transition. This model is represented in Figure 13 as a series of concentric shells around a spherical polystyrene domain; one should, however, consider the variation as a continuous one. If the interlayer were made more diffuse, one would expect it to contribute more significantly to the overall compliance. This could explain the deviation of $\log a_T$ from WLF behavior at low temperatures in the unannealed Shell sample.

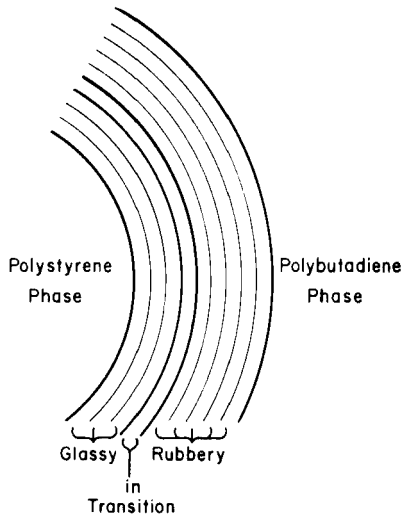


FIGURE 13 Schematic representation of interlayer model.

Including the interlayer in an additive compliance model gives

$$D'(\omega) = W_B(T)D_B'(\omega) + W_S(T)D_S'(\omega) + W_I(T)D_I'(\omega) \quad (8)$$

and

$$D''(\omega) = W_B(T)D_B''(\omega) + W_S(T)D_S''(\omega) + W_I(T)D_I''(\omega) \quad (9)$$

where $W(T)$ denotes the (now temperature dependent) weight or volume fraction of component X, and the subscripts B , S , and I represent the polybutadiene and polystyrene domains, and the interlayer, respectively. Neglecting the transition region (or, effectively, partitioning its contribution among the glassy and rubbery portions), gives

$$W_I(T)D_I'(\omega) = W_{IR}(T)D_{IR}'(\omega) + W_{IG}(T)D_{IG}'(\omega) \simeq W_{IR}(T)D_{IR}'(\omega) \quad (10)$$

where the subscripts *R* and *G* refer to the rubbery and glassy regions, respectively. We have here further assumed that the total compliance of the interlayer is approximately that of the rubbery portion. Similarly we may write

$$W_I(T)D_{IR}''(\omega) \approx W_{IR}(T)D_{IR}''(\omega) \quad (11)$$

although this is obviously a rather empirical way of representing the change in loss in the block copolymer from 40°C to 80°C.

At high temperatures, the interlayer is considered to be essentially rubbery and

$$W_{IR}(T) \simeq W_I(T) \quad T > 80^\circ\text{C} \quad (12)$$

Thus, values for $W_I(T)D_{IR}'(\omega)$ and $W_I(T)D_{IR}''(\omega)$ can be obtained by subtracting values at temperatures below the point where any interlayer effect can be seen (45°C) from values at the same frequency at high temperatures ($T > 80^\circ\text{C}$). This gives for Figure 4, then,

$$\log W_I(T)D_{IR}'(\omega) \simeq -3.0$$

$$\log W_I(T)D_{IR}''(\omega) \simeq -3.1 \quad (13)$$

The rubbery fraction of the interlayer, $W_{IR}(T)/W_I(T)$ is determined by comparing isochronal data from intermediate temperatures in Figure 4. This is done easily on the loss modulus data. The temperature dependence of the rubbery fraction at low $\omega a_T = 3$ is shown in Figure 14.

We now assume that the frequency dependence is related to the temperature dependence by a constant. A good reduction of the data was achieved by

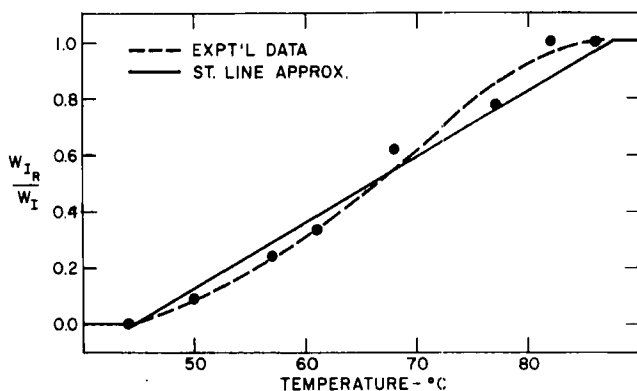


FIGURE 14 Temperature dependence of the rubbery fraction of the interlayer.

selecting a value of 10°C per decade. This constitutes only a rough approximation. In reality the relationship is certainly not constant. It should approach the often-used value of 3°C per decade⁹ at much longer times, but the variation is not too significant over the ±2 decades over which the data treated here extend.

The interlayer model is incorporated into the master curve by “correcting” the observed compliance at a given temperature and frequency by the contribution of the interlayer according to the approximate model discussed above. This treatment produces the master curves shown in Figure 15. The

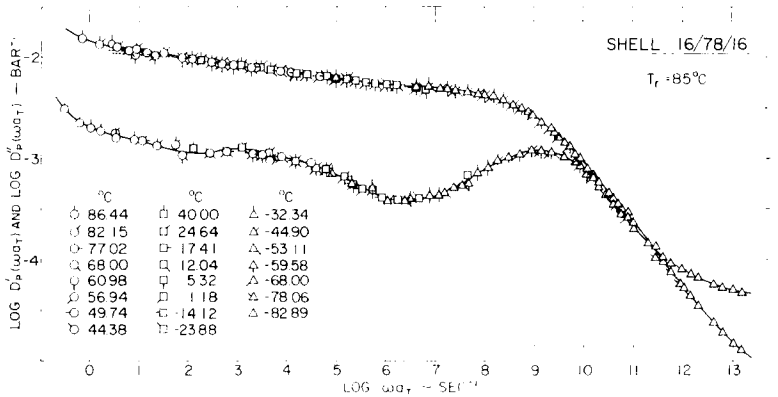


FIGURE 15 Master curves of the storage and loss compliance of Shell 16/78/16 in simple compression as functions of frequency at 85°C after interlayer correction.

data are reduced quite well into a single curve, although there is still some deviation as evidenced by the dashed lines in the storage compliance around $\log \omega a_T = 0.7$ and the scatter in the loss curve around $\log \omega a_T = 1$ to 2. This is not surprising considering the roughness of the model.

Even if the lack of superposition in Figure 4 were not due to an interlayer the approach used by us may still be appropriate. The compliance correction would then be interpreted as a correction to the assumed mechanical properties of the polystyrene phase; and the use of Eq. (11) to treat the loss data would be easier to defend. In any case, this method of representing the compliance data in the intermediate temperature regime does not affect the time-temperature relationships of the composite as a whole, leaving the mechanical properties of the composite consistent with the properties of the constituent homopolymers.

The thermorheological complexity of two-phase materials is illustrated strikingly by constructing a master curve at 25°C. This is shown in Figure 16.

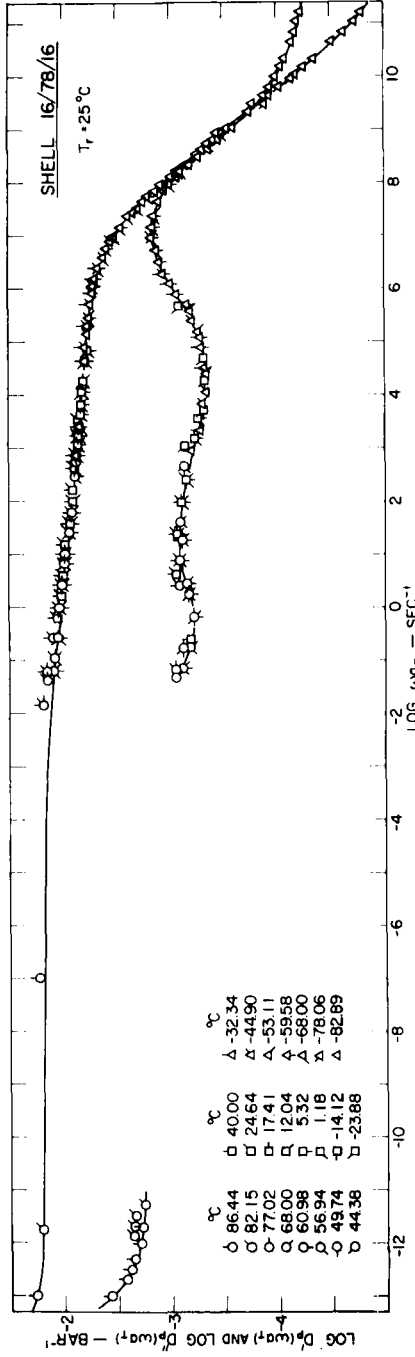


FIGURE 16 Master curves of the storage and loss compliance of Shell 16/78/16 in simple compression as functions of frequency at 25°C after interlayer correction.

The interlayer correction was also applied here. The polybutadiene transition has shifted approximately two decades because at 25°C the polybutadiene phase is still far above the glass transition. By contrast, the polystyrene transition has shifted approximately twelve decades because the polystyrene phase is glassy at 25°C. The intertransition plateau is accordingly lengthened. As with the master curves at 85°C, only polystyrene and polybutadiene shifts were applied to the loss data. Data suspected of containing significant contributions of both constituents were discarded. In the region $-11 < \log \omega a_T < -2$ the loss compliance must necessarily become quite low to satisfy the Kronig-Kramers relations. This is a necessary consequence of the lengthening and flattening of the intertransition plateau in this region, consistent with the increased separation of the loss peaks (cf. Figure 11).

NBS 10/30/10

This sample presents an entirely different picture. The empirical shift factors, referred to 0°C in Figure 8, are very revealing. Although the polybutadiene transition is very small in the master curve, the shift behavior is purely polybutadiene in nature and is nearly the same as that seen in the Shell 16/78/16 material. The WLF parameters describing the low temperature data are $c_1 = 13.36$ and $c_2 = 109.2^\circ\text{C}$ at a reference temperature of -80.91°C . At high temperatures, the mechanical behavior is dominated by polystyrene, apparently in the glassy state. In fact, the linear relationship used to describe the shifts of glassy polystyrene for Shell 16/78/16, the slope of which is based on Hideshima's data,¹⁹ shows remarkable agreement and is incorporated in Figure 8 as a dashed line. This intersects the WLF curve determined for the polybutadiene transition at 40°C. Thus, as explained in our earlier publication,⁷ the empirically shifted master curves in Figure 6 should be valid with good approximation at a reference temperature of about 40°C. This would make the locations of the two transitions on the logarithmic frequency axis consistent with the properties of the homopolymers corresponding to the constituents. Data in the 10–50°C region can not be positioned accurately, but they fall in the plateau region where horizontal shifts do not critically affect the appearance of the master curve.

A more rigorous analysis of the time-temperature superposition could be carried out in a manner similar to that used in the treatment of the data on the Shell 16/78/16 material, although an *additive modulus* model rather than an *additive compliance* model should reflect the presence of a continuous polystyrene phase more appropriately. For a meaningful analysis data without the arbitrary vertical shift would, however, be necessary. There is evidence that the mechanical properties in simple tension (and probably compression) may be drastically different from the shear properties when the polystyrene

forms a continuous phase as the material does not behave in an isotropic manner²⁰ and different models to represent the mechanical coupling are needed in each case. Specifically, shear deformation sees the phases coupled in series so that the compliance of the rubber phase dominates. Tensile deformation sees the phases coupled in parallel so that the modulus of the glassy phase dominates. Hence, the time-temperature shift behavior would differ for the two tests as well as the modulus. This might prevent a simple comparison between data obtained in shear and in compression. The high modulus and the additive modulus coupling may be responsible for the absence of an discernible interlayer effects in NBS 10/30/10.

Since the data cover a fairly small temperature range, the high temperature shift factors fall on a straight line also when plotted against the reciprocal of the temperature. The calculated activation energy, however, is about 91 kcal/mole, which is much higher than activation energies observed previously¹⁻³ for Kraton 102 in a similar temperature region. Since the NBS material seems to be genuinely representative of polystyrene glassy behavior, it seems likely that the intermediate temperature shifts observed previously in Kraton 102 are due to mechanisms other than relaxation in the glassy polystyrene phase.

Kraton 102

The shift factors, $\log a_T$, determined on the NBS 10/30/10 and the Shell 16/78/16 materials agree well with those for Kraton 102 if the difference in glass transition temperature of the two samples (5° and 3°C, respectively) is taken into account. The three WLF curves for the three materials are shown in Figure 17.

The shift factors for the polybutadiene glass transition seen in these three block copolymers show remarkable consistency and reproducibility. They are slightly steeper than the values determined by Maekawa, Mancke, and Ferry²¹ for homopolybutadiene. Their curve, shifted 5°C assuming a T_g of -93°C for the homopolybutadiene, is included in Figure 17. Kraus *et al.*²² have pointed out that a filler raises the apparent glass transition as seen in the mechanical properties by raising the rubbery modulus (i.e. the intertransition plateau in our case). This could perhaps account for the difference in the shift factors for homopolybutadiene and for the polybutadiene phase in block copolymers.

The pronounced difference in the shift factors seen here and those seen in the creep and stress relaxation experiments reported earlier³ and reproduced in Figure 17, is difficult to account for. These measurements were made on unannealed solvent cast films, and very much larger strains were used. These factors may have affected the response. The WLF equation determined by

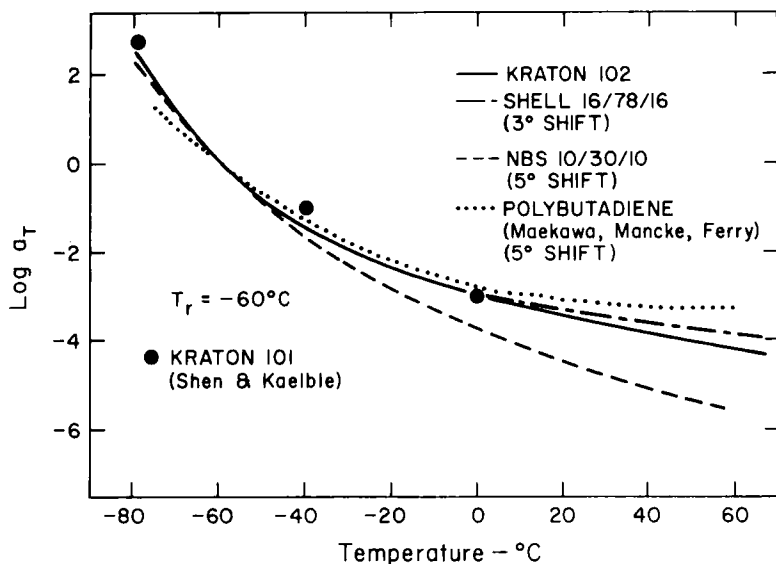


FIGURE 17 Comparison of WLF-equations for Shell 16/78/16, NBS 10/30/10, and Kraton 102.

Shen and Kaelble² for Kraton 101 does not agree with ours as reported here although their shift factors fall on our curve as again shown in Figure 17. They used the universal form of the WLF equation, however, which may not be appropriate, and apparently weighted their lowest temperature data more heavily.

Probably the most meaningful way to shift the data on Kraton 102 is to follow the scheme used for the Shell 16/78/16 data with no provision for an interlayer. In Shell 16/78/16 the polystyrene phase had no discernible effect on the shift factors below 80°C. Since there is evidence that the glass transition of the polystyrene phase is above 80°C, it is unlikely that the polystyrene phase would affect the Kraton 102 data below 50°C. Using, then, the WLF equation determined from Figure 9, and adding the Arrhenius expression, Eq. (11), which was used for Shell 16/78/16 for the region above 0°C, one obtains the compliance master curve shown in Figure 10.

Since we do not have data at higher temperatures we cannot make a more complete quantitative analysis. Nevertheless, we can begin to explain the results obtained previously for Kraton 101 and 102. In shifting relaxation modulus or creep compliance data one would not necessarily see any significant lack of superposition. The change in compliance with temperature due to the changing interlayer may be expected therefore to produce the relatively large shifts that were earlier³ interpreted as arising from contributions of the

glassy polystyrene. This also explains the rather low temperatures at which this behavior was observed to be significant in the transient experiments. We have seen that in Shell 16/78/16 the time dependence of the interlayer is of the order of 10°C per decade of time. Thus, the interlayer effect observed in the dynamic experiments at 50°C would be expected to appear 30° to 40°C lower in a transient experiment where the times are generally about four decades longer.

CONCLUSIONS

Despite the difficulties raised by the thermorheological complexity of block copolymers, data obtained as a function of frequency allow some interesting phenomena to be observed. The most noteworthy of these is the enormously long intertransition plateau in the storage compliance. The extent of the plateau depends on the temperature and arises from the almost 200°C separation of the glass temperatures of the two phases. The modulus in the plateau region is high because of the presence of the polystyrene phase and trapped entanglements in the polybutadiene phase. Differences in phase composition and morphology between the Shell materials and the NBS sample are clearly reflected. The Shell materials appear to present evidence for changes in the effective amount of the hard and soft phases as function of the temperature. In these materials the polystyrene domains act essentially as inert filler in the polybutadiene transition region and well into the intertransition plateau. The effect of an interlayer becomes noticeable above 40°C .

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