

Some Viscoelastic Properties of ABS Polymer

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Synopsis

The discrete relaxation spectrum of an ABS (acrylonitrile-butadiene-styrene) polymer at 190°C. was calculated by using results from tensile relaxation moduli and the principle of reduced variables. The shift factor was found to conform well to the WLF equation, and the free volume fraction at T_g was calculated to be 0.026 in good agreement with the universal value. The values of the thermal expansion coefficient of free volume were calculated to be $9.8 \times 10^{-4} \text{ deg.}^{-1}$ and $7.0 \times 10^{-4} \text{ deg.}^{-1}$, respectively, from the WLF coefficients and from dilatometric results. The width of the entanglement plateau of the relaxation spectrum was observed to be a factor of approximately 2 larger than that calculated from molecular weights between entanglement couplings determined either from rubber elasticity theory or from an assumed molecular model which discounts the presence of the butadiene in the ABS system. By using Pao's theory, flow curves at 190°C. were calculated both from the discrete relaxation spectrum and from the dynamic modulus. These curves were essentially identical. However, the stress values of these curves were found to be about a decade higher than those experimentally determined from capillary flow measurements. Nevertheless, the shapes of the curves are in good agreement, and an explanation is suggested for existing discrepancies. Flow instability, processing variables, and residual strains are discussed in light of the flow curves and the calculated recoverable shear strains.

Introduction

Dynamic mechanical studies on the viscoelastic properties of ABS (acrylonitrile-butadiene-styrene) polymer solids have been reported recently by several authors.¹⁻⁴ In view of the commercial interest in these polyblends, an investigation into the mechanical properties of this polymer melt was carried out with special emphasis on processing behavior. The present analysis attempts to describe the rheology of polyblend melts and compares steady capillary flow measurements with flow curves calculated from measurements on the distribution of relaxation times using a relation for shear stress previously derived⁵⁻⁷ from Pao's continuum theory.^{5,8,9}

Earlier studies^{7,10-12} have used these relations to discuss the rheology of bulk polyethylene melts. Thus, it is hoped that the results of this work can provide a basis for further understanding the behavior of other polyblends and certain filled polymer systems.

This paper will be concerned first with obtaining a discrete relaxation spectrum from the relaxation modulus, calculating a flow curve from the

spectrum, and subsequently with comparing this curve to experimental flow measurements. In addition, a flow curve will be calculated from the dynamic modulus by using Pao's theory in correlation form.⁷

Experimental

The material investigated in this study was a commercial ABS polymer.

Tensile stress relaxation measurements on dumbbell-type specimens, at temperatures between 90 and 140°C., were obtained by using an Instron testing machine equipped with an environmental chamber. Strains varied from 7.0×10^{-3} to 7.0×10^{-2} and the initial rate of strain was kept constant at 4.12×10^{-2} sec.⁻¹.^{*} Specimens were shaped from compression-molded plaques with a Tensil-Kut machine. Compression molding was carried out in such a manner as to avoid extensive orientation in the finished plaques.

Specific volume as a function of temperature was determined using accepted dilatometric techniques;¹³ steady flow measurements were obtained with a Sieglaff-McKelvey capillary flow rheometer, and dynamic oscillatory measurements were obtained by using a Maxwell orthogonal rheometer.¹⁴⁻¹⁶

Results and Discussion

Figure 1 shows the tensile relaxation modulus curves at different temperatures. In calculating the modulus from the stress relaxation measurements, Poisson's ratio was assumed to be $1/2$. In addition, the cross-sectional area of specimens was corrected for thermal expansion.

The curves of Figure 1 were subsequently shifted to a reference temperature T_0 of 96°C. according to the method of reduced variables,^{17a} to produce the plot shown in Figure 2. The vertical shift factor, $\log(\rho T/\rho_0 T_0)$, where T is the absolute temperature, ρ is density, and ρ_0 is density at the reference temperature, was calculated to be negligible, and the horizontal shift factor, $\log a_T$, was fitted to the WLF equation, represented by the solid line in Figure 3,

$$-\frac{T - T_0}{\log a_T} = \frac{C_2^\circ}{C_1^\circ} + \frac{1}{C_1^\circ} (T - T_0) \quad (1)$$

where C_1° and C_2° are experimentally determined constants. Values for C_2° and C_1° at $T = 96^\circ\text{C.}$ were found to be 37.3°K. and 11.8, respectively.

From these values the WLF coefficients C_2^g and C_1^g corresponding to the glass transition temperature, T_g , ($T_g = 85^\circ\text{C.}$, see Fig. 4) were calculated to be 26.3°K. and 16.8, respectively. These are in good agreement with accepted universal values.

The thermal expansion coefficient of free volume, α_f , and the free volume fraction, f_g , at T_g were calculated from the WLF coefficients to be $9.8 \times$

* The use of very high strain rates was forbidden by the mechanical limitation of the Instron.

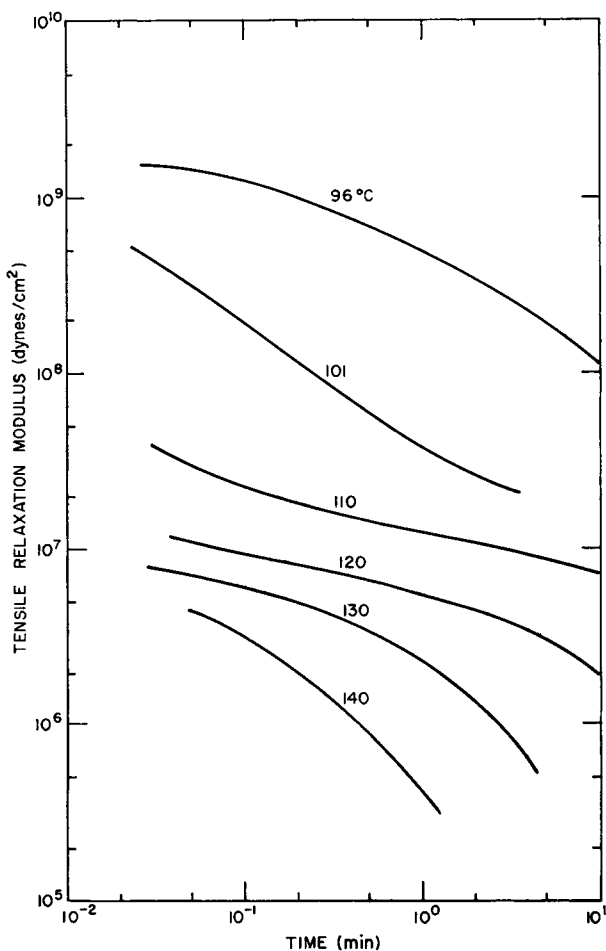


Fig. 1. Tensile relaxation modulus curves of ABS polymer at several temperatures.

$10^{-4} \text{ deg.}^{-1}$ and 2.6×10^{-2} , respectively. Moreover, α_f was determined to be $7.0 \times 10^{-4} \text{ deg.}^{-1}$ through the results of Figure 4 and the expression

$$\alpha_f \simeq \left(\frac{1}{v} \frac{\partial v}{\partial T} \right)_{T > T_g} - \left(\frac{1}{v} \frac{\partial v}{\partial T} \right)_{T < T_g} \quad (2)$$

where v is the specific volume (see Appendix).

The fact that the value of the fractional free volume at the glass transition temperature and its thermal expansion coefficient compare favorably with the universal values (0.025 and $4.8 \times 10^{-4} \text{ deg.}^{-1}$, respectively) implies that the temperature dependence of the mechanical properties of this polyblend is similar to that of many amorphous homopolymers above their glass transition temperatures. The reasonable agreement in the thermal expansion coefficients of free volume calculated in the two different manners supports the consistency of the experimental data.

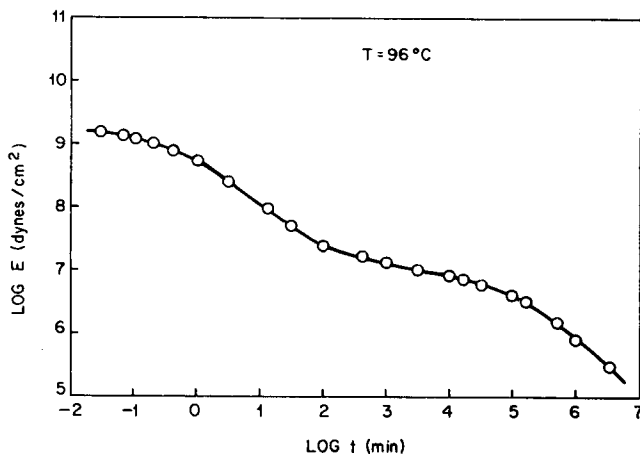


Fig. 2. Tensile relaxation modulus master curve at 96°C. for ABS polymer.

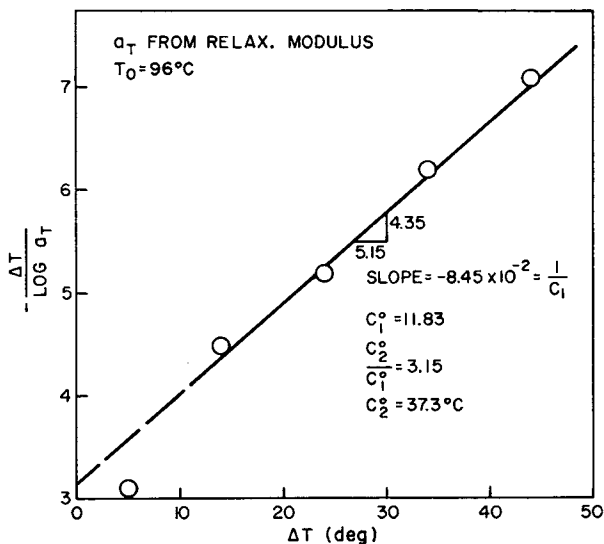


Fig. 3. WLF plot of ABS polymer with the use of a reference temperature of 96°C.

The relaxation spectrum was obtained from the relaxation modulus by successive approximations through the relation¹⁸

$$H(\tau) = -M(m) G(t) \left. \frac{d[\log G(t)]}{d[\log t]} \right|_{t=\tau} \quad (3)$$

where $H(\tau)$ is the continuous relaxation spectrum, $G(t)$ is the shear relaxation modulus,* t is time, τ is the relaxation time, and $-m$ is the slope of a doubly logarithmic plot of H against τ . The variable M is assumed to be

* Here $G = E/3$ because of the previous assumption on Poisson's ratio.

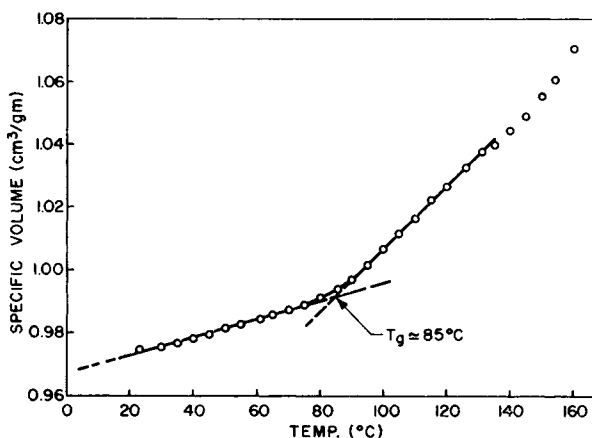


Fig. 4. Relationship between specific volume and temperature for ABS polymer.

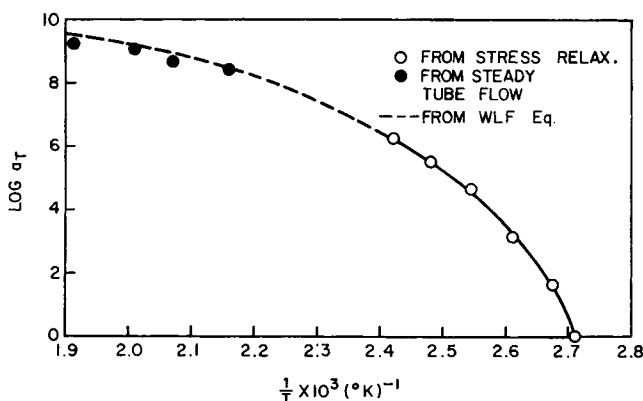


Fig. 5. Arrhenius type plot of shift factor a_T for ABS polymer.

1 in the first approximation on H ; in later approximations $M \equiv \Gamma(m-1)^{-1}$ where Γ is the gamma function. Two trials were sufficient to determine H . The spectrum was then shifted along the logarithmic τ axis to 190°C . by using a shift factor of -8.5 obtained through extrapolation of the WLF plot in Figure 3. The small vertical shift factor was again neglected. It is felt that the shifting of the spectrum to a higher temperature achieved in this manner is appropriate since the activation energies obtained from extrapolated values of a_T from the WLF plot agree closely with those obtained from capillary flow data in that temperature range (see Fig. 5).

The shifted spectrum is shown in Figure 6. If a monodisperse system is assumed, from molecular theory^{17c} the average molecular weight between entanglements coupling points, M_e , can be approximated from the width of the entanglement (rubbery) plateau Δ by using the relation

$$\Delta = 2.4 \log (M/2M_e) \quad (4)$$

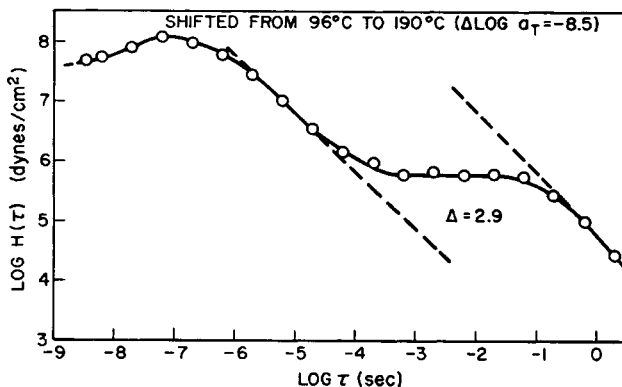


Fig. 6. Continuous relaxation spectrum of ABS polymer shifted from 96 to 190°C.

where M is molecular weight. By this method, on the basis of the molecular weight of the soluble phase of the blend,¹⁹ M_e was calculated at 3.2×10^3 .

By considering a model polymer system of acrylonitrile-styrene whose respective monomers are randomly distributed along the chain and considering the styrene to be present in amounts of 74% by weight¹⁹ the average molecular weight per atom of backbone chain was calculated to be 41.6. An entanglement spacing value of 673¹⁸ for bulk polystyrene was then used to calculate an M_e of 1.4×10^4 . Furthermore, from rubber elasticity theory^{17c} and the experimentally determined modulus, G_e , in the entanglement plateau zone, M_e for the polyblend was calculated to be 1.3×10^4 through the expression

$$M_e = \rho RT/G_e \quad (5)$$

By using either of the latter two values of M_e the width of the entanglement plateau is calculated to be approximately 1.5 for the model. This is approximately a factor of two lower than that actually observed for the polyblend. These findings indicate that the presence of the polybutadiene in the ABS system has an influence on the viscoelasticity of the system in that it extends the width of the entanglement plateau region of the relaxation spectrum. This has also been suggested by Takayanagi.²¹

A discrete relaxation spectrum can be approximated^{17b} from a continuous one by manipulating the relation

$$G_i(t) = \sum_{i=1}^n G_i e^{-t/\tau_i} = \int_{-\infty}^{\infty} H(\tau) e^{-t/\tau} d(\ln \tau) \quad (6)$$

to obtain

$$G_i \simeq H(\tau) \Delta(\ln \tau) \quad (7)$$

where G_i is the modulus of the i th relaxing element whose relaxation time is τ_i . The relaxation spectrum represented by discrete elements evenly spaced at intervals of 0.5 units along the logarithmic τ axis is shown

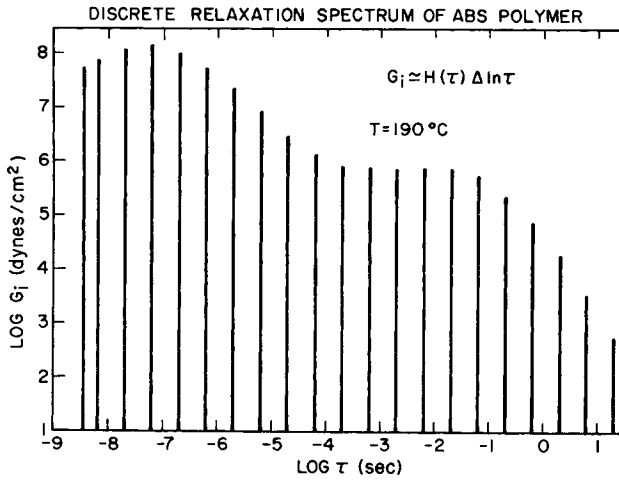


Fig. 7. Discrete relaxation spectrum of ABS polymer at 190°C.

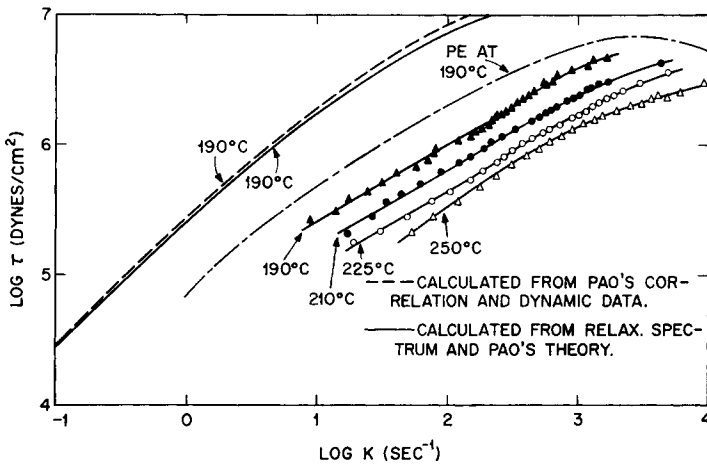


Fig. 8. Experimental and calculated flow curves for ABS polymer. A curve for linear polyethylene is also shown.

in Figure 7. The last few values of the terminal zone were obtained by using extrapolated values of the continuous spectrum.

The discrete relaxation spectrum was utilized for calculating the shear stress in steady flow through the expression⁷ derived from Pao's continuum theory

$$\tau_{12} = K \left[\sum_{i=1}^n \frac{G_i/\tau_i}{(1/\tau_i)^2 + K^2} \right] \left\{ 1 + \frac{1}{2} \left[\frac{2K \sum_{i=1}^n \frac{G_i}{(1/\tau_i)^2 + K^2}}{\sum_{i=1}^n \frac{G_i/\tau_i}{(1/\tau_i)^2 + K^2}} \right]^2 \right\} \quad (8)$$

where K is shear rate, τ_{12} is shear stress, and the remaining quantities have been defined earlier. In addition, the shear stress was calculated from dynamic measurements by using relations previously derived between dynamic oscillatory and steady-flow shear properties.⁷

The shear stress–shear rate results calculated as described above are shown in Figure 8. In this range of shear rates it is the rubbery plateau region of the spectrum which contributes most heavily to the stress. It is evident that the two calculated curves are almost identical; this implies that the relaxation spectrum obtainable from dynamic measurements agrees with that shown in Figure 6. For comparison, experimental flow curves at several different temperatures are also included in Figure 8.

It is clear that the stress values calculated from Pao's theory are higher (by a factor of $\simeq 6$) than those obtained from steady-flow experiments. A similar behavior was observed previously⁷ for polyethylene melts; however, the slopes of the calculated and experimental curves are nearly identical. This means that an excellent approximation of a steady-flow curve can be obtained by arbitrarily shifting the calculated curve along the abscissa after having determined a single value of steady-flow shear stress (for example, by measuring melt index).

The discrepancy between the experimentally determined steady-flow results and those calculated from the relaxation spectrum may be due to a slight variance of the spectrum in the entanglement zone with changing rate of shear. This possibility was first suggested by Osaki and co-workers²² and recently by Huseby and Blyler.⁷

The quantity to be squared in eq. (8) is a measure of the recoverable shear strain.⁷ For the ABS system this quantity is found to be lower than that of polyethylene⁷ under the same conditions, although, in the range of shear rate studied, the two polymers are observed to have similar flow curves. In addition the calculated recoverable shear strain did not pass through a maximum in the range of shear rates studied. It has been hypothesized that the occurrence of the maximum in the recoverable shear strain coincides with the onset of flow instability. However, the flow instability observed in polyethylene^{7,23} is not evident in either the experimental or calculated flow curves for the polyblend. Nevertheless, the occurrence of this instability at higher rates of shear is not discounted.

Summary and Conclusions

The discrete relaxation spectrum of an ABS polyblend at 190°C. was determined by using results from tensile relaxation moduli and the principle of reduced variables. The shift factor conformed well to the WLF equation. The free-volume fraction of the polyblend at the glass transition temperature was calculated to be 0.026 which is in good agreement with the universal value. The values of the thermal expansion coefficient of free volume were calculated to be $9.8 \times 10^{-4} \text{ deg.}^{-1}$ and $7.0 \times 10^{-4} \text{ deg.}^{-1}$, respectively, from the WLF coefficients and from dilatometric results. These results indicate that the temperature dependence of the

viscoelastic behavior of the polyblend is quite similar to that of many amorphous homopolymers above their glass transition temperatures.

The width of the entanglement plateau region was observed to be approximately twice as large as that calculated from average molecular weights between entanglement couplings determined either from rubbery elasticity theory or from an assumed model for the blend which discounted the presence of the butadiene (either free or grafted). Thus, it was concluded that the butadiene in the ABS system has the effect of widening the entanglement plateau region. Therefore, the rheological effect of the butadiene is quite different from that of an inert filler.

From Pao's theory and the determined discrete relaxation spectrum a flow curve at 190°C. was calculated which is almost identical to that calculated from the dynamic modulus using Pao's theory in correlation form. This implies that the relaxation spectrum obtained from relaxation modulus agrees with that obtainable from dynamic measurements. However, the shear stress values of the calculated curves were found to be about a decade higher than those experimentally determined from capillary flow measurements. An explanation is suggested for existing discrepancies.

In the range of shear rates studied ($1-10^5$ sec.⁻¹) the calculated recoverable shear strain of the ABS polyblend was found to be lower than that of polyethylene reported by other workers, although the two polymers have similar flow curves. However, within those shear rates, the flow instability which is characteristic of many polymers was not observed for the polyblend. Nevertheless, its occurrence at higher values of shear rate is not discounted.

In light of the experimental flow curves and the knowledge of the recoverable shear strain, it is concluded that the processing problems resulting from flow instability at high shear rates are probably less severe for ABS polymers than for polyethylene. Also, because of the lower recoverable shear strain and lack of crystallinity,²⁴ residual strains in an ABS polymer product should be lower than in one made from polyethylene under identical conditions. More extensive studies in this direction are planned for the near future.

Appendix

For an amorphous polymer let: v = specific volume, v_o = occupied (noncollapsible) volume, v_f = free volume, v_g = specific volume below T_g , v_l = specific volume above T_g , and f = fractional free volume, where T is the absolute temperature and T_g is the glass transition temperature.

The coefficient of thermal expansion of free volume is defined as

$$\alpha_f = \frac{\partial f}{\partial T} = \frac{(\partial v_f/v)}{\partial T} = \frac{1}{v} \frac{\partial v_f}{\partial T} - \frac{v_f}{v^2} \frac{\partial v}{\partial T} \quad (9)$$

or

$$\frac{1}{v} \frac{\partial v_f}{\partial T} = f\alpha + \alpha_f \quad (10)$$

where α is the coefficient of thermal expansion of the polymer.

The difference between the coefficients of thermal expansion in the liquid and the glassy states near T_g is

$$\begin{aligned} \Delta\alpha_{T \rightarrow T_g} &= \alpha_l - \alpha_g = \frac{1}{v_l} \frac{\partial v_l}{\partial T} - \frac{1}{v_g} \frac{\partial v_g}{\partial T} \\ &= \frac{1}{v_o + v_f} \frac{\partial(v_o + v_f)}{\partial T} - \frac{1}{v} \frac{\partial v_g}{\partial T} \end{aligned} \quad (11)$$

and since v_f is approximately constant below T_g , then

$$\frac{\partial v_g}{\partial T} \simeq \frac{\partial v_o}{\partial T}$$

therefore

$$\Delta\alpha_{T \rightarrow T_g} \simeq \frac{1}{v_o + v_f} \frac{\partial v_f}{\partial T} \quad (12)$$

Substituting eq. (10) in eq. (12) results in

$$\Delta\alpha_{T \rightarrow T_g} \simeq f\alpha + \alpha_f \quad (13)$$

where f is usually approximately $1/40$, so that at T_g

$$\alpha_f \simeq \Delta\alpha$$

The helpful discussions with Dr. S. Matsuoka are gratefully acknowledged.

References

1. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **13**, No. 1, 65 (1963).
2. M. Takayanagi, H. Harima, and Y. Iwata, *Mem. Fac. Eng. Kyushu Univ.*, **13**, No. 2, 57 (1963).
3. S. G. Turley, *Effect of Polymer Structure on Impact Properties*, Polymer Conference Series, Wayne State Univ., May, 1967.
4. R. M. Evans, H. R. Nara, and E. G. Bobaleck, *SPE J.*, **16**, 76 (1966).
5. Y. H. Pao, Jr., *J. Polymer Sci.*, **61**, 413 (1962).
6. L. L. Blyler, Jr. and T. W. Huseby, in preparation.
7. T. W. Huseby and L. L. Blyler, Jr., *Trans. Soc. Rheol.*, **11**: **1**, 77 (1967).
8. Y. H. Pao, *J. Appl. Phys.*, **28**, 591 (1957).
9. Y. H. Pao, *J. Polymer Sci. B*, **2**, 437 (1964).
10. T. W. Huseby and C. G. Gogos, *Polymer Eng. Sci.*, **5**, No. 3, 1 (1965).
11. L. L. Blyler, Jr. and T. W. Huseby, *J. Appl. Polymer Sci.*, **10**, 75 (1966).
12. T. W. Huseby, *Trans. Soc. Rheol.*, **10**: **1**, 181 (1966).
13. N. Bekkedahl, *J. Res. Natl. Bur. Std.*, **42**, 145 (1949).
14. B. Maxwell and R. P. Chartoff, *Trans. Soc. Rheol.*, **9**: **1**, 41 (1965).
15. L. L. Blyler, Jr. and S. J. Kurtz, *J. Appl. Polymer Sci.*, **11**, 127 (1967).
16. B. Maxwell, *Polymer Eng. Sci.*, **7**, 145 (1967).

17. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, (a) Chapt. 11; (b) Chapt. 3; (c) Chapt. 10.
18. J. D. Ferry and M. L. Williams, *J. Colloid Sci.*, **7**, 347 (1952).
19. B. D. Gesner, *J. Appl. Polymer Sci. A*, **3**, 3825 (1965).
20. R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).
21. M. Takayanagi, private communication.
22. K. Osaki, T. Tamura, M. Kurata, and T. Kotaka, *J. Phys. Chem.*, **69**, 4183 (1965).
23. T. W. Huseby, *Trans. Soc. Rheol.*, **10**: **1**, 1 (1966).
24. T. W. Huseby and H. E. Bair, *SPE Preprints, Ann. Tech. Conf.*, 12 (1966) I-2.

Received October 6, 1967