Viscoelastic Properties of Filled Polymers

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Rheological properties of carbon black filled polyisobutylene samples (of low and high molecular weight) have shed light on the relationship between the behaviour of disperse and polymeric systems. At sufficiently high filler concentration a structural skeleton seems to appear. This affects the properties.

INTRODUCTION

The specific rheological properties of highly filled polymeric systems depend on the ratio between the viscosity of the dispersion medium and the strength of structural skeleton, of filler. A large number of papers have been devoted to a detailed study of disperse systems with non-elastic dispersion media. The properties of such plastic disperse systems as greases,[1–3] bentonite clays[4] and bitumens[5] have been studied most thoroughly in this respect. A general description of the rheological characteristics of these systems has been given.[3,6] An investigation of plastic disperse systems made it possible to point out such fundamental features of their properties as the presence of a creep region involving flow of the system with unbroken structure and with a viscosity of the order of 10^{11} or 10^{12} poise (the viscosity of the dispersion medium being from a few to many thousand poise), passage through a yield point, to which corresponds a very sharp (jumpwise) decrease in apparent viscosity of several decimal orders, and flow with broken structure, when the stresses considerably exceed the yield point and the viscosity of the system approaches that of the dispersion medium in order of value. These peculiarities

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of rheological properties are common to a great variety of plastic dispersed systems, though the general regularity indicated may be more or less pronounced depending on their composition.

Another important system for studying rheological properties are polymer systems which display high elasticity as their main feature.[7] Until very recently the study of the rheological properties of filled polymer systems was confined to an examination of predominantly particular questions, although the existence of certain similarities of shape in the flow curves of plastic disperse systems and polymer melts was pointed out in reference.[8] Meanwhile a systematic study of the behaviour of filled polymer melts would make it possible to unify the description of the rheological properties of the two main classes of systems, the viscosity anomaly and viscoelasticity of which are the most important objects of study in present-day rheological investigations.

Being dispersed systems, filled polymers should obey the general laws of behaviour of such systems, but the high viscosity of the dispersion medium and its capacity for high-elastic deformation cannot but give rise to certain peculiarities in rheological properties. The presence of a disperse phase capable of forming a structural skeleton, should have its effect on the viscoelastic properties of the polymer.

On the basis of what has been said above, the object of this work can be formulated as a systematic investigation of the viscous and elastic properties of filled polymers having different viscosities and containing different amounts of filler, to establish the specific effect of polymer as the dispersion medium on the properties of the system and the general effect of filler on the viscoelastic properties of polymer.

EXPERIMENTAL

Materials

Rheological properties were studied mainly on a typical polymer—grade P-20 polyisobutylene—possessing the entire range of rheological properties inherent in polymer melts. The filler was acetylene black, which possesses high structurizing properties. The molecular weight of the polymer determined from its intrinsic viscosity in toluene, was 9.5×10^4. The initial viscosity of polyisobutylene at 20°C is close to 10^7 poise. This polymer has a wide range of relaxation properties, typical of polymeric systems, and a pronounced region of anomalously viscous flow. The rheological properties of polyisobutylene have been studied previously.[9] The black selected as the filler had a specific surface area of 110 m²/g (determined by the kinetic method) and a

fairly high structurizing ability (ASTM dibutyl phthalate absorption value 1.39 ml/g).

For comparison, the rheological properties of a low-molecular weight polyisobutylene (grade P-1) were studied. The chemical structure of this polymer is quite equivalent to that of its higher-molecular analogue, but its initial viscosity is much lower, being only 6×10^2 poises at 20°C. Owing to the low-molecular weight of this sample neither relaxation processes nor any deviations from Newtonian flow conditions were observed in it (in the experimental procedures used in this work). Hence, grade P-1 polyisobutylene is a typical hydrocarbon medium, and its mixture with acetylene black should be regarded as intermediate in properties between filled polymers and the typical disperse systems described in Refs. 1–3. Comparison of the results of measurement of the rheological properties of mixes based on P-1 and P-20 gives an insight into the specific influence of the polymeric nature of the dispersion medium. The mixes studied for both polymers contain up to 30 parts by weight of black per 100 parts of polymers.

P-20-black mixes were prepared on a set of microrolls, by masticating them for 10 minutes at room temperature; P-1 pastes were masticated with the black by hand. Good reproduceability (deviation of not more than $\pm 5\%$ from average values) of the points on the flow curves of the initial and masticated P-20 polyisobutylene (without black), and constancy of the intrinsic viscosity values of the corresponding samples are indications that no mechanical degradation of polymer occurs under the conditions of mastication of the mixture. All rheological measurements were conducted within the temperature range from room temperature to 100°C.

Methods

A set of rotational elastoviscometers, capillary viscometers, and shear plastometers was used for studying the rheology of the black-filled polyisobutylenes. A list of the instruments used in this work, indicating their working ranges, possible errors of measurement, and other general data, is given in Table I.

Results and Discussion

Viscous Properties and Yield Points of Filled Polymers
Figure 1 (a and b) shows the flow curves of black mixtures based on P-20 polyisobutylene at 22°C and 60°C for all the concentrations studied.

The flow curves obtained at room temperature (Figure 1a) are typical of both unfilled and filled polymers. Similar curves for unfilled rubbers have been described by G. M. Bartenev *et al.*[17] and in many other papers. It is evident from Figure 1a that as usual addition of filler to the polymer

TABLE I

Type of measurement	Working assembly	Conditions of measurement	Range of measurement			Percentage error of measurement		
			τ dyne/cm^2	$\dot{\gamma}$ sec^{-1}	γ_{el} arb. units	τ	$\dot{\gamma}$	γ_{el}
REV-1 rotational elastoviscometer[10]	Cone-plane	$\dot{\gamma} = Const$	$5 \times 10^3 - 10^6$	$10^{-5} - 1$	—	3	1	—
REV-3 rotational elastoviscometer[11]	Cone-plane	$\dot{\gamma} = Const$	$4 \times 10^3 - 10^6$	$10^{-4} - 1$	—	2.5	1	—
Rotovisco rotational viscometer (West Berlin)[12]	Cylinder-cylinder	$\dot{\gamma} = Const$	$4 \times 10^1 - 10^5$	$10^{-3} - 10^2$	—	3	1	—
Shear plastometer[13]	Plane-parallel ribbed plates	$\tau = Const$	$10^2 - 10^5$	$10^{-7} - 10^{-1}$	$\leqslant 0.1$	3	3.8	12
EM-1 elastometer[14]	Cone-plane	$\dot{\gamma} = Const$	—	$10^{-3} - 1$	> 0.2	—	—	15
KVPD-1 constant-pressure capillary viscometer[15]	Capillary	$\tau = Const$	$10^3 - 10^7$	$10^{-3} - 10^3$	—	1	4	—
AKV-2 automatic capillary viscometer[16]	Capillary	Variable pressure of uncoiling spring	$3 \times 10^3 - 3 \times 10^5$	$3 \times 10^1 - 2 \times 10^3$	—	1	4	—
KVPR constant discharge capillary viscometer	Capillary	Constant velocity of plunger in bomb	$4 \times 10^4 - 10^5$	$10^{-3} - 10^1$	—	3	1	—

increases the viscosity anomaly. The reasons for such a change in shape of the flow curve when filler is added become clear if the viscous properties of the mixtures are examined at 60°C (Figure 1b), where it is experimentally less difficult to investigate a wider range of shear rates and stresses than at 22°C. It can readily be seen that if only the range of shear rates above 10^{-3} sec^{-1} is taken into consideration (this being the range in which the rheological properties of filled polymers are usually studied), the flow curves at 22°C and 60°C do not differ qualitatively from one another. But the picture changes sharply when we pass to the range of low rates and stresses: with increasing filler content the flow curves run steeper, and with decreasing stress they become vertical (or almost vertical) straight lines. The higher the concentration of filler, the higher the stress values to which the position of these vertical lines corresponds. The presence of vertical sections on the flow curves may be related either to slippage of the system relative to the face of measurement, or to very abrupt (avalanche-like) destruction of the structural network.
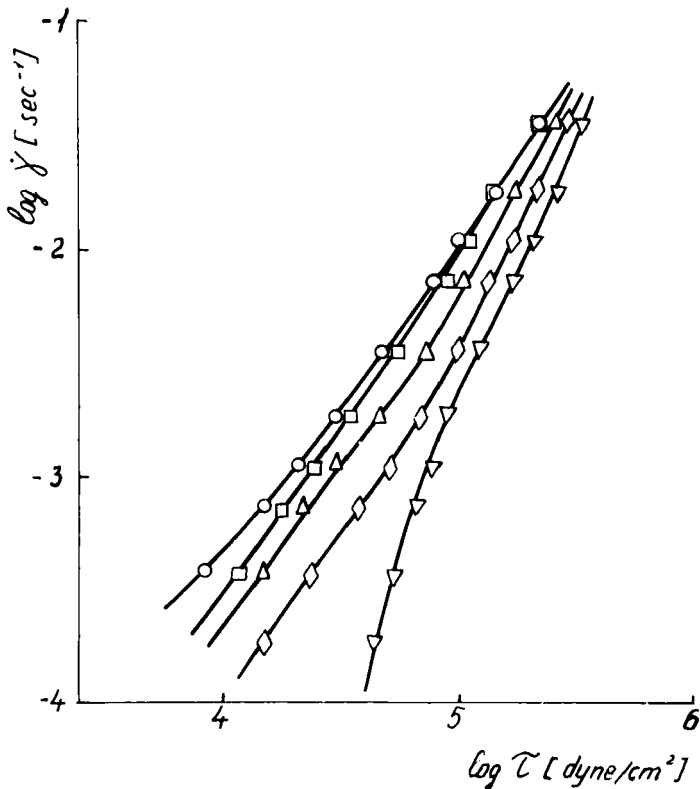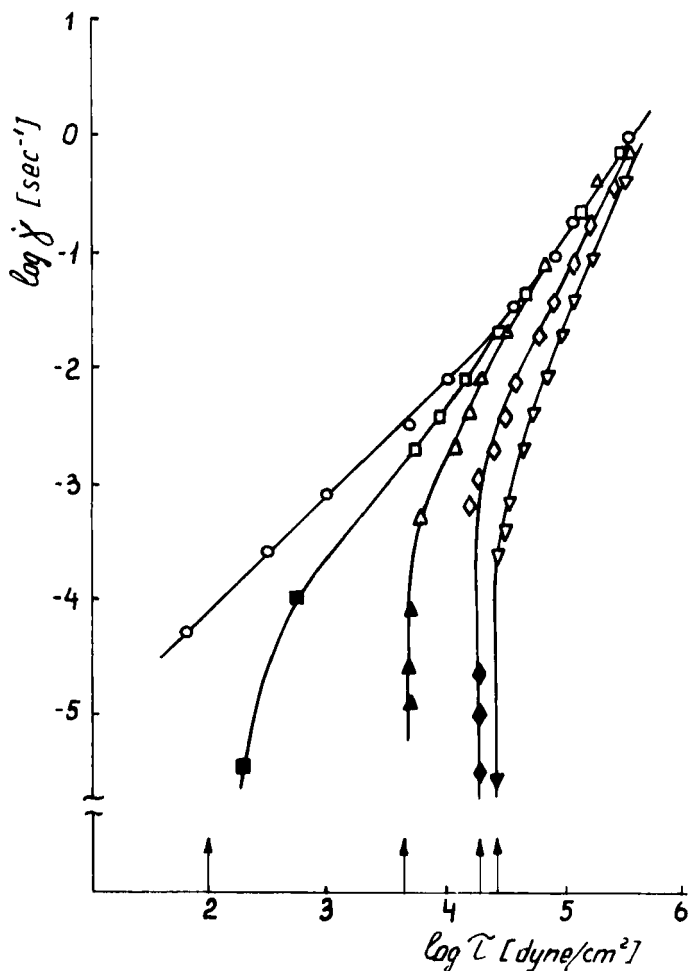

FIGURE 1(a)

(b)

FIGURE 1   Flow curves of filled P-20 polyisobutylene with different black contents (percent by volume): ○—pure P-20; □—2.5 percent; △—5 percent; ◇—9 percent; ▽—13 percent black; (a) at room temperature; (b) at 60°C.

   Black points were obtained on a shear plastometer with plane-parallel plates; all the rest were obtained on rotational viscometers; vertical arrows indicate yield points.

The former may be the case when the strength of structural skeleton exceeds adhesion of the system to the solid wall; then, if the measuring surface of the instrument is moving relative to the sample very slowly, the acting stresses are not high enough to break up the structural skeleton. But the other reason

for the vertical branches of the flow curves, namely, a sharp drop in viscosity within a narrow range of stresses, is no less typical of dispersed systems.[3,6] These sections correspond to passage through the yield point, when the system in which flow is retarded by the continuous rigid structural network of filler fails, resulting in a system with a broken filler structure, capable of irreversible deformation.

A convenient experimental method of studying the behaviour of systems at low shear rates is by measuring the strains caused by loading and unloading of a sample placed in the narrow gap between the plane-parallel plates of a shear plastometer. These experiments resulted in a set of strain-time curves, the system recovering elastically each time after the load was removed; the criterion of established equilibrium conditions was absence of strain within the resolution range of the method of measurement with respect to place shift (approx. 1.2 μ) over a time period of about 6 to 8 hours. It was found by this method that in the case of mixes containing 5.9 and 13 percent black there are stresses τ_m, below which no irreversible strain is detected in our experiments. At stresses above τ_m flow can be observed; the corresponding points are blackened in Figure 1b. The value of τ_m can be established to an accuracy of not worse the ± 6 percent.

Measurements of viscous properties on the shear plastometer carried out with smooth and with ribbed plates coincided. This shows that in the cases under consideration the vertical section on the flow curves is actually related to flow of the system, accompanied by the sharp drop in apparent viscosity within a narrow range of stresses, typical of disperse systems, and not to slippage of the sample relative to the solid surface.

According to the above estimate of sensitivity of the method used, it may be stated that the viscosity of the system at $\tau < \tau_m$ is not less than 10^{10} poises (for a polymer containing 5–13 percent black), because if the viscosity were lower, corresponding irreversible strains of the grease-creep type would be detectable by the methods used. Hence, the viscosity of filled polymers with unbroken disperse-phase structure is in any case not lower than the viscosity of intact plastic disperse systems.

We checked our estimates of τ_m values by relaxing the stress during 8 hours after cessation of steady-state flow.[18]

The corresponding yield point values are shown by arrows in Figure 1b. The τ_m value for the system containing 2.5 percent could be determined only by extrapolation of the stress versus shear rate dependence to $\dot{\gamma} \to 0$, because the error of stress assignment on the shear plastometer is a considerable fraction of the yield point value found by the relaxation method.

To complete our discussion of the yield points of P-20-base mixes when studying their viscous properties, we may point out that no flow was observed in samples tested on the capillary viscometer with stresses (calculated from

the pressure assigned) below τ_m. The transition to perceptible volume discharge is estimated to an accuracy not worse than 20 percent of τ_m (the calculation being made from the stress on the capillary wall).

Thus, lowering the viscosity of the dispersion medium in P-20 polyisobutylene by raising the temperature from 22 to 60°C enables us to pass from the region of shear rates remote from the yield point of the system to the stress range in which the existence of a structural skeleton can be detected relatively easily and the flow curves of the polymer systems come close to those of typical disperse systems based on low-molecular compounds.

It is interesting to note that the yield point and volume discharge values obtained in the flow region are independent of capillary radius. This is an indication of the absence of wall slippage effects. Hence, after passing through the yield point shear strains develop throughout the entire volume of the material.

The effects described above are still more pronounced if low-molecular P-1 polyisobutylene is used instead of P-20. The flow curves of P-1-base pastes (Figure 2a,b) are essentially more developed vertical regions of the flow curves observed for mixes of P-20 and black at 60°C. However, lowering the viscosity of dispersion medium makes the effect of the structural skeletons more pronounced, so that the vertical sections of the flow curves become predominant within the interval of shear rates studied. The existence of a second (lower) section on the flow curves is evidently related to dry friction of the material against the surface of the measuring assembly upon forced motion.

Measurement at very low deformation rates with a shear plastometer with corrugated plates gave the yield point values of 5.9 and 13 percent mixes of P-1 with carbon black (with an average error of ± 7 percent). These values are indicated in Figure 2a by the arrows at the abscissa axis. At shear stresses below τ_m slow flow with viscosities of the order of 10^9 poise were observed, which is typical of dispersed systems of broken structure.

Additional measurements made with constant-pressure or constant-discharge capillary viscometers gave more complete information on the rheological properties of the 13 percent mix (see Figure 2b). It is evident from the figure that the data obtained for different conditions of forcing the mix through capillaries of various radii practically coincide with those obtained with the rational instrument in the region of the second vertical branch with a stress spread of not more than ± 30 percent. Therefore, these data are a characteristic of the rheological properties of the mix under study.

The appearance of the extrudate produced at a given rate of discharge is also characteristic. At discharge rates below a certain critical value (indicated by an arrow in Figure 2b) the extrudate has a pronouncedly rough surface. If the discharge rate is increased the extrudate becomes smooth, as shown
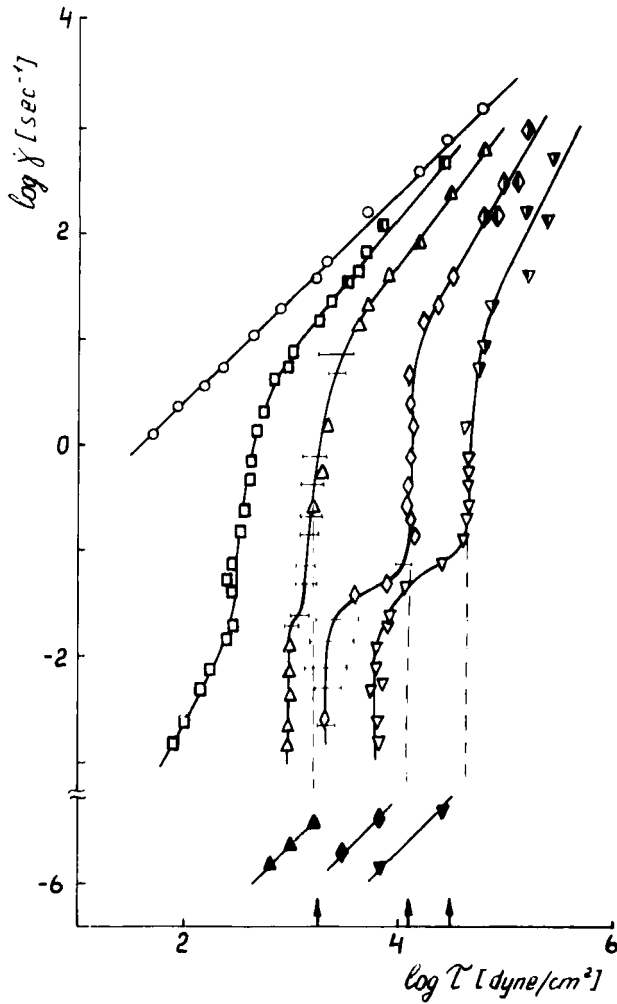
FIGURE 2a   Flow curves of P-1 polyisobutylene mixes with acetylene black at 60°C:
○—pure P-1; □—2.5 percent; △—5 percent; ◇—9 percent; ▽—13 percent black by volume.
    ○, □, ▽, ◇, △—"Rotovisco"; ◐, ◧, ▲, ◈—AKV-2; ◆, ▼—KVPD; ▲, ◆,
▼—plastometer.
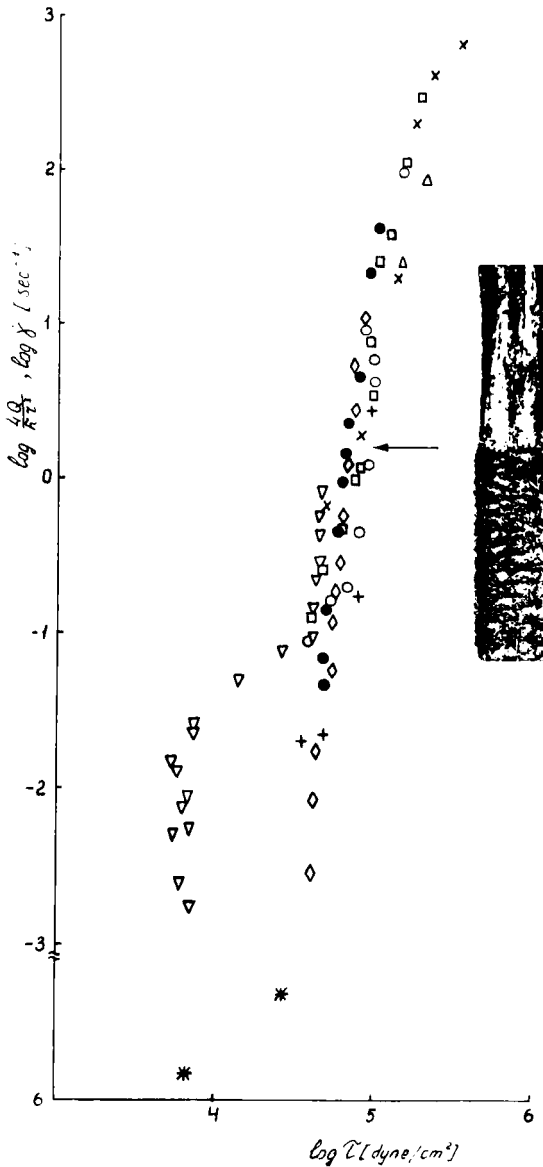   Vertical arrows indicate yield points.

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FIGURE 2b Rheological characteristics of 13 percent dispersion of carbon black in P-I at 60°C.

1. In log τ vs. log $\dot{\gamma}$ coordinates: ∇—"Rotovisco"; $*$—plastometer with plane-parallel plates.

2. In log τ vs. log $\dfrac{4Q}{\pi r^3}$ coordinates: $\triangle$—MV-2, capillary diameter $d = 0.8$ mm; KVPD, d(mm): $\times$—0.548, $\square$—0.974, $\circ$—2.075, $+$—3.92; KVPR, d(mm): $\bullet$—2.054, 2.1 $\diamond$—47.127.

in the photograph. In this respect the sequence of effects is the reverse of what is well known for polymer melts, where an increase in shear rate causes distortion of the smooth surface.

This suggests that a stress just slightly exceeding the yield point flow develops in the wall-adjacent layer, involving breakdown of its structure and, possible, slippage of the material at the capillary wall. At higher stresses volume flow becomes predominant. Such a sequence of effects accounts for observed appearance of extrudate, because in the case of thermoplast melts the sequence of deformation regimes is the reverse.

Some differences in the properties of mixes based on P-1 and P-20 are manifested in the shapes of the flow curves in the range of higher shear rates. In the case of P-1-base dispersions the region of flow of the system with maximally broken structure is relatively easy to reach. The corresponding branches of the flow curve are those close to the Newtonian ones at shear rates above $\sim 20\,\text{sec}^{-1}$ (see Figure 2a). In the case of the filled higher-molecular polyisobutylene (Figure 1) the flow remains sharply anomolously viscous, even if the structural skeleton of the disperse phase is destroyed. This is related to the specific viscous properties of the dispersion medium, since the macromolecules themselves are capable of forming a structural network which is gradually broken down as the stresses rise. Also related to the specific properties of the polymer is the strong convergence of the flow curves in the region of high shear rates, which is very typical especially of elastomers (cf. Ref. 19).

The change in viscosity of base P-1 pastes in the region of high shear rates (see Figure 3a,b) is essentially the well known effect of growth of the structural components of the resistance to deformation, and is displayed as a result of rupture of the bonds between structural elements, which are restored continuously in the flow, mechanical entanglement of structural skeleton fragments, etc.

Comparison of the dependencies shown in Figure 3a with the usual dependencies of specific viscosity $\eta_{sp} = \eta/\eta_0 - 1$, η_0 being the viscosity of the dispersion medium) on the filler concentration C, described for suspensions and model systems based on low-viscosity compounds, showed that in the case under consideration η_{sp} increases much more than is predicted even by such a strong dependence as is given by the Mooney equation.[20] Since the flow of P-1-base pastes in the region of high shear stresses is close to Newtonian flow, the dependence $\eta_{sp}(C)$ versus C should be the same for different stresses. In contrast (see Figure 3b), the functions $\eta_{sp}(C)$ for P-20-base mixes differ depending on the stress at which the viscosities are compared. Furthermore, the higher the stress, the weaker is the dependence of η_{sp} on C and the closer the stress to the yield point, the stronger is the effect of filling on the viscosity. All this can be readily understood by examining Figure 1, since the flow

curves diverge sharply at low stresses and almost converge in the region of high shear stresses.

Now let us examine the yield point values obtained (τ_m) in greater detail. The dependencies of the yield points on the concentration of the systems studied are shown in Figure 4. We take as the yield point of the 2.5 percent P-1-base mixture the stress corresponding to the vertical section on the flow curve (see Figure 2a), because experimental determination of this value is beyond the scope of the plastometer.

Obviously, despite a 10^5-fold difference in solvent viscosity, the τ_m values of the two systems studied are fairly close. This is an indication that the strength of structural skeleton plays a determinative role in the phenomenon under consideration. It is typical of both of the systems studied, that the yield point was detected only at concentrations above 2.5 or 3 percent, and that τ_m increased fairly sharply on further increase of filler content.
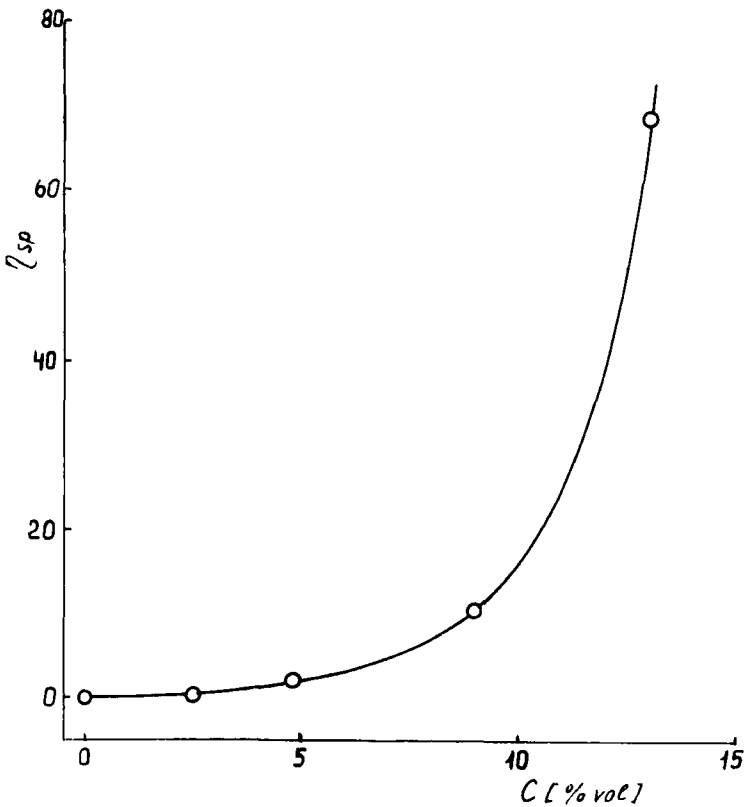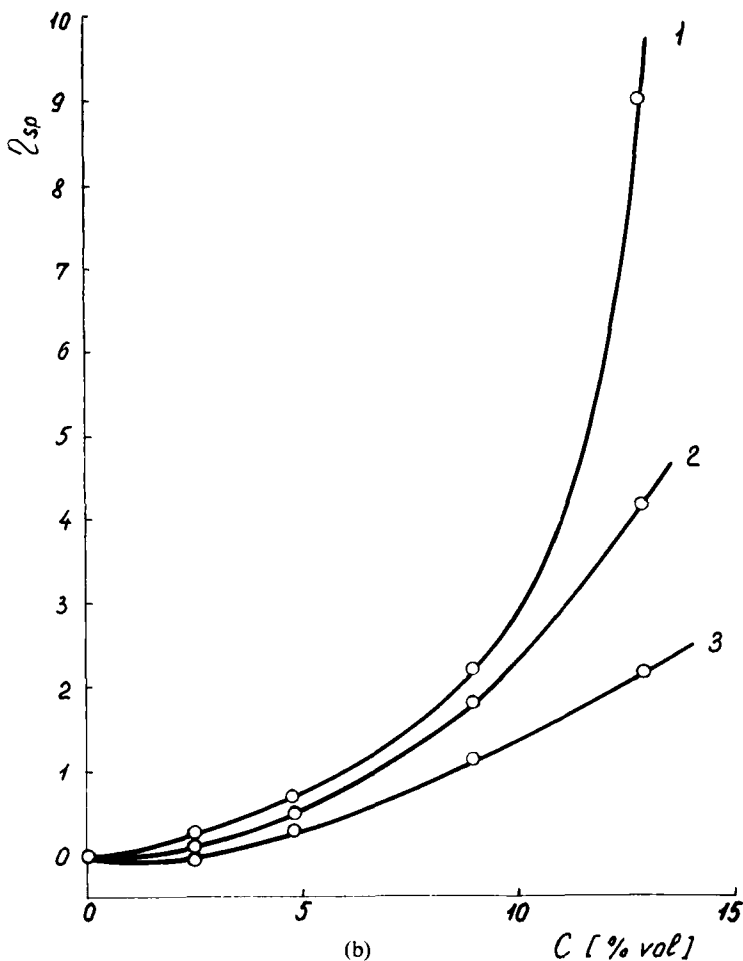

FIGURE 3(a)

FIGURE 3 Concentration dependence of specific viscosity: (a) for mix of P-1 with black at 60°C and $\tau = 10^5$ dyne/cm²; (b) for mix of P-20 with black at 22°C and $\tau = 1$— 6×10^4 dyne/cm²; 2—10^5 dyne/cm²; 3—2×10^5 dyne/cm².

The appearance of a yield point obviously corresponds to formation of a continuous three-dimensional structure of black particles. The exact concentration at which a continuous structural network forms depends on the nature of filler and on the interaction between filler and medium. The appearance of a yield point in rubber solutions at approximately 4.8 percent (by volume) black content in Ref. 21 was attributed to a three-dimensional structure composed of rubber macromolecules with filler particles
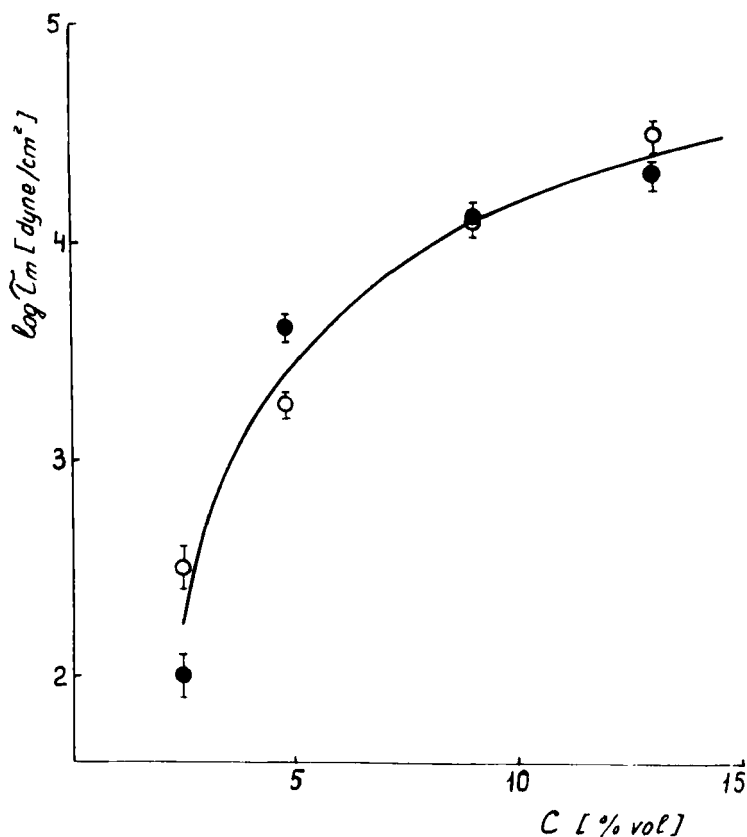
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FIGURE 4 Dependence of yield points of filled polyisobutylenes on black concentration at 60°C: ●—P-20, ○—P-1.

at its nodes. However, such concentrations of black are sufficient for coagulated black structures to appear.[22] In the experiment described above the P-1-base pastes have a yield point, and one can be detected at a filler content of 4.8 percent, although low-molecular P-1 polyisobutylene is hardly likely to have. Hence the appearance of a yield point even at relatively low filler contents should be related to its structurizing ability.

The determinative role of the strength of the structural skeleton formed by the filler particles in passing through the yield point of the system also becomes quite evident on comparing the flow curves of the same sample for temperatures varying from 22° to 100°C. This causes a change in viscosity of dispersion medium of 160 times. The data of Figure 5 suggest that the yield point depends little on the temperature.
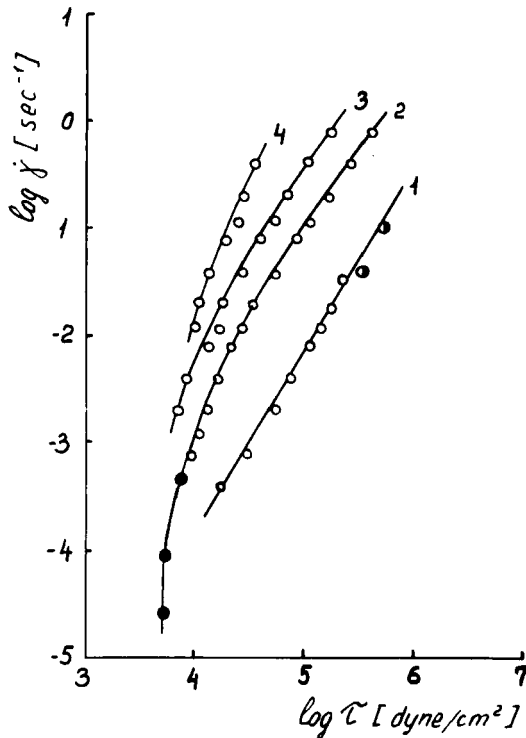
FIGURE 5   Flow curves of 5 percent mix of P-20 with black at different temperatures:
1—22°C; 2—60°C; 3—80°C; 4—100°C.
   Points were obtained: ○—on REV-1 and REV 3; ◑—on KVPD; ●—on a shear plasto-
meter with plane-parallel plates.

Direct measurements of the viscosity of a 5 percent P-1-base dispersion
at temperatures ranging from 22 to 60°C showed that the τ_m values are indeed
independent of temperature, though the deformations (obtained at $\tau = Const$)
corresponding to breakdown of the structure depend substantially on the
temperature. This is in general typical of thixotropic coagulation structures
to which black structures belong.[23]
   Now let us analyze the temperature dependence of the viscosity of filled
polymer. This problem has interested investigators for quite a long time,
not only in connection with practical questions of fabricating articles from
filled polymers, but also due to the fact that analysis of the temperature
dependence of viscosity gives an insight into the mechanism of flow of these
systems. Two contradictory points of view on this question are now under
discussion in the literature. References 17 advocate the idea that the activation

energy of viscous flow is independent of the filler content, and from this idea follows the opinion that the pure melt and the filled polymer have the same mechanisms of flow. However, Ref. 24 presents experimental data which contradict this idea.

Obviously, to be complete, analysis of the viscosity versus temperature dependence should be based on examination of the entire flow curve, including both the regions close to the yield point of filled systems and the structural branches of the flow curves. Before establishing the nature of the dependence of viscous properties on temperature it is necessary to determine strictly which viscosity values of such liquids as polymer systems are to be compared. It is usually the most correct to compare initial viscosities, because they are related to the molecular parameters of polymer. But in systems containing a sufficient amount ($>$ 2.5 percent in our case) of filler Newtonian flow regions are difficult to investigate.

The temperature dependence of the initial viscosity of polymer is known to be equivalent to their temperature dependence of apparent viscosities compared at constant shear stresses,[25] and the activation energy of viscous flow determined in this way is independent of the choice of stress at which the viscosities are compared. Hence, we shall compare η versus T dependencies at $\tau = Const.$ The dependence of $log\eta$ on $1/T$ for various stresses is plotted in Figure 6 for P-20 containing 4.8 percent black. Obviously, in the regions of high shear stresses the activation energy is constant and independent of stress. The activation energy of viscous flow of the P-20-base mixes studied, calculated at high stresses, is independent of filler content, being 14.5 $\pm$ 0.5 kcal/mol in all cases, i.e., it equals the activation energy of the pure polymer (cf. Ref. 9).

This result is in good agreement with the data obtained in Ref. 17 for filled rubbers, and therefore one may agree with the conclusion that the pure polymers and their mixes with fillers have the same flow mechanisms. However, as can be seen readily from Figure 6, this conclusion refers only to the region of fairly high stresses, where the structural skeleton of the filler is greatly broken.

At low shear stresses the $log\eta$ versus $1/T$ dependence is nonlinear, i.e., its nature differs from that of the same dependence in the region of high stresses. Owing to the change in mechanism of deformation on passing into the regions of low stresses, the activation energy will also change regularly; on approaching the yield point it cannot be determined correctly at all.

Thus, investigation of the viscous properties of filled polymers shows that the high viscosity of the dispersion masks the strength properties of the filler. Hence, in the stress region where flow of the polymer with a broken black network predominates, the properties of the system are determined by the viscosity of the dispersion medium. In the stress close to the yield
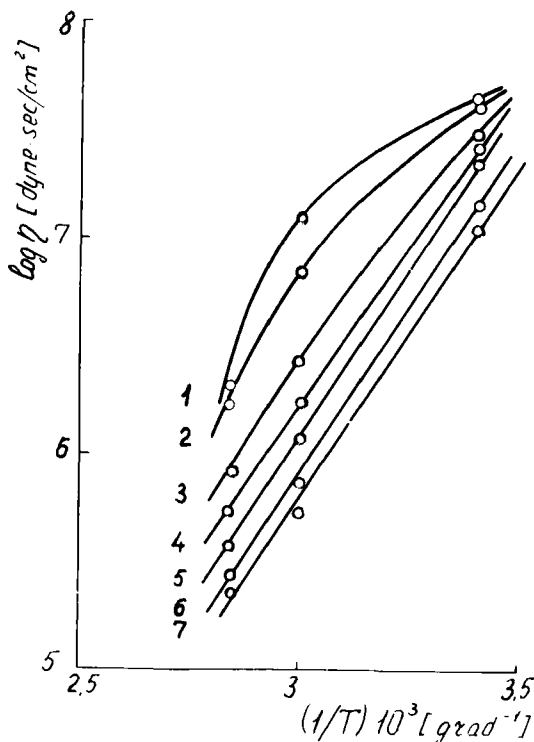
FIGURE 6   Temperature dependence of viscosity of 5 percent mix of P-20 with black at various shear stresses (dyne/cm²); 1—8 × 10³; 2—10⁴; 3—2 × 10⁴; 4—3 × 10⁴; 5— 5 × 10⁴; 6—10⁵; 7—1.5 × 10⁵.

point the properties of this system and, in particular, the temperature viscosity dependence are determined by overlapping of flow of the dispersion medium with breakdown of the structural skeleton. This results in the above described change of activation energy in passing from high to low stresses.

High Elasticity of Filled Polymers

Now we pass over to a discussion of experimental data on the effect of filler on the ability of P-20-base systems to display high-elastic strains.

It is characteristic of P-20 polyisobutylene that it has a linear region of mechanical behaviour, wherein its viscous properties are described by Newton's law, and its high-elastic properties, by Hooke's law. A study of the properties of P-20 at low stresses (from approx 10^2 to $> 10^4$ dyne/cm²) on a shear plastometer showed that at $\tau \leqslant 10^4$ dyne/cm² the viscosity and modulus

of elasticity G ($G = \tau/\gamma_{el}$ where γ_{el} are the equilibrium elastic strains measured for steady flow conditions at the stress τ) remain constant; the spread of experimentally determined viscosities is within ± 5 percent and of moduli, within ± 10 percent of the average values.

Measurements of the elastic strains of filled systems at $\tau < \tau_m$ (Figure 7) showed that in the absence of flow mixes behave like elastic bodies with stress-independent moduli.
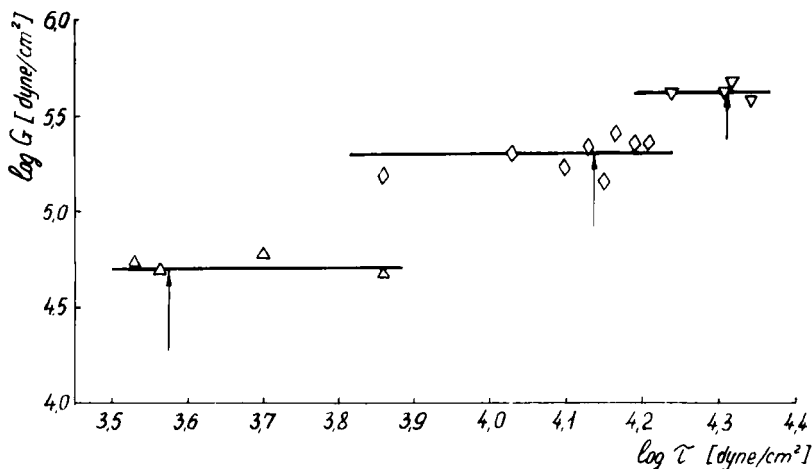

FIGURE 7   Dependence of elasticity modulus of filled P-20 on concentration at stresses close to yield points (vertical arrows indicate corresponding yield point values): △—5 percent; ◇—9 percent; ▽—13 percent black by volume.

It is very important that the modulus remains unchanged on passing through the yield point (in Figure 7 the stresses τ_m are indicated by vertical arrows). This is evidence that the elastic properties of the filled systems studied are determined completely by the elasticity of the polymer, because the abrupt destruction of the black structural skeleton on passing through τ_m has no effect on the elasticity of the system.

Elastic strains were measured mainly on an EM-1 rotational instrument by elastic "recoil" in the shear stress range 4×10^4 to 4×10^5 dyne/cm². The primary experimental data are given in Figure 8 as the γ_{el} versus τ, while Figure 9 shows modulus versus stress dependencies for systems with different filler contents. Although the elasticity of polymer-base disperse systems depend primarily on the properties of polymer, the black structure causes certain specific features in the elasticity of the system, especially at high stresses. This can be seen readily from Figure 9, where attention is drawn
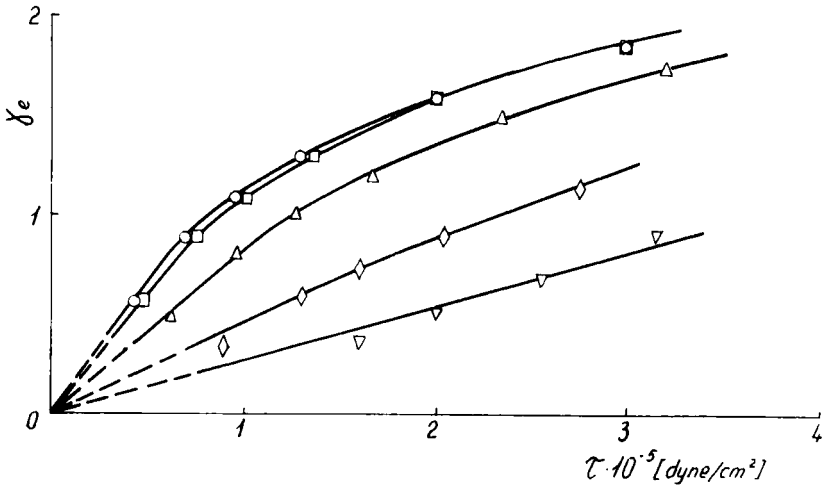
FIGURE 8   Dependence of elastic strain of P-20-black mixtures on shear stress: ○—pure
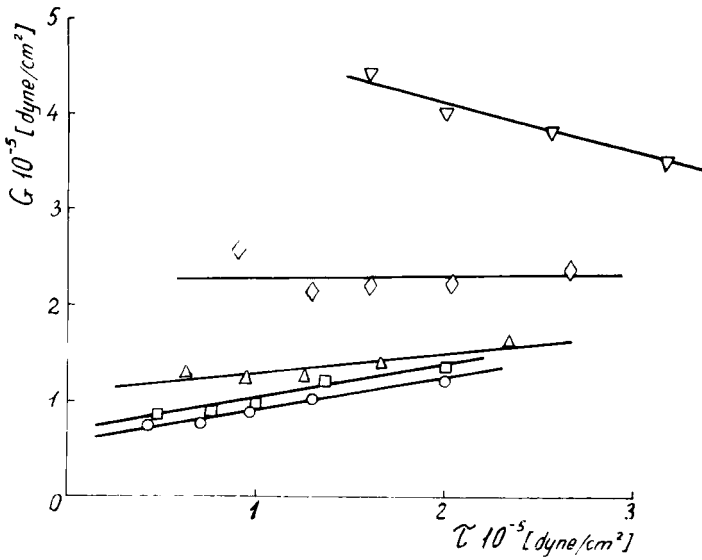P-20; □—2.5 percent; △—5 percent; ◇—9 percent; ▽—13 percent black by volume.

FIGURE 9   Variation of elasticity modulus of filled P-20 with increasing shear stress
at different black concentrations: ○—pure P-20; □—2.5 percent; △—5 percent; ◇—9
percent; ▽—13 percent black by volume.

to the different course of the change in elasticity modulus with increasing shear stress for different filler contents. At a black content up to 5 percent as typically with other polymeric systems, the modulus increases little with the stress; at 9 percent G is practically independent of stress, and at 13 percent black G decreases with increasing shear stress. This effect can be accounted for by assuming that deformation of filled polymers involves two simultaneous competing processes, namely, orientation of the macromolecular chains under the influence of the applied stress, and breakdown of filler structure. The former process, which is peculiar to polymer systems, favours increasing rigidity, and hence increasing modulus. The latter process results in a decrease in modulus compared to the value observed for unbroken structure. The filler itself increases the rigidity of the system and hence the absolute value of the modulus (see Figure 10). At a low black content the processes characteristic of the polymer matrix proper predominate; with increasing filler concentration structure breakdown becomes the prevailing process and this lowers the shear modulus. The decrease in rigidity of black-
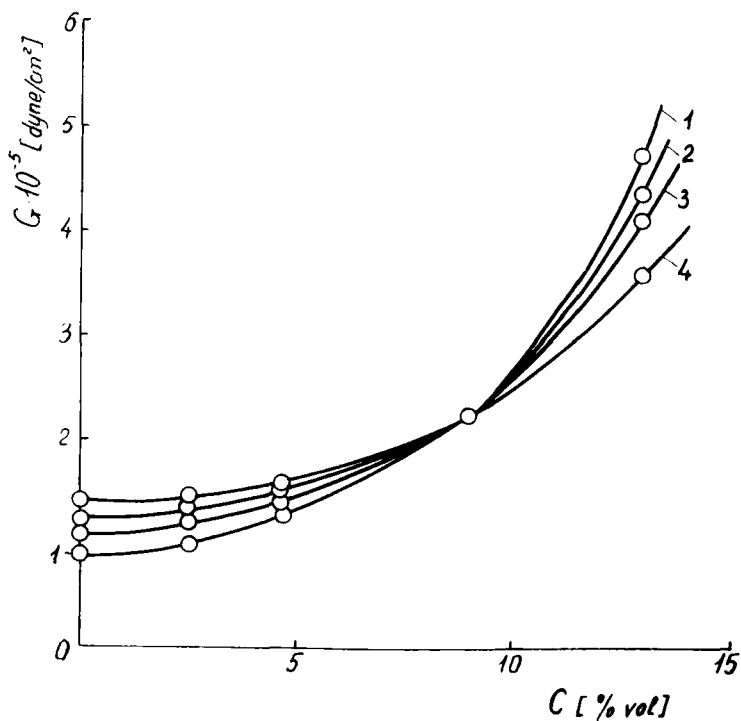

FIGURE 10 Concentration dependence of elasticity modulus for mixes of P-20 with black at different shear stresses (dyne/cm^2): 1—10^5; 2—1.5 $\times$ 10^5; 3—2 $\times$ 10^5; 4—2.5 $\times$ 10^5.

filled polymers with increasing intensity of mechanical influence is, in general, a fairly well known fact, although it has usually been studied under dynamic influence.[26] In this case an effect of similar importance is observed when steady flows occurring under the action of increasing stresses, are compared.

Measurement of the high-elastic strains of black-filled systems led us to the conclusion that addition of a solid filler to the polymer somewhat depresses the elasticity of the latter. This follows from the fact that the modulus grows with increasing filler content (Figure 10) and becomes still more evident from a comparison of the high-elastic strains measured during the flow of systems with different filler contents at $\tau = Const$. These data, presented in Figure 11, show that the presence of a structural network of the filler or its fragments retards the development of high-elastic strains.
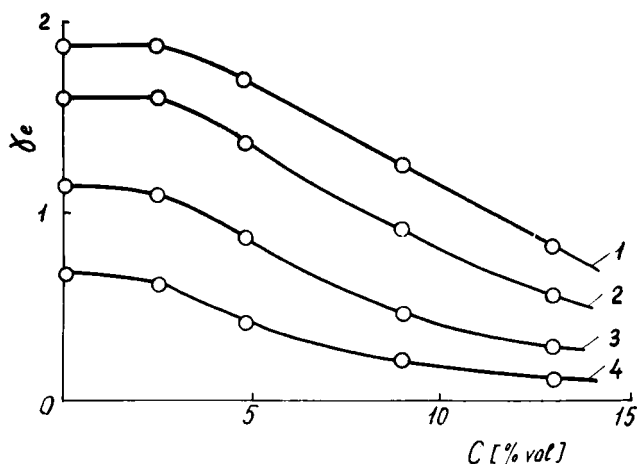

FIGURE 11   Variation of elastic strains of filled P-20 with black concentration at shear stresses (dyne/cm²): 1—3 × 10⁵; 2—2 × 10⁵; 3—1 × 10⁵; 4—5 × 10⁴.

Elastic Turbulence in Filled Polymers

The effect demonstrated in Figures 10 and 11 by the data obtained on rotational instruments, is quite essential in examining the flow of filled polymers through nozzles and capillaries. The addition of a filler to a polymer melt decreases swelling of the extrudate after emerging from the nozzle and makes "elastic turbulence" or "melt rupture" occur at higher critical stresses, because these defects are related in nature to the elastic strains developing during flow.[27]

To study these effects in greater detail, mixtures of P-20 with acetylene black were investigated on a constant-pressure capillary viscometer within

the shear stress range 10^5 to 10^7 dyne/cm^2. The extrudate diameter was measured at the capillary outlet and the change in quality of the extrudate surface with increasing stress was observed visually. The observations showed that two characteristic stress values or critical points can be singled out, the first τ_{cr}' corresponding to the appearance of dullness and roughness on the extrudate surface and the second τ_{cr}'' (at higher shear rates) corresponding to the appearance on the extrudate of periodic large flaws in the form of screw-like distortions of the surface with a large pitch (the pitch value depending on the filler content in polymer). The values τ_{cr}' and τ_{cr}'' were estimated to ± 25 percent. It should be pointed out that the change in appearance of the extrudate is not related to the beginning of non-Newtonian flow or any points on the flow curves.

Figure 12 shows the dependence of high-elastic recovery of the extrudate "a" (extrudate diameter to capillary diameter ratio) on the shear stresses in the system for all mixes studied. The black marks indicated in these figures by arrows I correspond to τ_{cr}' values, and those indicated by arrows II, to τ_{cr}'' values. It is evident from the figure that all the curves are of an extreme nature. At first a grows with the stress, the appearance of roughness on the extrudate surface having no effect on the course of this dependence. At a certain definite shear stress for each mix a reaches a maximum and then falls off. Passage through the maximum corresponds (to an accuracy of not worse than ± 25 percent) to the appearance on the extrudate of large periodic flaws, i.e., to the stress τ_{cr}''.

Examination of the values τ_{cr}' and τ_{cr}'' for mixes of different composition (Figure 13) reveals a definite difference in shape of their concentration dependencies. Increasing the rigidity of the system has a relatively weak effect on the τ_{cr}' values. At the same time τ_{cr}'' increases very greatly with increasing black content in the system. The concentration dependencies of the coefficients of elastic recovery of the extrudate a for the constant stress $\tau = 1.8 \times 10^6$ dyne/cm^2 (curve 1) which lies below τ_{cr}' and for both critical stresses τ_{cr}' and τ_{cr}'' (curves 2 and 3 respectively) are given in Figure 14.

In the experiments described above the high-elastic strains and moduli could be measured only at stresses below τ_{cr}' (see Figures 8 and 9). Hence, the critical high-elastic strains, which according to Ref. 27 determine the conditions at which unsteady flow conditions set in, could not be estimated.

We can now advance some qualitative ideas concerning the possible mechanism of the phenomena resulting in the above described dependencies of recovery coefficient a on stress and mix composition, and of critical parameters on filler concentration.

At the flow regimes designated by the general term "elastic turbulence" or "unsteady flow" at least two phenomena can be distinguished: small-scale periodicity and large-scale flaws.[27] We suggest that the former phenomenon
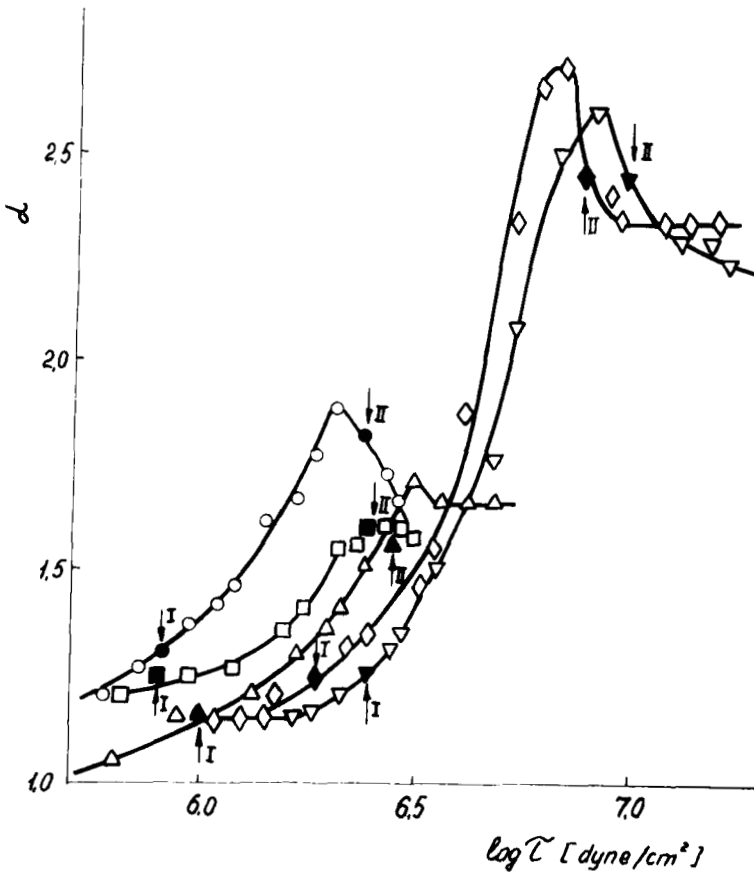
FIGURE 12   Variation of coefficient of recovery of extrudate a with shear stress for various mixes of P-20 polyisobutylene with black: ○—pure P-20; ☐—2.5 percent; △—5 percent; ◇—9 percent; ▽—13 percent black by volume.

may be due to periodic adhesion and detachment of the sample at the capillary exit, and the latter, to mixing or fracture of the material in the bulk.

The experimental data obtained are evidence in favour of the assumption that there are two kinds of "unsteady" flow of polymer systems, namely: the appearance of surface defects of the type of small-scale pulsations or surface dullness at lower stresses, and of bulk large-scale pulsations, at higher stresses. Evidently, both of these effects are related in one way or another to the relaxation and/or high-elastic properties of the system studied.

The dependence a on the stress τ and the filler concentration C is due to the following factors. The greater the stress, the larger are the accumulated

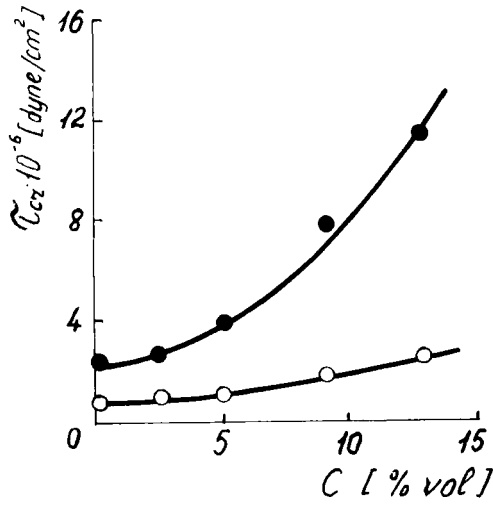**FIGURE 13**   Concentration dependence of critical stresses for P-20-black mixes corresponding to the appearance of "elastic turbulence": $\bigcirc$—$\tau_{cr}'(C)$; $\bullet$—$\tau_{cr}''(C)$.
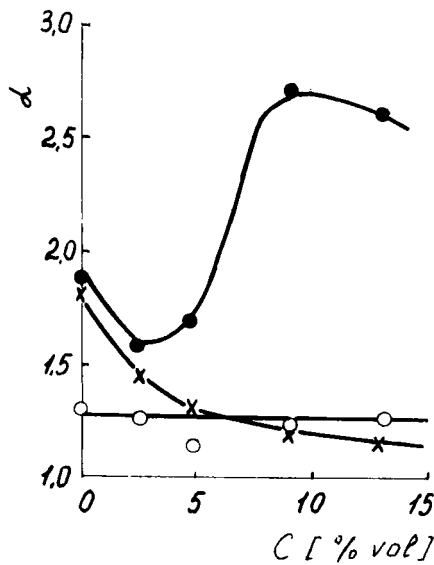
FIGURE 14   Dependence of coefficient of recovery of extrudate on black content in polymer at shear stresses: $\times$—1.8×10^6 dyne/cm^2; $\bigcirc$—τ_{cr}'; $\bullet$—τ_{cr}''.

high-elastic strains, and hence, a. The onset of conditions of periodic wall slippage at τ_{cr}' does not affect the nature of this dependence, because slippage over part of the capillary length is equivalent to effective reduction of its length, which with $\tau = Const$ results only in further increase of a.

The passage of the a versus τ dependence through a maximum at τ_{cr}'' is related to the fact that elastic recovery begins to occur inside the capillary throughout the entire volume of material. The retarding influence of the structural skeleton on development of "elastic turbulence" results in very strong dependence of τ_{cr}'' on the concentration when the black content is higher than 2.5 percent by volume (Figure 13). Since the values of τ_{cr}'' increase sharply with increasing filler content, this makes it possible for elastic strains in filled polymers to continue growing up to very high stresses, which also make it possible for a values to grow over a wide range of shear stresses (see Figure 12). This accounts for the high values observed for the coefficient of recovery of the extrudate at $C > 5$ percent (curve 3, Figure 14). Besides, the ideas given above are evidently qualitative evidence in favour of the assumption that the condition for the onset of unsteady flow conditions ($\gamma_{el} \approx 5$ to 7 units), suggested in Ref. 27 should be classed as a large-scale flow defects. This conclusion follows from the fact that the elasticity modulus changes greatly in the region of high concentrations, and it is τ_{cr}'' rather than τ_{cr}' that is as strongly dependent on concentration.

CONCLUSION

Our studies of the rheological properties of filled polymers have thrown light on the relationship between the behaviour of disperse and polymeric systems. A common feature of disperse systems, including polymer-base systems, may be the existence, at a sufficiently high filler concentration, of a structural skeleton which causes a yield point to appear. With increasing solid phase content the yield point rises. The yield point depends very little on temperature. Related to the existence of a shear yield point is the sharp difference in rheological properties between filled and unfilled polymer melts at low stresses. After passing through the yield point the effect of the structural skeleton of filler is the weaker, the higher the viscosity of the dispersion medium, i.e., of the polymer melt. Hence, highly viscous filled systems are quite analogous to polymer melts in peculiarities of behaviour at high shear rates. The activation energy of viscous flow is independent of stress and degree of filling only in the region of sufficiently high stresses; at low stresses the temperature dependence of the apparent viscosity of filled polymers varies in a complex manner due to the effect of the structural skeleton.

The elasticity of filled polymers is somewhat depressed in the presence

of the disperse phase, this being manifested as increase of the elasticity modulus with rising filler content. With increasing stress the elasticity modulus of highly filled polymers decreases, while that of unfilled polymer melts increases. Passage through the yield point, which is essentially a very sharp jumpwise decrease in viscosity of many decimal orders, is not accompanied by any change in elasticity of the system. Since addition of black to the polymer depresses its elasticity, the stresses corresponding to the appearance of "elastic turbulence" in filled polymers flowing through capillaries, increase noticeably with increasing solid filler content in the system.

Summary

Viscoelastic properties are studied in filled polymer systems with low-molecular polyisobutylenes having initial viscosities of 6×10^2 and 10^7 poises (at room temperature) as the dispersion media. The filler was acetylene black with a specific surface area of 110 m^2/g, noted for its high structurizing ability. It was added to the polymers in amounts ranging from 2.5 to 13 percent by volume. The black can form a three-dimensional structural skeleton, which causes the appearance in the filled polymers of a yield point up to approx 5×10^4 dyne/cm^2 in value. At low shear stresses the rheological properties were affected mainly by the presence of a yield point. Passage through the yield point results in a change in viscosity of at least five decimal orders. At the same time this has no effect on the display of elasticity, though the high elasticity of the filled systems is tangibly lower than that of the unfilled polymer.

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