RHEOLOGICAL PARAMETERS OF COAL TARS IN CYCLIC AND CONTINUOUS DEFORMATION

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Studies have been made on the prestationary and steady-state modes of flow, and the amplitude and frequency limits to linear behavior have been determined, while it has been shown that there is a structured framework consisting of dispersed-phase particles.

The viscoelastic parameters of coal tars used on roads determine the behavior of the tar—concrete mix widely employed in constructing road surfaces. This gives considerable interest to the deformation characteristics. One can relate the deformation characteristics to the structure in order to choose the optimum composition and the parameters of the components, and also to forecast the behavior under particular working conditions.

The literature carries virtually no information on the rheological behavior of tars, which are systems complicated in composition and structure. One can assume as approximation that road bitumens are the closest analogs to tars, whose properties have been described in some detail [1]. It has been shown [2] that the $\tau(t)$ dependence is monotone for a bitumen at relatively low shear rates, whereas peaks appear on the $\tau(t)$ curves at relatively high rates, because the system passes through the shear-strength limit, which is characterized by a quantity τ_{SS}, which is related to structure disruption, which occurs until a steady-state mode of flow is set up [3]. The value of τ_{SS} increases with the concentration of the dispersed phase and as the viscosity of the dispersion medium decreases. If we consider a bitumen as a material with a typical dispersed structure or as a system similar to a concentrated polymer solution [4], we can describe the behavior in various states of strain and can consider the relationship to the deformation of tar.

The tests were done on a compound tar widely used in making tar—concrete mixtures, which was made by fusing medium-temperature sinter (dispersed phase) with high-temperature tar (dispersion medium) in proportions providing a conditional viscosity parameter (C_{50}^{10} = 79 St) corresponding to the standard grade of tar D-6. The contents of the phase and the medium in the tar were correspondingly 47 and 53% by mass. The glass temperature of the tar was −5°C.

We examined the deformation of road coal tar with a VR-74 vibrorheometer [5] and a DKhP-2 mechanical spectrometer [6] under various states of deformation: periodic (cyclic), continuous shear at a constant rate, and with the periodic deformation superimposed on the continuous.

The experiments were performed with shear rates in the range 10^{-2}–10^{2} sec^{-1} at frequencies from 10^{-4}–10^{3} Hz at temperatures T from 0 to +80°C.

The VR-74 and DKhP-2 were used to determine the following: the dynamic characteristics (the components of the complex dynamic shear modulus), namely the elastic and loss moduli, and also the absolute value of the complex dynamic viscosity and the variations in these quantities as functions of circular frequency, strain amplitude, strain-rate amplitude, and temperature in periodic deformation; we also measured the stationary characteristics: the dependence of the shear stress on time and shear rate in continuous deformation, and the dependence of the shear stress on time and rate under conditions of periodic deformation superimposed on continuous.

These various modes of deformation provided different sorts of information on the behavior. The small-amplitude deformation gives information on the rheological parameters in the case of undisturbed structure, while increasing the amplitude enables one to evaluate the

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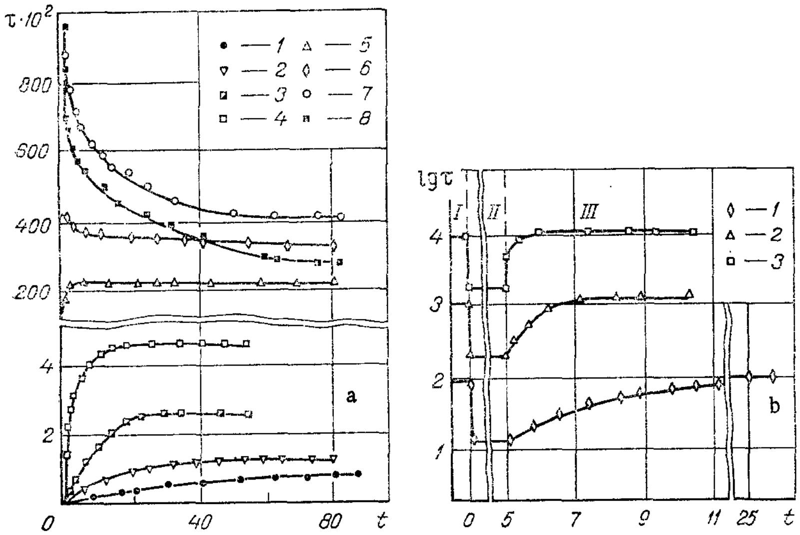

Fig. 1. Dependence of the shear stress τ (Pa) on deformation time t (sec) for tars of grade D-6 (a), curves 1-8 being for strain rates $\dot{\gamma}$ (sec^{-1}) correspondingly of 1) $2.4 \cdot 10^{-2}$; 2) $6.0 \cdot 10^{-2}$; 3) $1.2 \cdot 10^{-1}$; 4) $2.4 \cdot 10^{-1}$; 5) $1.2 \cdot 10^{-1}$; 6) $2.4 \cdot 10^{1}$; 7) $6.0 \cdot 10^{1}$; 8) $1.2 \cdot 10^{2}$; also shear stress τ (Pa) as a function of deformation time t (sec) under conditions of periodic deformation at frequency $\omega = 44$ sec^{-1} and amplitude $\gamma_0 = 6.5 \cdot 10^{-1}$ superimposed on steady-state flow (b); curves 1-3 for shear rates $\dot{\gamma}$ (sec^{-1}) correspondingly of: 1) $2.4 \cdot 10^{-2}$; 2) $6.0 \cdot 10^{-1}$; 3) $6.0 \cdot 10^{0}$; I) part before vibration; II) vibration applied; III) after vibration; T = 20°C.

limiting conditions under which vibration disrupts the material. The experiments with continuous deformation provide the traditional relationships for the rheological characteristics [$\tau = f(t)$, $\tau = f(\gamma)$, etc.]. Finally, when small-amplitude strain is superimposed on continuous, one can establish the effects of shear stress and rate on the relaxation and thixotropic characteristics.

We first consider the data from continuous deformation. Figure 1a shows that up to shear rates of 20 sec^{-1} there is a smooth change in the shear stress up to the region where steady-state flow occurs. At $\gamma > 20$ sec^{-1} (on curves 6-8), one gets pronounced peaks, which indicates a limiting shear strength, whose absolute value increases with the strain rate. Prominent peaks are characteristic of systems having low-viscosity dispersion media (a substantial part is then played by the rigidity of the torsion system) [7]. As the temperature is raised, the shear stress in the steady-state flow mode decreases, and the shear-strength limit also decreases. As the temperature is raised, the peaks on the τ(t) curves degenerate and vanish at 60°C, and steady-state conditions are attained at lower τ.

Therefore, on drawing up the general laws for τ(t) for dispersion-type bitumens [8, 9] and tars, we can say that the regularities are qualitatively similar, particularly in that there are limits to the shear strength, which, in turn, reflects the structured framework.

The behavior of the rheological characteristics is important in evaluating the effects of vibration, as these are recorded with periodic deformation at various frequencies and amplitudes superimposed on the steady-state strain, where one expects changes in the viscosity because of the additional structure-element destruction (superanomalies). Figure 1b shows $\tau = f(t)$ curves recorded under these conditions. The shear stress is reduced when periodic strain is applied, and the stresses gradually return to the original level after it is removed. The time required to reach the original τ decreases at the strain rate increases, which means that the main factor disrupting the structure is the strain amplitude, while the duration does not play an important part.

The τ(t) curves with cyclic strain superimposed on continuous flow are qualitatively similar for coal tar and bitumen. The tar shows a sharp reduction in the shear stress, whereas the bitumen shows a smooth fall, whereas the latter also shows a more prolonged re-

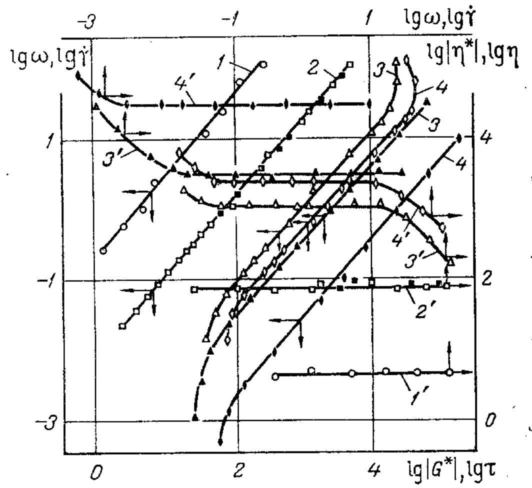

Fig. 2

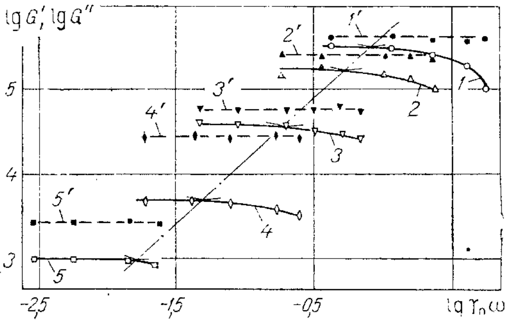

Fig. 3

Fig. 2. Flow curves $\tau(\dot{\gamma})$ (1–4, open points), curves for the absolute value of the complex dynamic shear modulus $|G^*|$ (Pa) (2–4, filled points), and absolute value of the complex dynamic viscosity $|\eta^*|$ (Pa·sec) (2'–4', filled symbols) as a function of circular frequency ω ($\sec^{-1}$); effective viscosity η (Pa·sec); shear rates $\dot{\gamma}$ ($\sec^{-1}$) (1'–4', open symbols): 1, 1') T = 80; 2, 2') 60; 3, 3') 40; 4, 4') 20°C.

Fig. 3. Dependence of the elastic modulus G' (Pa) (curves 1–5) and the loss modulus G" (1'–5', dashed lines) on the amplitude of the strain rate $\gamma_0\omega$ ($\sec^{-1}$); curves 1–5 for frequencies ω ($\sec^{-1}$), respectively: 1) 62.8; 2) 31.4; 3) 6.28; 4) 3.14; 5) 0.31. T = 20°C.

covery of the stress to the initial values. These differences are due to the lower viscosity of the dispersion medium in the tar by comparison with the bitumen and, consequently, the thixotropic recovery in the tar is more rapid. Figure 1b also shows that the tar has an internal structural framework formed by the particles of dispersed phase.

We should note that in [10] it proved impossible to identify the structural framework in tar of D-6 grade at temperatures below room temperature. Evidently here considerable importance attaches to the scope for making measurements at sufficiently low strain rates.

Figure 2 shows flow curves for D-6. Up to high stresses of about $3 \cdot 10^4$ Pa, the flow is almost Newtonian. There are sharp changes in $\tau(\dot{\gamma})$ at 20 and 40°C in the region $\tau > 3 \cdot 10^4$ Pa, which are evidently due to the viscosity superanomaly effect [11].

The following conclusions are drawn from the continuous-strain experiments. The rheological behavior of tar is substantially dependent on temperature. At room temperature or below, there is a structural framework formed by the crystalline phase of the anthracene present in the dispersion medium and by the dispersed phase in the sinter, and one observes a turning-point behavior of τ at certain values of $\dot{\gamma}$ in the prestationary state of strain, while $\tau(\dot{\gamma})$ shows clearly that there is a yield point $\tau_{yp} = 0.7 \cdot 10^2$ Pa (Fig. 2, curves 3 and 4). Deformation at $\tau > \tau_{yp}$ or elevated temperature will disrupt the framework, so the material behaves like a Newtonian liquid over fairly wide ranges in τ and $\dot{\gamma}$. The decisive effect then comes from the viscosity of the dispersion medium, while the fragments of the disrupted structure (dispersed phase) act as a structureless filler. One can use the Shvedov–Bingham model [12] to describe the viscoelastic behavior of tar of this composition up to high $\dot{\gamma}$ at room temperature or below. The tar has a yield point, and the shape of the rheological curves is dependent on the shear stress and shear rate, the deformation time, and the structure strength, i.e., attainment of an equilibrium state is very important.

We now consider the results obtained with periodic strain, particularly the relationship between the dynamic and stationary characteristics.

Figure 3 shows how the elastic modulus and loss modulus (dashed lines) vary with the strain-rate amplitude (temperature 20°C). The $G'(\dot{\gamma}_0)$ curves have two ranges: linear and nonlinear strain, which are separated by the dot–dash line. As the frequency increases, the

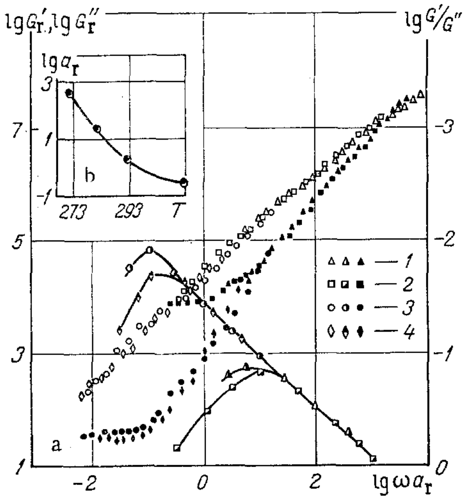

Fig. 4. Effects of reduced frequency ωa_r (sec^{-1}) on the reduced values of the dynamic elastic modulus G'_r (Pa) (1-4, filled points), the loss modulus G''_r (Pa) (1-4, open points), and the parameter G'/G'' (1-4, half-filled points) (a) and dependence on temperature T (°K) for the temperature coefficient of reduction a_r (b). Reduction temperature 20°C: 1) T = 0; 2) 10; 3) 20; 4) 40°C.

boundary of the linear region shifts to larger $\dot{\gamma}_0$. At the same time, the $G''(\dot{\gamma}_0)$ curves show that the loss modulus is not affected by $\dot{\gamma}_0$. It seems that a nonlinear range in $\dot{\gamma}_0$ for G" would occur at higher γ_0. Similar relationships were obtained for other temperatures.

The bounds to linear strain in tar provide curves indicating how the elastic and loss moduli vary with the circular frequency under conditions of nondestructive testing over a wide range in ω, which enables one to extend the results from 0 to 40°C by using the temperature—time superposition method [13], where the reduction temperature T_r was taken as 20 °C (Fig. 4). The moduli increase with the circular frequency. A feature of $G'_r(\omega a_r)$ is that there are yield points, which correspond to constant values of G'_r, which can be identified at all the temperatures used. This again shows that there is a framework structure. A distinctive feature of a tar relative to a macromolecular polymer is that there is no highly elastic plateau in the $G'(\omega)$ or maximum on $G''(\omega)$, whereas the attainment of constant G' or a turning point in G" in the region of the vitreous state should occur for higher frequencies. However, the temperature dependence of the reduction coefficient a_r is qualitatively similar to the curves obtained for polymer systems. Curves 1-4 (Fig. 4) show the dependence of the dimensionless parameter (essentially the reciprocal of the mechanical loss angle tangent) on the circular frequency. The prominent peaks on these curves correspond to circular frequencies representing the yield point at the corresponding temperature. This form of $G'/G'' = f(\omega)$ has not been reported beofre and may serve as a criterion for obtaining the yield point in the disperse systems.

In studies made on polymer systems [14] and bitumens [9], there was found to be an empirical correlation between the characteristics determined in stationary flow and with periodic shear strain at small amplitudes. This correlation was used for tar, assuming equivalence between the shear rate and the circular frequency, to draw up $\tau(\dot{\gamma})$ and $|G^*|(\omega)$ curves, as well as curves for the dynamic viscosity $|\eta^*| = f(\omega)$ and the effective viscosity $\eta = f(\omega)$ (Fig. 2). At room temperature, there is a correlation between $|G^*|(\omega)$ and $\tau(\dot{\gamma})$ only at low strain rates (curves 3-3' and 4-4'), while as the temperature rises the $\tau(\dot{\gamma})$ and $|G^*|(\omega)$ curves come together, and they coincide at 60°C (curves 2-2') throughout the strain-rate range. Therefore, there is similarity in these relationships only in the region of Newtonian behavior for tar, as in the case of bitumens of all structural and rheological types [1]. If the system contains a structured framework, the correlation between the dynamic and stationary characteristics is only qualitative over wide ranges in ω and $\dot{\gamma}$, as in the case of filled polymers.

Therefore, this similarity in rheological characteristics between tar and dispersion-type bitumens is due primarily to similarities in structure, since there is a structured framework at low temperatures, which is formed by the free-carbon and asphaltene fractions respectively, while, in addition, the structural state of the tar is related to the proportions of dispersed phase and dispersion medium, as well as the chemical natures of all the components.

NOTATION

η^*, complex dynamic viscosity; γ_0, deformation amplitude; ω, angular frequency; f, vibration frequency; ω_r, reduced frequency; $\dot{\gamma}_0$, strain rate amplitude; G^*, complex shear modulus; G', elastic modulus; G'', loss modulus; $G^* = G' + i\ G'' = \eta^*\cdot i\omega$; τ, shear stress; τ_s, shear strength; τ_{yp}, yield point; $\dot{\gamma}$, shear rate; η, effective viscosity; $\eta = \tau/\dot{\gamma}$; a_r, temperature reduction coefficient; G_r', reduced elastic modulus; G_r'', reduced loss modulus.

LITERATURE CITED

1. V. A. Zolotarev, "Fundamental rheological properties of bitumens and asphalt-concretes," in: Applied Rheology and Flow in Dispersed Systems [in Russian], Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk (1981), pp. 24-32.
2. G. V. Vinogradov, V. A. Zolotarev, A. N. Bodan, et al., "Features of the viscoelastic behavior of bitumens of various structural and rheological types under conditions of continuous deformation," Kolloidn. Zh., 40, No. 4, 629-634 (1978).
3. G. V. Vinogradov and V. P. Pavlov, "Flow and strength in structure disperse systems," Kolloidn. Zh., 20, No. 2, 248-253 (1958).
4. V. A. Zolotarev, Working Life in Road Asphalt-Concretes [in Russian], Vysshaya Shkola, Kharkov (1977).
5. V. I. Brizitskii, Yu. G. Yanovskii, D. A. Mustafaev, et al., " The VR-74 vibrorheometer," Abstracts for the All-Union Seminar on Instrumental Methods in Rheology [in Russian], VDNKh, Moscow (1977), pp. 38-40.
6. L. P. Ul'yanov, V. M. Neimark, Yu. G. Yanovskii, et al., "An instrument for examining the dynamic characteristics of polymers at low and infralow frequencies," Zavod. Lab., 39, No. 11, 1402-1404 (1973).
7. G. V. Vinogradov, "Some problems in the rheology of highly concentrated dispersed systems," Proceedings of the Military Armored Tank Brigade Academy: Information Issue [in Russian], No. 57 (1959), pp. 1-25.
8. V. A. Zolotarev and E. A. Verebskaya, "Effects of structure and production technology on the rheological properties of bitumens, " in: Machines and Technologies for Handling Rubbers, Polymers, and Rubber Mixtures [in Russian], Issue 1, Yaroslavl Polytechnic Inst. (1978), pp. 62-68.
9. V. A. Zolotarev, A. I. Isaev, and G. V. Vinogradov, "The viscoelastic parameters of bitumen during continuous and cyclic deformation," Inzh.-Fiz. Zh., 29, No. 2, 332-340 (1975).
10. V. I. Bratchun, "Structural features of coal tars," Izv. Vyssh. Uchebn. Zaved., Stroit. Arkhitektura, No. 8, 65-69 (1983).
11. V. P. Pavlov and G. V. Vinogradov, "A generalized rheological characterization of plastic dispersed systems," Kolloidn. Zh., 23, No. 3, 424-429 (1966).
12. W. L. Wilkinson, Non-Newtonian Liquids [Russian translation], Mir, Moscow (1964).
13. J. D. Ferry, Viscoelastic Properties of Polymers, Wiley (1970).
14. Yu. G. Yanovskii and A. Ya. Malkin, "Polymer property correlation in continuous and periodic strain," in: Advances in Polymer Rheology [in Russian], G. V. Vinogradov (ed.), Khimiya, Moscow (1970), pp. 52-78.