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TIME-DEPENDENT VISCOELASTIC CHARACTERISTICS OF MIXTURES OF POLYBUTADIENES DIFFERING IN MICROSTRUCTURE*

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UDC 532.135:536.4

A dynamic method has been used to examine the rheological behavior of binary mixtures of polybutadienes (PB) differing in microstructure.

One can use the viscoeleastic behavior of a polymer in small-amplitude periodic deformation (dynamic testing) to describe features of the transition from one physical state to another on the basis of nondestructive tests (for fluid, rubber-type, leathery, and vitreous states), and in that way one can determine changes in characteristics such as the accumulation modulus G' and the loss modulus G". From the practical viewpoint, there are two experimental approaches: with varying temperature and constant frequency or with varying frequency at a fixed temperature. In both cases, one obtains a rheological evaluation of the state and defines the limits to it from measurements on the moduli.

Fundamental parameters such as the maximum Newtonian viscosity η_0, the elasticity A°_G, and the quasiequilibrium reversible shear compliance J°_e are very important to the viscoelastic behavior of a polymer system. The linear theory indicates that these quantities are usually derived from the dependence on frequency ω of the above moduli in the region of the flowing state, i.e., where G' is proportional to ω^2 and $G'' \sim \omega$. According to [1], this corresponds to deforming the polymer with the structure unchanged. Then

$$\eta_0 = \lim_{\omega\to 0} G''/\omega;\ A^0_G = \lim_{\omega\to 0} G'/\omega^2;\ J^0_e = A^0_G/\eta_0^2.$$

However, a wide-ranging rheological technique is required to attain the flow state for a macromolecular system, particularly at low frequencies, which involves considerable difficulties. New scope for estimating the initial parameters is opened up by the temperature dependence of the moduli recorded at relatively low frequencies to determine with high accuracy not only the absolute values of η_0, A°_G in a single experiment in the flow state but also the temperature dependence of these. Therefore, the simpler experiment (temperature scanning at constant frequency) provides a large volume of very important information.

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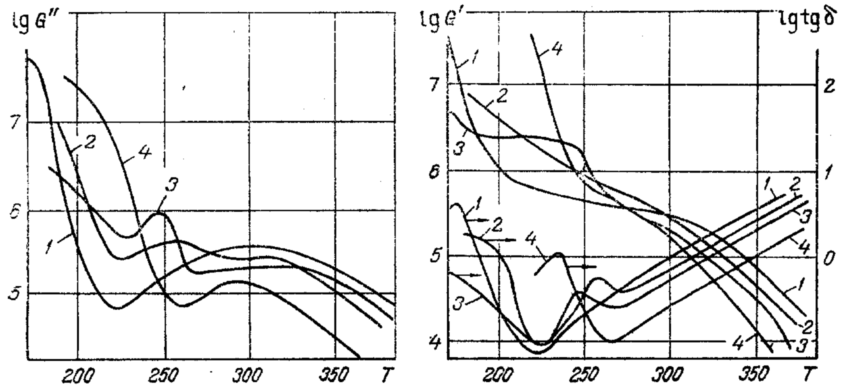
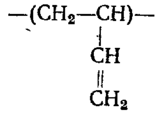


Fig. 1. Dependence of G' and G" (Pa) and mechanical loss tangent tan δ on temperature T (K): 1) 1,4 PB; 2) 20% 1,2 PB; 3) 40% 1,2 PB; 4) 1,2 PB.

TABLE 1. Polybutadiene Characteristics

Characteristic	1,4-polybutadiene	1,2-polybutadiene
Molecular structure	$-(CH_2-CH=CH-CH_2)-$	 $-(CH_2-\underset{\underset{\underset{CH_2}{\Vert}}{CH}}{\vert}{CH})-$
Microstructure, %		
1,2-links	7,3	84
1,4-trans	46,7	7,8
1,4-cis	46,0	8,2
Molecular mass		
M_w	111047	135000
M_w/M_n	1,15	1,2
T_g, °C	—96	—35
[η], 25 °C, toluene	1,32	1,28

A mixture or solution of polymers from the same homological series and having the same structure shows [2] sharp changes in the initial elastic characteristics A°_G, J°_e in the region of 0.5 mass % of the macromolecular component.

It has been found [3] that there is a peak on the G"(ω) curve at contents up to 80% of the macromolecular component at not very low temperatures for PB mixtures identical in structure, which corresponds to the transition from the flow state ot the highly elastic one in the frequency range where this occurs for the low-molecular component. As the temperature rises, a plateau appears in the frequency dependence of the loss modulus, which extends to the entire frequency range between the peaks for the two components. Consequently, signs of individual component behavior in the mixture become less pronounced as the temperature is reduced, namely because of reduced activity in the macromolecular component. On the other hand, the peak in the loss modulus for the macromolecular component degenerates as the low-molecular one is introduced, and at relatively low c (about 20%) one sees the transition to the highly elastic state of the macromolecular component only from the changes in shape in the G'(ω) and G"(ω) curves at low frequencies. At frequencies corresponding to the peak loss for the high-molecular component, G' and G" are reduced by less than a factor two by the addition of up to 50% of the low-molecular component.

These features led us to examine the behavior of mixtures of polybutadienes differing in microstructure over wide ranges in temperature, frequency, and composition on the basis of the above approach in evaluating the viscoelasticity. We used 1,2 and 1,4 polybutadienes similar in molecular mass (MM) and having narrow molecular-mass distributions (MMD). Table 1 gives the characteristics. The mixtures were prepared by dissolving the components together in benzene at room temperature. The experiments were performed with the DKhP-2 mechanical spectrometer [4] for use in dynamic tests on polymers.

Figure 1 shows the temperature dependence of G' and G" together with tan δ = G"/G' derived for a circular frequency log ω = 0.8 for the initial specimens (curves 1 and 4) and mixtures of them (20 and 40% 1,2 PB, curves 2 and 3). It is clear that the initial specimens have turning points on the tan δ(T) curves corresponding to the glass temperatures of 177 and 238°K for 1,4 and 1,2 PB correspondingly. The descending branches of the G'(T) and G"(T)

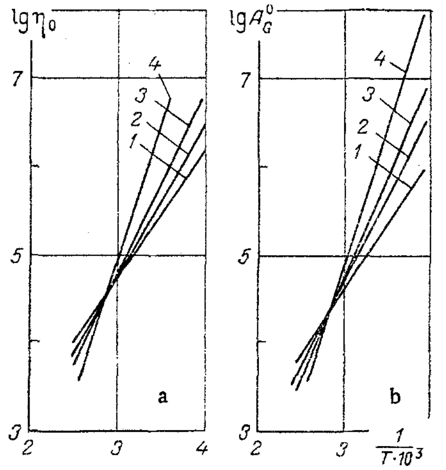


Fig. 2

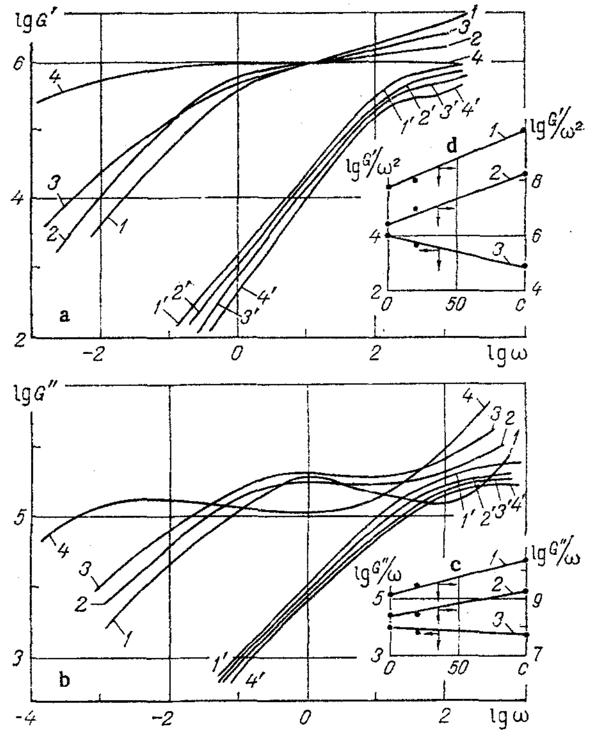


Fig. 3

Fig. 2. Temperature dependence of the initial maximal Newtonian viscosity η_0(Pa•sec) (a) and the elasticity coefficient A°_G (b): (1-4) see Fig. 1.

Fig. 3. Frequency dependence of G' (a) and G" (b) in Pa for the specimens at temperatures in °K of: 1-4) 253; 1'-4') 383. In the insets we show the dependence of the viscosity G''/ω (c) and the elasticity coefficient G'/ω^2 (d) on the concentration c of 1,2 PB in % in the mixture.

curves at elevated temperatures are related to the attainment of the flow state. The mixture gives a tan δ(T) curve with two peaks, whose positions correspond approximately to the glass temperatures for the initial specimens. This tan δ(T) pattern is characteristic of incompatible polymers [5]. The flow-state region is only slightly responsive to change in mixture structure: the tan δ(T) curves change in slope only slightly at elevated temperatures (curves 1-4 are practically parallel). The G"(T) and G'(T) curves taken over a wide temperature range are complicated: there is a plateau together with broad peaks corresponding to the highly elastic, transitional, and fluid states, with G' and G" falling considerably at elevated temperatures in the region of the fluid state and increasing as the temperature decreases in the leather-type state (transitional to the vitreous one). Well above the glass temperature of one of the components, the viscosity is almost independent of the composition in these incompatible mixtures, and in that respect the system may be taken as compatible. The G'(T) results for the fluid state were used in calculating η_0(T) and A°_G(T) as shown in Fig. 2. The η_0(T) and A°_G(T) relations are described by straight lines with different slopes which range from 1.6 to 3. The η_0(T) and A°_G(T) lines for the mixtures are intermediate between those for the initial PB. The activation energies for viscous flow in 1,4 and 1,2 PB are 8 and 14 kcal/mole correspondingly, which shows that the microstructure has a considerable effect.

At $T > T_g + 50$, the viscosity is an additive function of the composition: $\lg \eta_m = c \lg \eta_1 + (1 - c) \lg \eta_2$, where c is the weight proportion of the added component, while η_1 and η_2 are the component viscosities.

We also plotted G' and G" as functions of ω (Fig. 3) for various temperatures to determine the features of the viscoelastic behavior in various regions (the highly elastic rubber-type state and the leather-type one). As examples we show data for 253°K (curves 1-4) and 383°K (1'-4'). The dynamic characteristics characterize the viscoelastic behavior in different ways. At 253°K they enable one to characterize the behavior of a mixture in the fluid state (the descending branches at the lowest frequencies) as highly elastic [plateau in G' (ω) and maxima in G"(ω)] and transitional to the leather-type state (rising branches at high

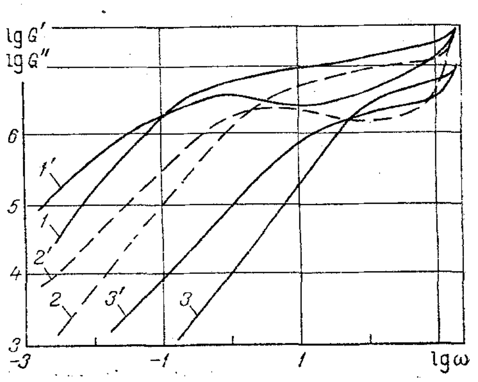


Fig. 4. Dependence of G' and G" on frequency ω (sec^{-1}) for a mixture containing 20% 1,2 PB at temperatures in °K of 1) 253; 2) 293; 3) 383.

frequencies). The features corresponding to the transition from one state to another are fairly pronounced for the initial materials, but are not so for the mixtures. The most marked difference in behavior between the initial materials and the mixtures occurs in the transition from the fluid state to the highly elastic one. The curves for the initial materials and the mixtures differ little in virtually all states at elevated temperatures. The differences in the temperature coefficient of viscosity between the initial components mean that the temperature dependence of G'(ω) and G"(ω) for 1,2 PB is more pronounced than that for 1,4 PB, and therefore there is a change in the sequence of the curves at elevated temperatures (compare curves 1-4 with 1'-4'), which agrees well with the behavior of G'(T) and G"(T) at low and high temperatures (Fig. 1). At 383°K, there is close similarity between the G'(ω) and G"(ω) for the initial PB and the mixtures, and the behavior of the curves indicates that there is not a very prominent region for the highly elastic state in the frequency range used. One expects that at these temperatures the system would pass almost instantaneously from the fluid state to the induced vitreous one as the frequency increases [6].

Therefore, the difference between the components are largely eliminated at elevated temperatures in these systems derived from a single homologous series. Interest attaches to the concentration dependence of η_0 and A°_G, which is also shown in Fig. 3 (c and d). Curves 1, 2, and 3 are for 253, 293, and 383°K correspondingly. The viscoelastic parameters are clearly dependent on the component concentrations, at $T \leqslant T_g + 50$ we find $\eta \sim c^{0.3}$, but at higher temperatures the dependence is very different and is $\eta \sim c^{-0.1}$. As regards A°_G, we find $A^\circ_G \sim c^{0.6}$ at 253-283°K and $A^\circ_G \sim c^{-0.3}$ at 383°K. An important point is that the slope of $(\eta_0^\circ, A^\circ_G) = f(c)$ changes at 383°K, which is evidently due to difference in the contributions from the components to the flow.

We compared the G'(ω) and G"(ω) curves for the mixture containing 20% 1,2 PB at different temperatures (Fig. 4). Curves 1 and 1', 2 and 2', and 3 and 3' correspond to 253, 293, and 383°K. The main tendency is that the highly elastic state region varies with temperature. The length and height of the plateau increase considerably as the temperature is reduced and ω_{max} shifts to lower frequencies (by more than two orders of magnitude).

These wide-range temperture relationships enable one to characterize the fluid state, which is particularly important for describing the initial behavior. One can estimate all the major initial constants, which until recently was possible only by processing dynamic characteristics recorded at low frequencies. However, it should be borne in mind that the temperature dependence is much easier to record than the frequency one. This can be applied to mixtures as well as to individual polymers.

At $T \leqslant T_g + 50$, the viscoelastic characteristics of linear-polymer mixtures are determined to a considerable extent by the properties of the component with the higher glass temperature. At $T > T_g + 50$, the individual properties hardly make themselves felt.

These regularities are important in working processes, since the extension of the fluid region and the change in plateau height at elevated temperatures should enable one to increase the upper limits to the strain rates in processing, which opens up ways of accelerating the process.

NOTATION

G', G", storage and loss moduli, real and imaginary components of the complex modulus, Pa; η_0, initial (larger Newtonian) viscosity, Pa•sec; A°_G, initial elasticity coefficient, Pa; J°_e, (quasi) equilibrium reversible shear compliance, Pa^{-1}; ω, circular frequency, sec^{-1}; tan δ, mechanical loss tangent; T, temperature, °K; T_g, glass temperature; c, concentration of minor component, mass %; ω_{max}, circular frequency corresponding to maximum in G"(ω).

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DYNAMIC VISCOSITIES OF BENZENE—CHLOROBENZENE SOLUTIONS

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532.133

Measurements are reported on the dynamic viscosities of benzene—chlorobenzene solutions.

Sound design of equipment for producing chlorobenzene and improved efficiency in producing it from benzene require reliable data on the thermophysical parameters of benzene—chlorobenzene solutions over wide ranges in temperatures and pressure. The literature carries data only on the densities of these solutions at 298.15-353.15°K and atmospheric pressure [1].

We have measured the dynamic viscosities of benzene—chlorobenzene solutions having molar concentrations of 25-75, 50-50, and 75-25% over the range 290.15-550.15°K at pressures of 1-40 MPa. A Golubev—Petrov capillary viscometer (fifth form) was used [2]. See [2] on the methods of performing the measurements, thermostating the viscometer, and processing the results.

The temperatures were measured to ±0.01-0.02% with a PTS-10 standard resistance thermometer. The pressures were produced and measured by means of MP-60 and MP-600 piston-load gauges of accuracy class 0.05. The flow time was measured with and SDSpr-1 timer having a scale division of ±0.1 sec. The flow time was measured not less than three times for each point.

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