

Viscoelastic Behavior of Interpenetrating Polymer Networks: Poly(ethyl Acrylate)—Poly(methyl Methacrylate)

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Synopsis

The creep behavior of a series of poly(ethyl acrylate)—poly(methyl methacrylate) interpenetrating polymer networks was investigated. For comparison purposes, some stress relaxation data were included. Master curves containing a single broad transition covering approximately 20 decades of time were found for midrange compositions. Although the time-temperature superposition principle and the WLF equation should not strictly apply, reasonable agreement was found over a large portion of shift factor versus temperature plots. Application of a modified Tobolsky-Aklonis-Dupre glass-rubber theory suggested that the breadth of the transition could be attributed to a near continuum of phase compositions in the material, each phase composition making its specific contribution to the relaxation spectrum. Whether or not these phase regions are so small as to arise from random concentration fluctuations in an otherwise compatible polymer pair remains unknown.

INTRODUCTION

Interpenetrating polymer networks, IPNs, contain an especially intimate mixture of two polymeric components. Although not chemically bound to each other, they cannot be separated because of their unique morphology.¹

The IPNs, like polyblends and block copolymers, usually exhibit a greater or lesser degree of phase separation. However, the polymer incompatibility problem recently has received renewed attention, and several polymer pairs^{2,3} were shown to exhibit partial, perhaps total, compatibility.

In the previous paper of this series,⁴ IPNs containing poly(ethyl acrylate) and poly(methyl methacrylate) were shown to exhibit a single, broad glass transition. The present paper considers the creep behavior of this system. Some stress relaxation data are also presented for comparison. A modified Tobolsky-Aklonis-Dupré⁵⁻⁷ theory of molecular

relaxation behavior in the glass transition region is applied in an effort to clarify the phase relationships existing in this system.

MATERIALS AND INSTRUMENTATION

The synthesis of these materials has been previously described.^{1,4} In brief, a solution of ethyl acrylate monomer, containing tetraethylene glycol dimethacrylate (TEGDM) for crosslinking and benzoin for activation, was polymerized photochemically for 24 hr. The recipe for the PEA and the PMMA was 2 ml TEGDM and 0.3 g benzoin per 100 ml monomer. After vacuum drying the homopolymer to remove traces of remaining monomer, controlled quantities of methyl methacrylate plus TEGDM and benzoin were swelled in, followed by a second photopolymerization and vacuum drying. In each case, clear, transparent materials were obtained. To insure compositional uniformity, only center portions of samples were used. IPNs containing 0, 27.6, 49.4, 66, and 100% by weight poly(ethyl acrylate), the other component being poly(methyl methacrylate), were prepared.

A modified Gehman torsional tester⁸ was equipped with a constant-temperature silicone oil bath to allow creep studies in torsion. After each run, the sample was removed and heated above its glass transition temperature for 10 min to allow relaxation to occur. Stress relaxation studies were carried out on a stress relaxometer.⁹ In both cases, the temperature could be held constant to $\pm 0.5^\circ\text{C}$ between -50°C and 125°C . The experiments employing the Gehman tester were between 5 sec and 1 hr long, those employing the stress relaxometer were between 1 min and a few days' duration.

RESULTS

In all cases, the creep data were converted to relaxation data. The semiempirical treatment of Ferry¹⁰ was employed for this purpose. Representative plots of the log of the time-dependent Young's modulus, as $\log 3G(t)$ versus log time, are presented in Figures 1, 2, and 3. Since all the samples were crosslinked, the modulus approached a constant value at higher test temperatures. This is known as the rubbery plateau region.

A comparison of Figures 2 and 3 with Figure 1 shows immediately that the IPN transition is broader than for normal homopolymers. Although it is well known that the standard time-temperature superposition principle¹¹ and the WLF equation do not strictly apply to broadened transitions, it is still instructive to construct master curves, as has been done by Takayanagi.¹²

The reference temperature of PEA was selected as -40°C , and T_{ref} for PMMA was $+30^\circ\text{C}$. The reference temperatures for the intermediate compositions were chosen as close as possible to 30°C . The master curves are shown in Figures 4 to 8. Data from stress relaxation experiments are superimposed on Figure 7. Note the single, broad transition appearing

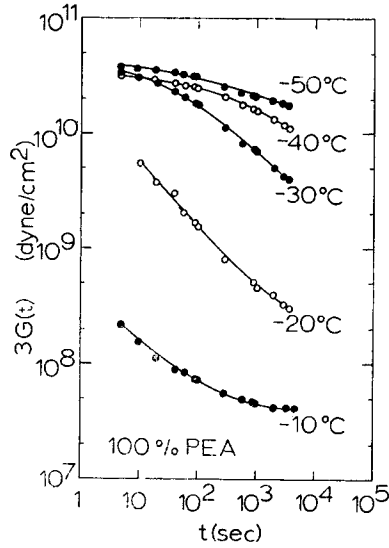


Fig. 1. $\log 3G(t)$ vs $\log t$ relaxation data for the poly(ethyl acrylate) homopolymer.

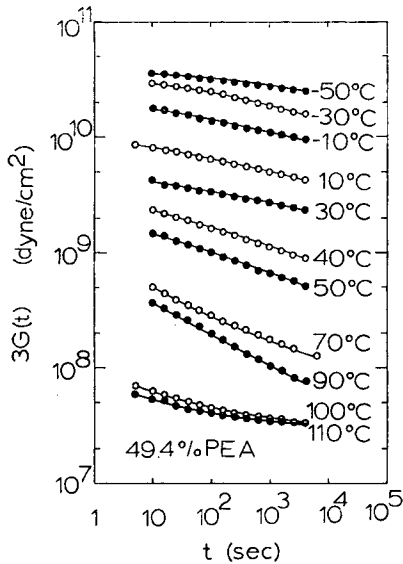


Fig. 2. $\log 3G(t)$ vs. $\log t$ for an IPN containing 49.4% PEA. The temperature range necessary to cover the relaxation spectrum is much wider than for Figure 1.

in the intermediate IPN compositions. This result is analogous to the modulus-temperature data reported by Sperling and co-workers.⁴

The empirical shift factors for the 49.4% PEA IPN are compared to the theoretical WLF values in Figure 9, 20°C being chosen as close to the classical glass transition temperature (based on ref. 4, Fig. 4). For a classical homopolymer, the shift factor covers about 8 decades of time

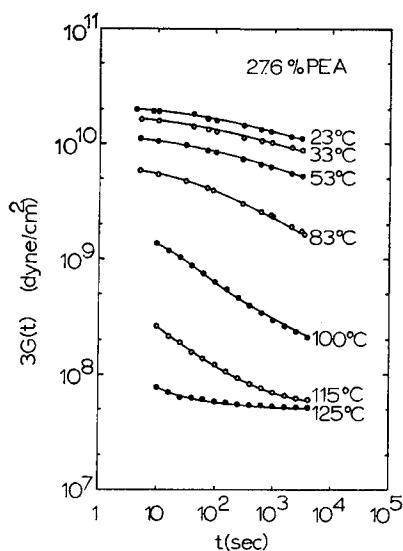


Fig. 3. Log $3G(t)$ vs. log t relaxation data for an IPN containing 27.6% PEA, 72.4% PMMA.

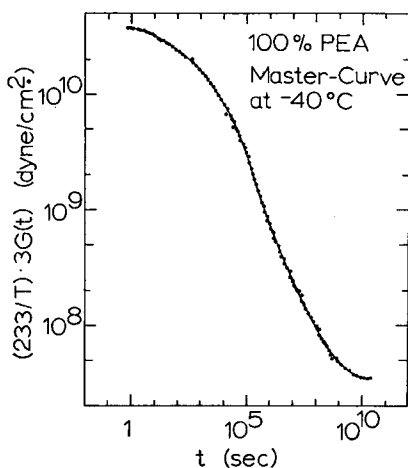


Fig. 4. Master curve prepared from Figure 1, employing -40°C as the reference temperature. As with most amorphous homopolymers, the transition covers about ten decades of time. Note the temperature correction to the modulus, as required by elasticity theory.

in a temperature interval of approximately 50°C . This corresponds to the central portion (20° to 70°C) of Figure 9. Surprisingly, the WLF equation fits the center and lower portions of the data quite well. The reason lies in the value of the derivative $-d \log (t/t_0)/dT$. The slopes (perhaps by accident) are nearly equal because the IPN transition covers both a broader time scale and temperature range. The increased breadth

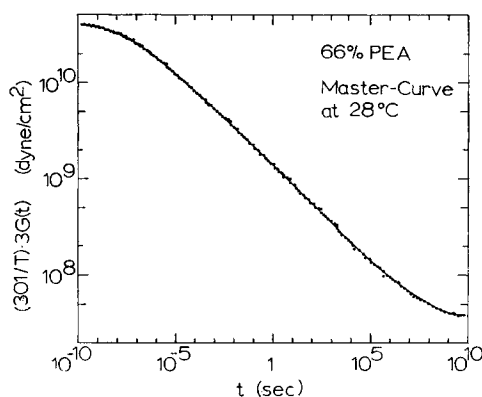


Fig. 5. At 66% PEA, the master curve covers about 18 decades of time.

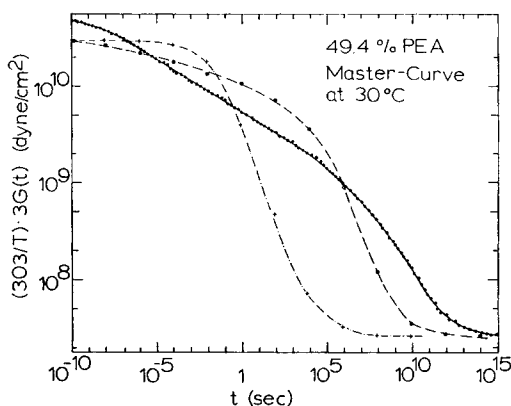


Fig. 6. For this midrange IPN composition of PEA and PMMA, the transition covers 23 or 24 decades of time. Dashed line represents eq. (4) and Figure 11, as discussed in the text. Dotted line represents eq. (3), τ_{min} being taken as the midpoint in Figure 10.

of the IPN transition becomes apparent on observing the upper portion of Figure 9, which does not have an analog in the WLF formulation.

MATHEMATICAL ANALYSIS

In 1964, the time-dependent relaxation modulus $E_r(t)$ was interpreted by Tobolsky and Aklonis as the sum of two Rouse functions.⁶ One, R_1 , is associated with torsional vibrations and internal rotations. The other, R_2 , is associated with an entangled network of Gaussian segments. The R_1 function was derived to be

$$R_1 = \frac{E_1 \tau_{min}^{1/2}}{2} t^{-1/2} [\Gamma_{t/\tau_1}(1/2) - \Gamma_{t/\tau_1 Z_1^2}(1/2)] \quad (1)$$

where E_1 is the tensile modulus (3×10^{10} dynes/cm²) in the glassy state, τ_{min} is the minimum relaxation time, $\Gamma(1/2)$ is the tabulated incomplete

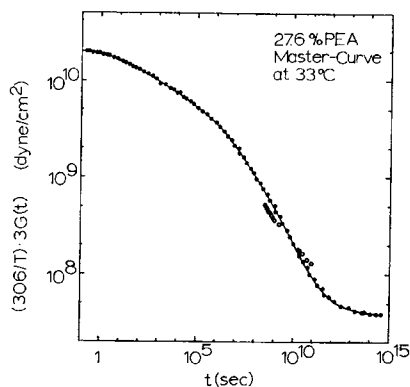


Fig. 7. Master curve for an IPN of 27.6% PEA at 33°C reference temperature, as obtained from creep experiments. Stress relaxation data (open circles) are included for comparison. Although slight differences exist, the stress relaxation data tend to confirm the creep data.

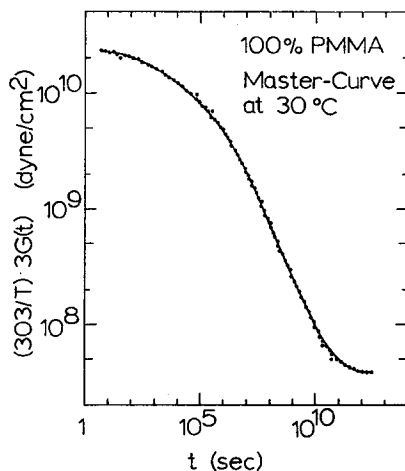


Fig. 8. This pure PMMA master curve resembles Figure 4, except that the higher temperature is required for the higher glass-rubber transition temperature of PMMA.

gamma function of argument $1/2$, τ_1 is the first normal mode relaxation time, t is the time, and Z is the number of Gaussian segments in a polymer molecule.

In a later paper, Tobolsky⁵ approximated this function with

$$R_1 = \frac{E_1 \tau_{min}^{1/2}}{\tau_{min}^{1/2} + t^{1/2}} \quad (2)$$

For the PEA and PMMA homopolymers, a modified form of the double Rouse function will be employed:

$$E_r(t) = \frac{E_1 \tau_{min}^{1/2}}{\tau_{min}^{1/2} + t^{1/2}} + R_2 \quad (3)$$

The factor R_2 represents the modulus in the rubbery plateau region of the master curve; it has the value of approximately 4×10^7 dynes/cm² for the present samples.

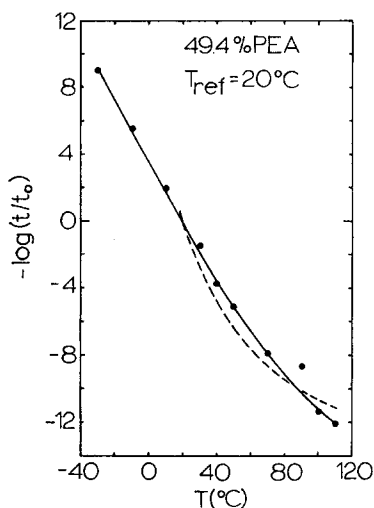
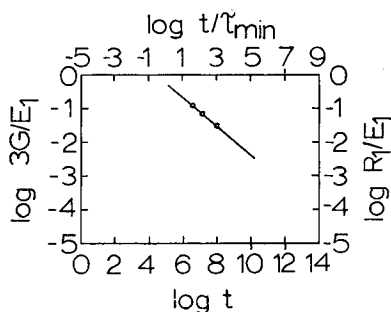


Fig. 9. Comparison of experimental shift factors vs. those predicted by the classical WLF formulation. Although agreement is good over the portion covered by theory, this result may be fortuitous.



Sliding-over Process(100%PMMA)

Fig. 10. Illustration of sliding-over process for PMMA used in the Tobolsky-Aklonis-Dupré theory to estimate τ_{min} for homopolymers. A value of τ_{min} equal to 10 sec is required for $3G/E_1$, to fit the theoretical curve given by the axes given below and on the right.

Because of the unusual breadth of the transition in the IPNs, it will be assumed that each sample consisted not of a single composition but of a continuous range of compositions. Each composition region will be assumed to have its own characteristic relaxation time. The average

composition, of course, will be equal to the overall composition. A number of simple distributions were analyzed by use of the formula

$$E_r(t) = 3G(t) = E_1 \cdot \sum_{i=1}^n \frac{w_i \tau_{min_i}^{1/2}}{\tau_{min_i}^{1/2} + t^{1/2}} + R_2 \quad (4)$$

where w_i is the frequency for composition i , normalized to satisfy

$$\sum_{i=1}^n w_i = 1 \quad (5)$$

The values of τ_i appearing in eq. (4) were evaluated as follows. For homopolymer, the single value of τ_{min} was obtained⁶ by use of a plot of $\log (R_1(t)/E_1)$ versus $\log (t/\tau_{min})$. By sliding tabulated values of eq. (2) over a plot of the experimental values of $\log (3G/E_1)$ versus $\log t$ in the transition region, the values of τ_{min} which gave the best fit were selected. This

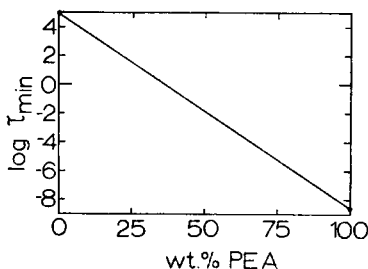


Fig. 11. The τ_{min} values at 0 and 100% PEA, estimated at 30°C, were obtained as explained in the text. τ_{min} values of intermediate phase compositions were estimated from this $\log \tau_{min}$ -composition empirical graph.

is illustrated in Figure 10 for PMMA. For pure PMMA τ_{min} was estimated at +30°C to be 1×10^5 sec. The value of τ_{min} for pure PEA was estimated at -20°C to be 1×10^{-1} sec. τ_{min} for pure PEA at +30°C was calculated by use of the WLF equation

$$\log \frac{\tau_T}{\tau_{T_g}} = \frac{-17.44 (T - T_g)}{51.6 + T - T_g} \quad (6)$$

to be 4.46×10^{-9} sec (T_g was assumed equal to -20°C).

The above method for determining τ_{min} is applicable to homopolymers when a slope of $-1/2$ is obtained in the transition region. This method cannot be used with the intermediate IPN compositions since slopes significantly less than $-1/2$ were found. It was therefore assumed that $\log \tau_{min}$ varied as a linear function of weight per cent PEA, Figure 11. This assumption is quite arbitrary and was made for the sake of simplicity. Other τ_{min} distributions, such as $\log \tau_{min} - \log$ composition, gave the same or poorer results, as discussed below.

DISCUSSION

Of the several phase distributions studied (Gaussian, etc.), the simplest, which assumed all compositions to have equal weight, gave the best fit. A distribution containing nine equally spaced compositions of equal weight covering the entire composition range yielded the dashed line in Figure 6. For comparison, a curve based on eq. (3) is shown as the dot-dashed line.

Only distributions which included the whole range of compositions from 0 to 100% by weight PEA reasonably approximated the form of the master curve. As can be seen from Figure 6, even this last yielded an imperfect fit to the experimental data. However, the assumption of a single relaxation time results in a much poorer fit. This suggests that the actual composition distribution, although it may be quite complex, will have to include the whole continuous range of compositions.¹³

Alternately, the PEA-PMMA IPNs may be considered to be compatible and to consist of one thermodynamically stable phase. The original Rouse-Bueche theory^{14,15} requires approximately 50 mers to undergo coordinated motion for the glass transition relaxation phenomenon to occur. This corresponds to a volume of ca. 10,000 Å³. Due to the chain characteristics of polymers, however, volumes of 100,000 Å³ or more will be required to average out random concentration fluctuations for even ideally compatible IPNs. If the minimum volume required for independent contributions to the relaxation spectrum is the same or smaller than that required to yield homogeneous overall compositions, a broadened transition will result. If this last is true, the above mathematical treatment will still be as valid as if phase separation actually existed. This point is the subject of continued investigation.

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