Temperature Dependence of Dynamic Mechanical Properties of Mixed Polymer Systems

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INTRODUCTION

The behavior of a bulk polymer subjected at a constant temperature above its glass transition temperature to an impressed sinusoidal deformation, $A \sin \omega t$, can be characterized by a dynamic modulus which is comprised of two terms, viz., an elastic component representing the fraction of the applied stress in phase with the strain, and a viscous component representing the fraction of the applied stress 90° out of phase with the strain. If the response of the bulk system is observed over a sufficiently wide range of frequency it is found that the elastic component, $E_1(\omega)$, exhibits an inflection over a relatively narrow frequency range, and that the viscous component, $E_2(\omega)$, exhibits a maximum in the same narrow frequency range. At frequencies above and below this narrow range the magnitudes of $E_1(\omega)$ and $E_2(\omega)$ are only slightly dependent on frequency. This behavior has been described mathematically[1] by the integral equations:

$$E_1(\omega) = \int_{-\infty}^{\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} H(\ln \tau) \, d \ln \tau \qquad (1)$$

$$E_2(\omega) = \int_{-\infty}^{\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} H(\ln \tau) \, d \ln \tau \qquad (2)$$

where $H(\ln \tau)$ is a weighting function describing the number of structural units with relaxation times in the logarithmic interval $\ln \tau$ to $\ln \tau + d \ln \tau$. The definition of $H(\ln \tau)$ from data obtained in static experiments (creep and stress relaxation) and dynamic experiments can be readily carried out to a first approximation[2] and, with somewhat greater difficulty, to higher approximations.[3] In the first approximation the distribution function $H(\ln \tau)$ is defined at each $\tau = 1/\omega$ by the negative slope of a plot of the elastic component against $\ln(1/\omega)$, or by the magnitude of the viscous component.

In other experiments it has been observed that the behavior of a bulk, amorphous polymer responds to an increase in temperature much as it would to a decrease in frequency of the cyclic stress applied. Analysis of this temperature dependence has led to the following expression[4] which relates the dynamic modulus measured at a temperature T to that measured at a standard temperature T_0 (usually 25°C.) and the densities of the polymer at the respective temperatures:

$$E_T(\omega) = (T\rho/T_0\rho_0) \, E_{T_s}(\omega a_T) \qquad (3)$$

As a result, a single master curve is obtained along which data for a given polymer at all temperatures and frequencies fall. The success of this empirical approach is evidenced by the large number of communications appearing in the recent literature, each describing one or more such master curves.

Although treatment of viscoelastic data according to eqs. (1) through (3) has been successfully carried out for a number of polymers, little progress has been made towards defining specific molecular motions within a given polymer which give rise to the observed response. It is the purpose of the present communication to present a theory which relates the behavior of amorphous polymers, at temperatures in the region of their glass transition temperatures, to their molecular composition.

THEORY

It is postulated that corresponding to each possible mechanical mode of motion in the polymer system there exists a characteristic temperature. Well below this characteristic temperature the motion is purely elastic ($\tau \rightarrow \infty$) and well above this characteristic temperature the motion is completely free, i.e., the mode reacts as a liquid with very low viscosity ($\tau \rightarrow 0$). Only in the vicinity of its characteristic temperature does the

mode react as an energy-dissipating mechanism. In particular, it is postulated that the relaxation time τ of a given mode at any temperature T is related to the relaxation time τ_k of the mode at its equilibrium transition temperature T_k according to the following equation:

$$\tau = \tau_k \exp (\Delta H/R) (1/T - 1/T_k) \qquad (4)$$

where ΔH is the enthalpy change associated with the equilibrium transition, R is the well-known gas constant, and τ_k is a temperature-independent constant when strain amplitudes are small. The entropy change associated with the transition has been replaced by $\Delta H/T_k$, and the enthalpy change has been utilized here so as not to preclude the possibility of a volume change accompanying the transition. If no volume change occurs, the enthalpy change reduces to an energy change. It should be noted that although it is not correct to identify the characteristic temperature with the equilibrium glass transition temperature, T_g, defined dilatometrically, it is necessary that T_k be a reproducible temperature defined for an equilibrium transition occurring at the frequency involved in the experiment.

It follows from eq. (4) that the distribution function $H(\ln \tau)$ will take the form $H(1/T_k)$, which describes the number of modes with reciprocal characteristic temperatures in the interval $1/T_k$ to $1/T_k + d(1/T_k)$. In addition, the following relations, parallel in structure and derivation to eqs. (1) and (2), will result:

$$E_1(1/T)$$
$$= \int_0^\infty [q^2/(1 + q^2)]H(1/T_k)\, d(1/T_k) \quad (5)$$

$$E_2(1/T) = \int_0^\infty [q/(1 + q^2)]H(1/T_k)\, d(1/T_k) \quad (6)$$

For the sake of clarity the variable $q = \omega\tau_k \exp (\Delta H/R) (1/T - 1/T_k)$ has been introduced.

In order to facilitate a discussion of the dependence of both $E_1(1/T)$ and $E_2(1/T)$ on temperature as predicted by eqs. (5) and (6), the kernels $q^2/(1 + q^2)$ and $q/(1 + q^2)$ are plotted against reciprocal absolute temperature in Figure 1. The curves were calculated for a single relaxation mechanism with $\tau_k = 0.55$ msec. and $T_k = 233°K$., and for the frequencies ($f = \omega/2\pi$) 10, 100, and 1000 cycles/sec. A value 10^4 (°K.) was chosen for the parameter $\Delta H/R$.

It is immediately obvious that the integrand of eq. (5) will be zero at reciprocal absolute temperatures much below that at which the inflection in $q^2/(1 + q^2)$ occurs. At reciprocal absolute tem-
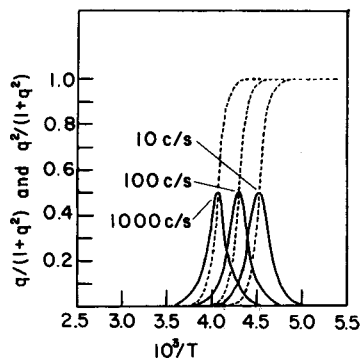

Fig. 1. Plot of the kernels $q/(1 + q^2)$ (——) and $q^2/(1 + q^2)$ (- - -) against reciprocal absolute temperature for a single relaxation mechanism.

peratures much above that of the inflection the integrand of eq. (5) assumes a constant value. Similarly, the integrand of eq. (6) will be nonzero only at reciprocal absolute temperatures in the vicinity of the maximum in $q/(1 + q^2)$. The magnitudes of $E_1(1/T)$ and $E_2(1/T)$ observed experimentallly, will, of course, reflect the sum (or integral) of the contributions at each temperature of all relaxation mechanisms $H(1/T_k)$. The assumption of linear additivity of the contributions is, of course, implicit in the forms of eqs. (5) and (6), as it is in the forms of eqs. (1) and (2). Plots of $E_1(1/T)$ and $E_2(1/T)$ should therefore reflect the general characteristics of the respective curves in Figure 1, i.e., $E_1(1/T)$ will exhibit a sigmoidal inflection and $E_2(1/T)$ a maximum. Furthermore, for a mixed polymer system multiple inflections and maxima should be observed provided the experimental temperature range is sufficiently broad and the characteristic temperature ranges of the components are sufficiently distinct.

It is also shown in Figure 1 that the temperature range in which each mechanism contributes significantly is governed by the parameter ω, the frequency of the applied deformation. It follows that the sum of the contributions will be similarly governed by ω, i.e., the inflection in $E_1(1/T)$ and the maximum in $E_2(1/T)$ will be shifted to lower values of reciprocal temperature by increased values of ω. It should be noted in this regard, however, that a tenfold increase in ω leads to a linear decrease in reciprocal temperature for the relaxation mechanism described in Figure 1. In general, a logarithmic increase in ω will lead, according to eqs. (5) and (6), to a linear decrease in the reciprocal temperature scale.

The shapes of the kernels in Figure 1 are such that, as a first approximation, $d/d(1/T) [q^2/$

$(1 + q^2)]$ and $q/(1 + q^2)$ can be replaced by the Dirac delta-function, $\delta(1 - T/T_k)$. It follows that the distribution function $H(1/T_k)$ will be defined by:

$$H(1/T_k)$$
$$= (R/2\Delta H)\frac{dE_1(1/T)}{d(1/T)}\bigg|_{T=T_k} = (1/\pi)\,E_2(1/T)\bigg|_{T=T_k}$$
$$(7)$$

It appears, therefore, that measurements of $E_1(1/T)$ and $E_2(1/T)$ over a temperature range which includes one or more transition temperatures should, by defining $H(1/T_k)$, afford a measure of the quantity and molecular composition of the components within a given polymer system.

EXPERIMENTAL

A series of model compounds of utility in assessing the validity of the proposed treatment of viscoelastic data were prepared and their dynamic mechanical properties measured over a 200° temperature range at essentially constant frequency. A vibrating reed technique was chosen because of its particular suitability for studies over a wide temperature range and at constant frequency.

Materials

The polymers utilized in the present study consisted of polybutadiene and copolymers of butadiene and styrene. The resonant frequencies encountered in a vibrating reed apparatus are rigidity-controlled, and, of course, the glass transition of any polymer is characterized by a marked change in rigidity. Consequently, to achieve sufficient rigidity of the specimens above their glass transition temperatures, i.e., to ensure that the resonant frequency did not vary over more than a twofold range for a given material, these rubbery polymers were incorporated into polystyrene whose glass transition and loss of rigidity occur at a temperature above those of the rubbery polymers. The mixing of polystyrene with each of the rubbery polymers was carried out via mill-blending for 10 min. at 165°C. on a standard, two-roll rubber mill. The blended materials were flash-molded in a mold with cavities of the proper dimensions. No attempt was made to vary systematically the degree of dispersion of the rubber component through a variation in the length of milling time. However, it seems reasonable to assume, in the absence of crystallinity,

that intramolecular near-neighbors exert a more profound influence on the motion of a given segment of the rubber chain than do intermolecular near-neighbors. As a result, the degree of dispersion of the rubber component after mill-blending should have little effect on the observed magnitudes of $E_1(1/T)$ and $E_2(1/T)$ corresponding to the rubber component.

The following rubbery polymers were utilized in this investigation:

(a) Naugapol 1504, ex Naugatuck Chemical Corporation, 12% bound styrene, "cold" recipe, glue-acid coagulated.

(b) S-1006, ex Shell Chemical Company, 23.5% bound styrene, "hot" recipe, intrinsic viscosity 2.1 dl./g.

(c) Pliolite 2104, ex Goodyear Rubber Company, emulsion polybutadiene, 60 wt.-% solids, salt-acid coagulated.

(d) Experimental copolymers made using a "hot" recipe. Butadiene/styrene charge ratios were such as to yield copolymers, PR-1 through PR-6, with various levels of bound styrene in the range 33 to 62 wt.-%.

Each of the above rubbery polymers was incorporated at a level of 20 wt.-% in crystal-grade polystyrene. In the case of S-1006 and PR-6, additional specimens were prepared with loadings other than 20 wt.-%. Styron 666, from Dow Chemical Company, was utilized as the polystyrene matrix.

Specimens

Polymer samples in the form of reeds with dimensions of the order 4.5 × 0.30 × 1.25 cm. were used. A coil of five turns of #40 magnet wire was wrapped around the perimeter of each
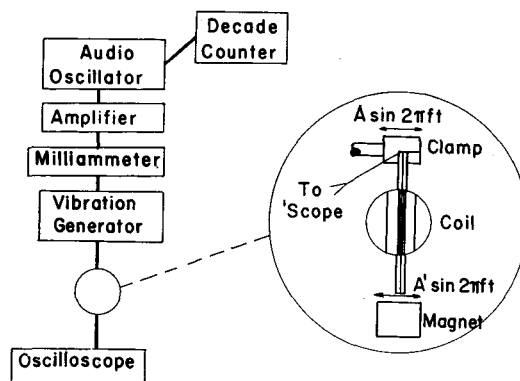

Fig. 2. Block diagram of apparatus with detail of specimen clamping and coil for amplitude measurement.

specimen (Fig. 2). Care was taken to ensure that the coil was accurately located on the specimen edges midway between the specimen faces. Since no extension or compression occurred along the locus of the coil during lateral vibrations of the specimen, the coil did not contribute to the Young's modulus, E_1, measured in the experiment. In addition, since the mass of the wire was negligible compared to that of the specimen, the presence of the wire had no effect on the characteristic frequencies of the system.

Apparatus

The source of oscillatory motion, $A \sin 2\pi ft$, applied to the clamp (Fig. 2) was a Goodman's Model 390A vibration generator which was supplied with alternating current power originating from a Hewlett-Packard Model 206A audio signal generator and amplified by means of a McIntosh 60-w. amplifier. The current supplied to the vibration generator, which was directly proportional to the force exerted upon the specimen clamped to the armature of the vibration generator, was measured by means of a Weston Model 625 thermomilliammeter. The frequency of the voltage across the vibration generator was monitored by means of an Erie Model 400 decade counter. An Alnico magnet located near the free end of the specimen induced a voltage $A' \sin 2\pi ft$ in the 5-turn coil wrapped around the specimen. The magnitude of this induced voltage, after amplification in a Tektronix Model 123 preamplifier, was observed on the screen of a Hewlett-Packard Model 130 oscilloscope.

The specimen and magnet were enclosed in a well-insulated thermostat whose temperature was maintained constant at low temperatures by passing dry, compressed nitrogen at controlled rates through a copper coil immersed in liquid nitrogen, and at elevated temperatures by means of a controlled heater within the specimen chamber. The temperature was regulated to within at least $\pm 0.1°C$. at temperatures below ambient, and somewhat more closely at temperatures above ambient.

Method

The frequency of the force applied to the specimen via the vibration generator was tuned to the resonant frequency, f_r, of the specimen. The current, i_r, supplied to the generator was adjusted to give a 60 mv. deflection on the oscilloscope screen. As the frequency, f, of the applied force was varied in discrete steps above and below the

resonant frequency, the current to the vibration generator was increased so as to maintain the 60 mv. deflection on the oscilloscope. Since the induced voltage, proportional to the product of amplitude times frequency, was kept constant, the amplitude of vibration was inversely proportional to frequency. Consequently, the ratio amplitude/unit force was proportional to $(1/if)$. The data were normalized to $(1/i_r f_r)$ and plotted against frequency to obtain a dispersion peak. In general, the complete dispersion peak was not determined but rather a triangle defined by the five points $(i_r f_r)$, $(\sqrt{2} i_r f_1)$, $(\sqrt{2} i_r f_2)$, $(2 i_r f_3)$, and $(2 i_r f_4)$. The band widths Δf_1 and Δf_2 at the amplitude ordinates of 0.707 (half power) and 0.500, respectively, were measured and averaged $(2\Delta f = \Delta f_1 + \Delta f_2/\sqrt{3})$, and the elastic and viscous components of the dynamic modulus were calculated according to the following equations:

$$E_1 = B[f_r{}^2 + (\Delta f)^2/2] \qquad E_2 = Bf_r \, \Delta f$$

$$B = 38.4\rho l^4/d^2$$

where ρ is the density, l the specimen length and d the specimen thickness. Dispersion triangles were obtained at suitable temperature intervals over the temperature range -130 to $80°C$. Over this temperature range resonant frequencies in the range 200 to 300 cycles/sec. were observed for the materials studied. No corrections for variation of density with temperature were applied to the data obtained in these experiments.

Experimental Error

The mechanical properties measured according to the present techniques are subject to an experimental error which is estimated to be $\pm 3\%$ for E_1 and $\pm 6\%$ for E_2. The errors arise from the limiting accuracies in the measurement of specimen length and thickness, of frequency, and from the fact that the (small) change in density with temperature was not taken into account. An additional error, significant only as regards E_2, arises from the limiting accuracy in current measurement, and from the fact that a complete dispersion peak was not defined at each temperature.

RESULTS AND DISCUSSION

Linearity of Viscoelastic Behavior

It was not necessary in the present investigation to determine the absolute value of the amplitude

of vibration in order to calculate the elastic and viscous components of the dynamic modulus. However, since the voltage induced in the coil was kept constant, the absolute value of the amplitude of vibration varied inversely with frequency during a given experiment. Although the frequency range necessary to define a dispersion peak at a given temperature was small (ca. 8 cycles/sec., or 3%) the variation in resonance frequency, and consequently amplitude, over the entire temperature range was of the order 70 to 100 cycles/sec., or ca. 30 to 50%. It was necessary, therefore, to determine whether the polymers being studied exhibited linear viscoelasticity, i.e., whether $E_1(1/T)$ and $E_2(1/T)$ were independent of strain amplitude in the range of strain amplitudes studied (<0.4%). The data obtained at 22°C., i.e., at frequencies, and consequently amplitudes, approximately midway between the extreme values in a given experiment, indicate that a tenfold increase in amplitude has no effect within experimental error on the measured properties of a typical sample (Table I).

TABLE I

Variation with Amplitude of the Dynamic Mechanical Properties of a Typical Sample at 22°C.

Amplitude	Resonant frequency, cycles/sec.	Band width at $^1/_2$ power, cycles/sec.	$E_1 \times 10^{-10}$, dynes/ cm.^{2}	$E_2 \times 10^{-8}$, dynes/ cm.^{2}
A^a	258.5	4.57	2.28	4.04
$2A$	258.5	4.57	2.28	4.04
$5A$	258.5	4.57	2.28	4.04
$10A$	258.5	4.67	2.28	4.07
$20A$	257.5	5.32	2.26	4.69
$50A$	257.0	5.70	2.24	4.99

[a] Sufficient to give 60 mv. deflection on oscilloscope, generally $A < 0.2$ mm.

Presentation of Data

Although $E_1(1/T)$, the elastic component of the dynamic modulus, is subject to a lesser experimental error than $E_2(1/T)$, the viscous component, the form of $E_1(1/T)$ is that of a cumulative distribution while the form of $E_2(1/T)$ is that of a differential distribution which, in general, affords a more graphic presentation of data than does a cumulative distribution. It is the author's opinion that in cases where the differential curve is obtainable directly from experimental data without geometric differentiation, it is preferable to present the data in this form despite the fact that the as-

sociated experimental error is somewhat higher than that associated with the integral curve. Consequently, the following discussion will be concerned only with the differential distribution, i.e., with the viscous component of the dynamic modulus. It should be made clear, however, that in electing to treat only the viscous component we are not neglecting data which would afford additional information regarding the mechanisms for absorption of mechanical energy. It was shown earlier that to a first approximation $E_2(1/T)$ is proportional to the derivative of $E_1(1/T)$ with respect to reciprocal temperature and, consequently, the mechanical properties of the polymer system can be defined entirely by $E_2(1/T)$ plus a value of $E_1(1/T)$ at one temperature, this value being necessary to define an integration constant. It should be noted, in this regard, that the use by many authors of the ratio $E_2(1/T)/E_1(1/T)$ versus temperature affords a less clear definition of the distribution $H(1/T_k)$ than does $E_2(1/T)$ versus temperature, despite the fact that the ratio is insensitive to the experimental errors in determination of specimen density and dimensions.

$E_2(1/T)$ for Butadiene–Styrene Polymers

In Figure 3, $E_2(1/T)$ is plotted against reciprocal absolute temperature for samples representative of those studied. The peak in each case corresponds to the rubbery polymer present, while, as shown by the data for polystyrene in the absence of added rubber, the incipient peak at high temperatures corresponds to the onset of the α-transition within the homopolymer matrix. Further, it can be seen that the homopolymer matrix contributes a significant "background" absorption of
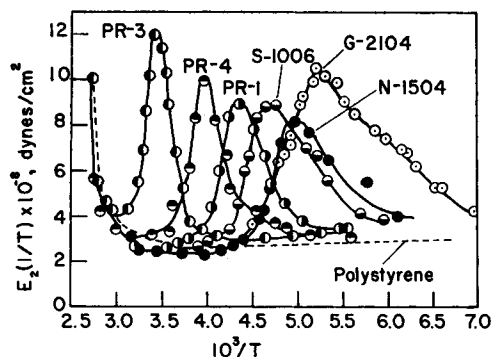

Fig. 3. Dependence of viscous component of the dynamic modulus on reciprocal absolute temperature for polystyrene and some representative rubbers with the following mole fractions of styrene: PR-3, 0.39; PR-4, 0.25; PR-1, 0.17; S-1006, 0.11; N-1504, 0.05; G-2104, 0.00.

Sample[a]	Amount incorporated in Polystyrene, wt.-%	Modal transition temperature T_k', °K.	Area under peak, relative units	Bound styrene,[b] mole fraction
S-1006	10	218	0.77	0.11
	20		1.52	
	30		2.34	
	40		3.46	
PR-6	7	238	0.41	0.21
	11		0.65	
	15		0.90	
	19		1.09	
PR-5	20	336	—	0.69
PR-3	20	291	0.87	0.39
PR-4	20	253	0.95	0.25
PR-2	20	239	0.97	0.22
PR-1	20	231	0.97	0.17
N-1504	20	203	1.50	0.05
G-2104	20	192	2.58	0.00

[a] Samples described in experimental section.

[b] Averaged data obtained via infrared and refractive index.

mechanical energy over the entire temperature range. Additional evidence in this regard was obtained through the study of samples of S-1006 and PR-6 which were not incorporated into polystyrene but which had been lightly cured with dicumyl peroxide to achieve specimens of suitable dimensional stability. The magnitude of $E_2(1/T)$ for these rubbers was found to be about 6×10^8 dynes/cm.[2] at -100°C. and essentially zero at about 20°C. Consequently, for loadings in the region of 20 wt.-%, the rubbers contribute at most 1.2×10^8 dynes/cm.[2] to the observed magnitude of $E_2(1/T)$ at low temperatures. In order to correct for the background absorption of energy by the polystyrene matrix, a technique similar to that used with spectroscopic and diffraction data
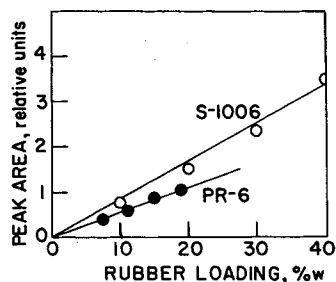

Fig. 4. Plot of area under peaks against rubber loading for the rubbery polymers S-1006 and PR-6.

was used. A tangent, parallel to the absorption curve for the polystyrene matrix, was drawn to the low and high temperature limits of the peak and the area under the peak was determined using the tangent as a reference baseline.

In Table II the modal temperatures T_k', i.e., the temperature of maximum $E_2(1/T)$, for the materials shown in Figure 3 and for the other materials studied are given along with the areas under the peaks and the mole fractions of styrene. As shown in Figure 4, a plot of the area under the peaks against the respective loadings of S-1006 was found to be linear. The data for sample PR-6, also shown in Figure 4, were found to be linear for loadings in the range 7 to 19 wt.-%. It is concluded that the area under the peak for a given rubber affords a direct measure of the quantity of the rubber present giving rise to the peak.

As can be seen from the other data in Table II, the area per unit weight of rubber is not a constant among the various rubbers studied. This result is not unexpected since the approximation leading to eq. (7) requires values of ΔH large enough to permit the substitution of $\delta(1 - T/T_k)$ for $q/(1 + q^2)$ and precludes the inclusion of a parameter describing the variation of ΔH with styrene content, which variation must surely exist, particularly over the broad range of styrene content of the materials studied.

However, some insight into the molecular structures giving rise to the observed peaks is gained through a plot of the reciprocal modal temperatures $(10^3/T_k')$ against logarithmic mole fraction of styrene as shown in Figure 5. It is apparent from the linearity of the curve, at least at high bound styrene levels, that the effect of a copolymerized diluent, butadiene, on the characteristic temperature of polystyrene parallels the depression of the melting point of a crystalline polymer by a noncrystallizing, copolymerized diluent.[5] We conclude that the temperatures of the peaks in $E_2(1/T)$ afford an estimate of the average molecular composition within a given homologous polymer series. It is important to recognize, however, that the presence of a nonpolymeric diluent will probably result in a further lowering of the characteristic temperature, since a nonpolymeric diluent is known to depress the melting point of a crystalline polymer.[5] Erroneous conclusions regarding the composition of the copolymer may therefore result if the presence of the diluent is not taken into account. Fragmentary evidence has been obtained in this regard; a
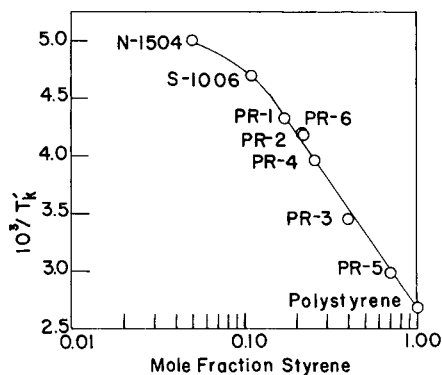
Fig. 5. Plot of reciprocal modal temperatures against mole fraction of styrene for the materials studied.

detailed study of the effect of nonpolymeric diluents is planned and the results will be reported in a subsequent communication.

In addition to nonpolymeric diluents, chain ends are known[5] to depress the melting point of crystalline polymers. It is to be expected that chain ends, if present in sufficient quantity, would exert a parallel influence on the measured rigidity of polymer chains. In this regard a quantitative relation between the relaxation spectrum $H(\ln \tau)$ and polymer molecular weight has been developed elsewhere.[6] Data were obtained from stress relaxation experiments ("zero" frequency) and a shift factor calculated such that the relaxation curves for samples of the same polymer of differing molecular weight coincided. However, in the present investigation, frequencies in the range 200 to 300 cycles/sec. were encountered, leading to a time scale of 0.005 to 0.003 sec. It is felt that this time scale precluded the motion of complete molecules, particularly since all the polymers in the present study had a number-average $\overline{DP}$ in excess of 500. Molecular weight, therefore, is considered to be at most only a moderate factor as regards the values of $E_2(1/T)$ observed in this investigation.

With the exception of sample PR-5, all the copolymers studied are richer, on a molar basis, in butadiene than in styrene, and consequently sequence lengths of butadiene greater than that of the average composition have higher probability than do sequence lengths of styrene greater than that of the average composition. One would therefore expect the peaks to be skewed in the direction of long sequences of butadiene, i.e., in the direction of low temperatures. The peaks shown in Figure 3 are asymmetric; in each case the area under the curve is greater for temperatures below

the modal temperature than for temperatures above the modal temperature. In addition, as the average composition approaches 0.5 mole fraction, the population density of sequence lengths corresponding to the average should increase, and the number of long sequences of butadiene should decrease. As shown in Figure 3, the peaks progressively increase in height and become more symmetrical with increasing styrene content. We conclude that the shape of the $E_2(1/T)$–reciprocal temperature peak is indicative of the distribution of molecular structures about the average composition. This conclusion is, of course, in agreement with eq. (5) which shows that $E_2(1/T)$ is directly proportional to the distribution function $H(1/T_k)$.

It was mentioned above that the present treatment of viscoelastic behavior fails in one respect, viz., the area per unit weight of rubber is not a constant among the materials studied. As noted above, it is felt that this failure is a result of the approximation leading to eq. (7) and not a result of a basic error in eqs. (5) and (6). However, as described earlier it was found that $E_2(1/T)$ for the polystyrene matrix, and for the samples of S-1006 and PR-6 not incorporated into polystyrene, was not zero below the transition temperature range of these materials but was constant for each and independent of temperature. This finding suggests that eq. (6) be modified on the right-hand side by the inclusion of a parameter which is a positive constant below the transition temperature region and is zero above this region. Equation (5) would be modified by the inclusion of the product of this parameter times a linear function of temperature. Since there are at present no theoretical grounds for the inclusion of this parameter, no attempt has been made here to modify eqs. (5) and (6) in this manner. Furthermore, for rubber loadings in the region 20 wt.-%, neglect of the low temperature "tail" entails only a minor error in the measured area under the peaks corresponding to the rubber component.

CONCLUSIONS

Data obtained for a homologous series of butadiene–styrene polymers substantiate a proposed treatment of the temperature dependence of viscoelastic properties of polymers. In particular it has been shown that the area under the peak observed in a plot of the viscous component of the dynamic modulus against reciprocal absolute tem-

perature affords a direct measure of the quantity of the rubber present in a mixed polymer system. In addition it has been shown that the temperature of the peak is, for high levels of bound styrene, directly related to the mole fraction of styrene present. Further, it has been found that the shape of the peak is indicative of the distribution of sequence lengths of butadiene and styrene about their average sequence lengths.

The treatment fails in one respect, as a result of a simplifying approximation, in that the area per unit weight of rubber is not a constant among the rubbers studied. In addition, the treatment fails to predict a nonzero value for the viscous component of the dynamic modulus at temperatures below the transition region.

Although in the present investigation experimental evidence has been obtained only for butadiene–styrene polymers, it is felt that the theory proposed is of general applicability. Necessary conditions are that the transition temperatures of the components be distinct, that monomeric diluents, if present, be taken into account, and that an experimental technique be used whereby frequency is kept essentially constant.

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Synopsis

The temperature dependence of the viscous component $E_2(1/T)$ of the dynamic modulus is reported for a homologous series of butadiene–styrene copolymers incorporated at various levels in styrene homopolymer. By the use of a vibrating reed technique based on resonance tuning, the frequency of the applied deformation was maintained essentially constant throughout the temperature range which included the glass transitions of the copolymers. It is shown that, when $E_2(1/T)$ for such mixed polymer systems is plotted against reciprocal absolute temperature, the area under the peak corresponding to a given copolymer affords a direct measure of the quantity of the copolymer present. Further, the temperature of maximum $E_2(1/T)$ is related to the mole fraction of bound styrene in the copolymer, and the shape of the peak is related to the statistical sequence lengths of styrene and butadiene in the copolymer.

Résumé

On rapporte la dépendance thermique du composant viscosimétrique $E_2(1/T)$ du module dynamique pour une série homologue de copolymères butadiène-styrène incorporés à différents taux dans du homopolystyrène. Par l'emploi d'une technique de vibration par résonance, on maintient constante la fréquence de la déformation appliquée à travers l'échelle de température qui inclut la transition vitreuse des copolymères. On montre que, lorsque $E_2(1/T)$ pour de tels systèmes de polymères mélangés est portée en diagramme en fonction de l'inverse de la température absolue, la surface en dessous du pic correspondant à un copolymère donné, donne une mesure directe de la quantité de copolymère présent. En outre, on rapporte la température $E_2(1/T)$ maximum à la fraction molaire de styrène lié dans le copolymère, et on rapporte la forme du pic aux longueurs des séquences statistiques de styrène et de butadiène dans le copolymère.

Zusammenfassung

Die Temperaturabhängigkeit der Viskositätskomponente, $E_2(1/T)$, des dynamischen Moduls wird für eine homologe, Reihe, zu verschiedenem Ausmass einem Styrolhomopolymerem beigemischter Butadien-Styrolcopolymerer mitgeteilt. Mittels eines Schwingröhrchenverfahrens, das auf Resonanz-abstimmung beruht, wurde die Frequenz der angewandten Deformation im wesentlichen im ganzen Temperaturbereich einschliesslich der Glasumwandlungstemperatur des Copolymeren konstant gehalten. Es wird gezeigt, dass beim Auftragen von $E_2(1/T)$ gegen die reziproke, absolute Temperatur für ein solches polymeres Mischungssystem der Flächeninhalt unter dem, einem bestimmten Copolymeren entsprechenden Maximum ein direktes Mass für die Menge des vorhandenen Copolymeren liefert. Weiters steht die Temperatur für das Maximum von $E_2(1/T)$ in Beziehung zum Molenbruch des im Copolymeren gebundenen Styrols und die Gestalt des Maximums zu der statistischen Sequenzlänge des Styrols und Butadiens im Copolymeren.