

VISCOELASTIC PROPERTIES OF A BITUMEN UNDER CONTINUOUS AND CYCLIC DEFORMATION

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An investigation was conducted on viscoelastic properties of a bitumen at various amplitudes and frequencies of the stresses acting on it; it established the effect of the amplitude of the deformation rate on the absolute value of the complex and effective viscosity.

The viscoelastic properties of bitumens are of decisive importance for problems involving their processing, transport, and application and have a considerable effect on the operating properties of the materials obtained from the bitumens. The methods of rotational and capillary viscosimetry [1] are widely used for determining the viscosity properties of bitumens under conditions of continuous shear deformation. At the same time, it is known that the techniques of the linear theory of viscoelasticity [2] are applicable to bitumens, and by using these techniques it is possible to carry out an investigation of the dynamic viscoelastic characteristics of bitumens (the elastic modulus and the loss modulus) [3-8]. Another feature of the viscoelastic behavior of bitumens is that the principle of temperature-frequency superposition [2-4] is applicable to it. On the basis of these factors, it can be assumed that the rheological behavior of bitumens should be similar in many respects to the behavior of polymer systems.

The purpose of the present investigation is to extend the experience accumulated in the study of polymer systems under cyclic deformation at large amplitudes to a specific class of viscoelastic materials, namely, bitumens.

Methods and Objects of the Investigation

In the measurement of the dynamic characteristics we used a vibrorheometer with coaxial cylinders [9] operating in a forced-oscillation regime in the 6-110-Hz frequency range. The measurements were made at various deformation amplitudes and various circular frequencies. The harmonic deformation regime was maintained fairly closely. In addition, the vibrorheometer was used for determining the effective viscosity in stationary shear flow and with oscillations imposed on the stationary flow. In order to find the effective viscosity, we also used the ACV-5 automatic capillary viscosimeter [10]. The dynamic measurements were made in a temperature range from -10 to +55°C, and the stationary measurements between 25 and 45°C.

The object investigated was a specimen of oxidized bitumen whose group composition, determined by absorption chromatography, is characterized by the following percentages: 13.9% asphaltenes, 33.6% resin, 13.2% paraffin-naphthene hydrocarbons, 21.7% light and medium aromatic hydrocarbons, and 17.6% heavy aromatic hydrocarbons.

The indicators of the standard bitumen tests have the following values: needle penetration depth at 25°C: 72, 1/10 mm; ring-and-ball softening temperature: 49°C; ductility at 25°C: 100 cm; Fraas brittleness temperature: 12°C; penetration index; 0.2.

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## Results of the Investigation and Their Evaluation

The dynamic characteristics of bitumens depend in large measure on temperature. As the temperature goes down, the inclination of the graphs of the elastic modulus and loss modulus as functions of frequency, decreases. At the lowest temperatures investigated the elastic modulus remained virtually unchanged as the frequency was varied. At the same time, the variation of the loss modulus with frequency was complicated in nature.

The viscoelastic properties of bitumens depend not only on the frequency, but also on the amplitude of the imposed stress. The region of linearity is maintained up to deformation amplitudes of the order of 1-2%, a fact that largely distinguishes bitumens from other dispersed systems, for which these deformations cause nonlinear behavior. The modulus of elasticity is reduced considerably more as the amplitude of the deformation velocity increases than is the loss modulus. This is a general law for the appearance of nonlinear behavior in polymer and dispersed systems.

The displacement of the dynamic characteristics is independent of frequency when a change is made from one temperature to another, and this suggests the possibility of using the method of temperature-time superposition [11] for the bitumen investigated. The value of the reduction coefficient is independent of the choice of the parameter used in determining it — the modulus of elasticity, the loss modulus, or, as will be shown below, the variation of stresses with shear velocity.

It is noteworthy that the method of temperature-time analogy is also applicable to large amplitudes of deformation; here it is necessary to use the reduction coefficient obtained for the linear region, and the displacement of the  $G'(\dot{\gamma}_{\max})$  and  $G''(\dot{\gamma}_{\max})$  curves must be made along the axis of deformation-velocity amplitudes.

In connection with this, in our investigations the function  $\alpha_r(T)$  was used for the reduction of data obtained in the linear and nonlinear regions for all frequencies.

The results of this reduction to a temperature of 35°C are shown in Fig. 1a, b in the form of generalized graphs of the moduli of elasticity and loss as functions of the reduced frequency for various amplitudes of the deformation velocity. The envelopes  $G'(\omega_r)$  and  $G''(\omega_r)$  refer to the linear region of deformation. Two segments can be distinguished on them. Corresponding to the low frequencies we have a region of flow in which the elastic modulus and the loss modulus increase as the frequency increases. In this region both moduli increase at about the same rate with frequency. For higher frequencies the modulus of elasticity is stabilized and its curve continues as a plateau, while the loss modulus reaches a maximum, after which it goes through a minimum and begins to increase. Similar complicated variations of the loss modulus with frequency are characteristic for linear polymers of high molecular weight, when the molecular weight is 10-20 times that of the polymer chain between the linkage nodes [12].

The modulus of elasticity in the plateau region is equal to  $5 \cdot 10^7 - 6 \cdot 10^7$  dyn/cm<sup>2</sup> for the bitumen studied, while for the bitumens investigated in [3] the modulus of elasticity in the plateau region was characterized by values of  $2 \cdot 10^9 - 3 \cdot 10^9$  dyn/cm<sup>2</sup>. It is difficult at this point to explain such a sharp difference between the moduli of elasticity in this region. However, by analogy with polymers, we may make the assumption that the difference is related to the differences in the rigidity of the bitumen, which is determined by its group composition and the quality of its asphaltenes. As is known, in curved-chain polymers the moduli of elasticity in the plateau region are higher than in the case of rigid-chain polymers [13]. From a comparison of the moduli of highly viscous and road-grade bitumens it may be assumed that bitumens with high mobility and flexibility of their asphaltene macromolecules are characterized by a higher value of the moduli of elasticity on the plateau.

In Fig. 1 it can be seen that when the graph passes into the nonlinear region of deformation, there is a truncation of the low-frequency part of the graphs of  $G'(\omega_r)$  and  $G''(\omega_r)$ , which increases with increasing amplitude of the deformation velocity. Such a truncation of the curves of elastic modulus and loss modulus as a function of frequency has also been noted in the investigation of polymer systems in regimes of deformation at large amplitudes.

From the data shown in Fig. 1a, b, using the method of Ninomiya and Ferry [14], we calculated for the linear region the spectrum of relaxation times of the bitumen. For low and high frequencies the spectral functions found on the basis of  $G'(\omega_r)$  and  $G''(\omega_r)$  differed by as much as 30% and 50%, respectively. The averaged results of the calculations are shown in

Fig. 1c. The relaxation spectrum of the bitumen has a shape that is characteristic of highly molecular polymer systems. In the region of long relaxation times the tangent of the angle of inclination for the bitumen studied is equal to  $-0.8$ . Rouse's theory [15], developed for polymer solutions, yields a value of  $-1/2$  for the tangent of the angle of inclination in the final zone. The same value is given for the tangent in [8] for asphalt systems. However, our data indicate that the viscoelastic behavior of a bitumen may differ from the behavior predicted by the Rouse theory. As the relaxation times decrease, the distribution function reaches a maximum, passes through a minimum, and begins to increase. By analogy with polymers, the growth of the distribution function in the region of small relaxation times is apparently related to the beginning of the transition to vitrification. Another indication of this is the increase in the loss modulus as frequency increases after the graph passes through a minimum (Fig. 1b). Figure 1c clearly illustrates that the distribution function is more complicated than the Gaussian function which was assumed in [3, 4] to be applicable to bitumens. Consequently, the hypothesis of a Gaussian distribution of relaxation times for bitumens should be examined very carefully, since it does not take account of the contribution made by the small relaxation times.

Within the present study, great interest attaches to the investigation of the effect produced by the amplitude of the deformation velocity on the variation of  $|\eta^*|$  as a function of  $\omega$ . The data shown in Fig. 2 indicate that the effect of the amplitude of the deformation velocity causes a decrease in  $|\eta^*|$ , and this decrease becomes greater as  $\dot{\gamma}_{\max}$  increases. At the same time, we can observe an increase in the frequency at which the transition to the linear region takes place. It follows from this that the nonlinear deformation of a bitumen means that the region in which  $|\eta^*|$  is independent of frequency is reduced and displaced in the direction of larger values of  $\omega$ . Similar results have been obtained for polymer systems [16].

The above-described data relate to a regime of cyclic deformation. Let us now consider the experimental results obtained during stationary flow of the bitumen and the imposition of oscillations on the stationary flow; we consider, in particular, the interaction between dynamic and stationary characteristics. Investigations on polymer systems have shown that there exists an empirical correlation between the characteristics determined in stationary flow and cyclic shear deformation with small amplitudes [17, 18]. By using for the bitumen the principle of equivalence of shear velocity and frequency, we were able to compare the functions  $\tau(\dot{\gamma})$  and  $G''(\omega)$ .

Figure 3 shows the results obtained by testing the bitumen by the methods of rotational and capillary viscosimetry and by a dynamic method. Over the entire range of shear velocities and temperatures we observe satisfactory agreement between the data of the rotational and capillary viscosimetry. A feature of the viscosity behavior of the bitumen investigated is that up to stresses of  $2.5 \cdot 10^6$  dyn/cm<sup>2</sup> it displays practically Newtonian flow [the angle of inclination of the  $\tau(\dot{\gamma})$  curve is approximately  $45^\circ$ ]. The data shown in Fig. 3 in the large-velocity region relate to the  $G''(\omega)$  curves obtained by direct measurements. The data presented here show that when  $\omega = \dot{\gamma}$ , we have  $G'' = \tau$ . This important fact must be investigated further for other types of bitumens. Nevertheless, it may be assumed that the shear stress cannot exceed the maximum value of the loss modulus. This has been noted on a number of occasions in the investigation of monodispersed polymers [12]. However, a verification of this assumption in the case of bitumens involves considerable experimental difficulties, since we must apply high shearing stresses (more than  $1.5 \cdot 10^7$  dyn/cm<sup>2</sup>).

Since the behavior of the bitumen is Newtonian over a wide range of shear velocities, we were able to combine continuous and cyclic deformations in such a way that we could neglect the effect of constant shear velocity on the structure of the bitumen and clarify the effect produced only by the parameters of the cyclic deformation on the maximum Newtonian viscosity of the bitumen. At the same time, using only cyclic deformation, we pursued the objective of showing whether the effect of the cyclic deformation on the absolute value of the complex viscosity is equivalent to the amplitude of the deformation velocity on the viscosity in stationary flow.

The experiments were carried out in the following way: we specified a constant shear velocity, and after steady-state flow had begun we superimposed on the stationary flow a cyclic deformation with various values of amplitude and frequency in the plane of the flow. As a result of this, we observed a decrease in torsional moment (shearing stress). The values of torsional moment obtained in steady-state flow for given parameters of cyclic de-

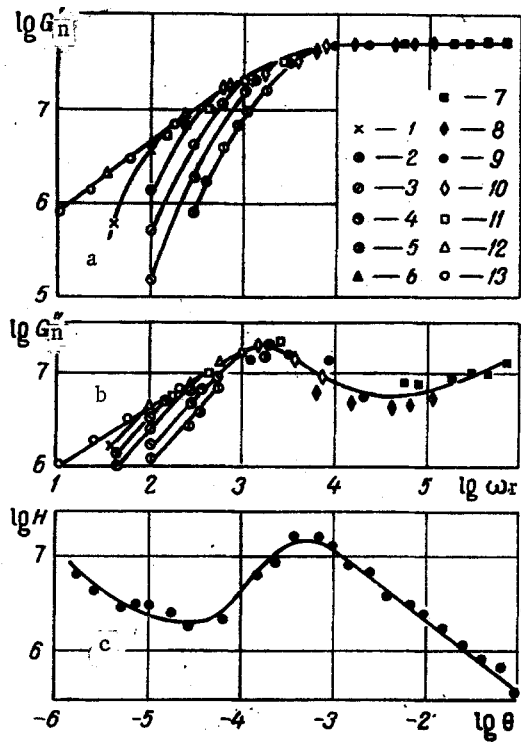


Fig. 1

Fig. 1. Reduced moduli of elasticity (a) and loss moduli in dyn/cm<sup>2</sup> (b) as functions of reduced frequency in sec<sup>-1</sup> in the linear and nonlinear regions, for various amplitudes of the deformation velocity  $\log \dot{\gamma}_{\max}$  (sec<sup>-1</sup>): 1) 0; 2) 0.5; 3) 1.0; 4) 1.5; 5) 2.0. Temperature, °C: 6) 10; 7) 0; 8) 10; 9) 20; 10) 25; 11) 30; 12) 35; 13) 40. Relaxation spectrum of  $\theta$  in sec, H in dyn/cm<sup>2</sup> (c). Reduction temperature 35°C.

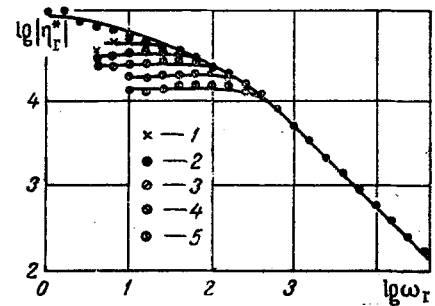


Fig. 2

Fig. 2. Absolute value of the complex viscosity (in poise) as a function of frequency in the linear region and for various amplitudes of the deformation velocity  $\log \dot{\gamma}_{\max}$  (sec<sup>-1</sup>): 1) 0; 2) 0.5; 3) 1.0; 4) 1.5; 5) 2.0.

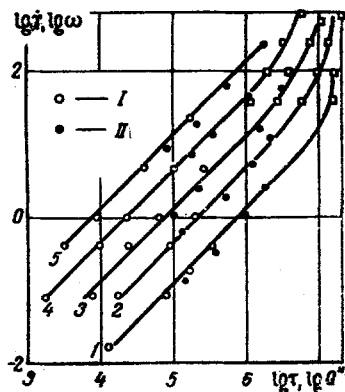


Fig. 3

Fig. 3. Stresses in dyn/cm<sup>2</sup> as functions of the shear velocity in sec<sup>-1</sup> and loss modulus as a function of frequency for various temperatures: 1) 25°C; 2) 30°C; 3) 35°C; 4) 40°C; 5) 45°C. I and II denote the rotational and capillary viscosimeters, respectively.

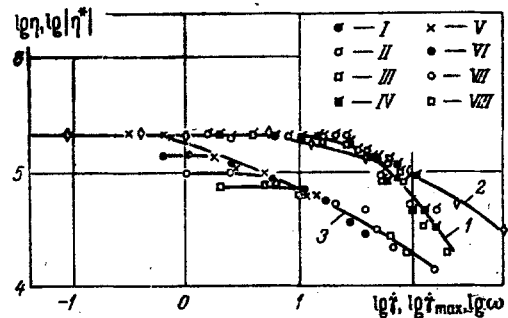


Fig. 4

Fig. 4. Curves showing: 1) effective viscosity as a function of the amplitude of deformation velocity for various shear velocities, sec<sup>-1</sup> [I)  $1.6 \cdot 10^{-2}$ ; II)  $8 \cdot 10^{-2}$ ; III)  $4 \cdot 10^{-1}$ ; IV)  $9.6 \cdot 10^{-1}$ ]; 2) effective viscosity as a function of shear velocity; 3) absolute value of complex viscosity as a function of the amplitude of deformation velocity for different frequencies [V) 6, VI) 16, VII) 40, VIII) 80 Hz].

formation were used for constructing a curve of effective viscosity versus deformation-velocity amplitude (Fig. 4, curve 1). The experiment showed that irrespective of the parameters of cyclic deformation and shear velocity, when this value is small, the factor determining the decrease in viscosity is the amplitude of the deformation velocity. This decrease is observed above some critical value of the amplitude of deformation velocity, which is independent of the shear velocity.

The same figure shows the effective viscosity as a function of shear velocity in the absence of cyclic deformation (curve 2) and the absolute value of the complex viscosity as a function of the amplitude of deformation velocity in the absence of stationary flow (the family of curves 3). As the amplitude of the deformation velocity increases after reaching its critical value, the graph of  $|\eta^*|$  as a function of  $\dot{\gamma}_{\max}$  passes to the envelope, where there is no longer any change in  $|\eta^*|$  as a function of frequency. This envelope characterizes the nonlinear regimes of deformation. A comparison of the envelope of the graph of  $|\eta^*|$  as a function of  $\dot{\gamma}_{\max}$  (curve 3) and the graph of  $\eta$  as a function of  $\dot{\gamma}$  (curve 2) shows that the nonlinear regimes of cyclic and continuous deformation are equivalent, since a displacement of these curves along the abscissa axis remains constant over a wide range of deformation velocities. This conclusion arrived at for a bitumen is in good agreement with previously published data on the investigation of polymers and their solutions [16, 19]. However, this comparison does not answer the question of what kind of viscosity (effective or complex viscosity) is more sensitive to cyclic deformation with large amplitudes. The answer to this question can be obtained by examining curves 1 and 3 simultaneously. It follows from this examination that the complex viscosity is the more sensitive parameter, since the critical value of amplitude of deformation velocity at which the decrease of  $|\eta^*|$  begins is less by more than one order of magnitude than the corresponding critical value for the effective viscosity. Investigation of a saturated solution of polyethylene [20] has shown that the effective viscosity decreased at an amplitude of cyclic deformation which was less by a factor of 1.5-3 than the amplitude at which the complex modulus components decreased. This difference is apparently due to the adopted scheme of imposing oscillations on stationary flow (in [20] the oscillations were imposed in a plane perpendicular to the stationary flow) or to the specific features of the systems investigated. Even though we have noted a large difference between the critical amplitudes of the deformation velocity, further increase leads to a sharper drop in the effective viscosity than in the complex viscosity.

A comparison of curves 1 and 2 indicates that the effective viscosity, for small values of  $\dot{\gamma}_{\max}$  and  $\dot{\gamma}$ , is more sensitive to an increase in the deformation velocity. However, as the intensity of the imposed action increases, the effective viscosity decreases more sharply for cyclic deformation than for continuous deformation. Consequently, cyclic deformation is a stronger factor in reducing the effective viscosity than is continuous shear flow.

The physical nature of the phenomena taking place during cyclic deformation and during simultaneous cyclic and continuous deformation is not yet clear. Nevertheless, it is known that stationary deformation at low shear velocity does not change the relaxation spectrum of the material, as a consequence of which the viscosity, which is an integral characteristic of the relaxation spectrum, is constant. In our experiments on cyclic deformation and on the imposition of cyclic deformation on stationary flow with low shear velocity, the reduction in complex viscosity and effective viscosity is due only to the absence of any vibrational stress. From this it follows directly that the variation of the relaxation spectrum of the material is due only to the effect of the amplitude of the deformation velocity. However, the values of  $\eta$  and  $|\eta^*|$  become equal at very different values of  $\dot{\gamma}_{\max}$ , which indicates the complex nature of the variation of the relaxation spectrum under vibration. This question will require further theoretical and experimental investigation.

The similarity of the rheological variations of bitumens and amorphous polymers which has been established in the present study is a result of the characteristics of the bitumen structure, which is characterized by the presence of supermolecular formations in the shape of fibrillae or globules (depending on the type of bitumen). The effect of stresses or deformations leads to a rearrangement of the formations formed by the most highly molecular compounds of the bitumen, namely, the asphaltenes, and the orientation of newly arriving complexes and individual macromolecules in the flow process, which can be proved by direct electron-microscopic investigations [21].

The analogy observed in the viscoelastic behavior of the two systems compared in our study is an important argument in favor of the recently developed theory [22] that bitumens

are solutions of high-molecular-weight substances — asphaltenes and solid resins with an average molecular weight of 1000-4500 and, according to [23], as much as 15,000 in a medium of petroleum oils and resins with an average molecular weight of 500-600.

The structural state of the bitumens depends on the concentration of asphaltenes, the ratio of resins and hydrocarbons, and the chemical nature of all the components of the bitumen. The bitumen investigated in the present study is characterized by a high Traxler dispersion index (about 2.7), which indicates the low degree of development of such a bitumen and the absence of a network of asphaltenes. This has a bearing on such features of the bitumen investigated as its transition to a pure Newtonian liquid at temperatures of about 40°C and the practical absence of high elasticity and the direct transition from the viscoplastic to the vitrified state. The region of transition from one state to the other is blurred and shifted in the direction of high temperatures: for a circular frequency of 40 sec<sup>-1</sup> it lies in the temperature range between +20 and 0°C, and for a circular frequency of 630 sec<sup>-1</sup> it lies between +10 and +30°C.

The high value of the vitrification temperature of the bitumen, found from the variation of the modulus of elasticity as a function of temperature, is due to the liquid-like structure of the resins dissolved in the hydrocarbons and the small influence of the asphaltenes on the structural transition [24].

The variation of the temperature interval in which the bitumen passes from the viscoplastic to the vitrified state as a function of frequency illustrates the relaxation mechanism of this transition, and the absolute value of the transition temperature shows that the vitrification temperature is much higher than the brittleness temperature found by the standard method.

#### NOTATION

$\eta^*$ , complex viscosity;  $\eta'$ , dynamic viscosity;  $\eta''$ , imaginary component;  $\eta^* = \eta' + i\eta''$ ;  $\gamma_0$ , deformation amplitude;  $\omega$ , circular frequency;  $f$ , frequency of oscillations;  $\omega = 2\pi f$ ;  $\omega_r$ , reduced frequency;  $\dot{\gamma}_{\max}$ , amplitude of deformation velocity;  $\dot{\gamma}_{\max} = \gamma_0\omega$ ;  $G^*$ , complex shear modulus;  $G'$ , modulus of elasticity;  $G''$ , loss modulus;  $G'' = \eta''\omega = G' + iG''$ ;  $\tau$ , shearing stress;  $\dot{\gamma}$ , shear velocity;  $\eta$ , effective viscosity;  $\eta = \tau/\dot{\gamma}$ ;  $\alpha_t$ , reduction coefficient;  $\theta$ , relaxation time;  $H(\theta)$ , relaxation spectrum.

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