Physical Chemistry

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1965

SovietRxiv

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Abstract

Full Text

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TRANSITION OF EXTERNAL FRICTION TO VISCOUS FLOW DURING SURFACE MELTING OF POLYMERS

(Presented by Academician V. A. Kargin, February 5, 1965)

Polymers, under the influence of changes in temperature, undergo various phase transformations; moreover, transitions to a number of states—glassy, highly elastic, and fluid—are of specific importance for them. The study of external friction should be a sensitive means of detecting changes in their state and represents one variant of the thermomechanical method. On the other hand, this also has important practical significance because in a number of works ([1,2]) the formation of a melt layer during friction of thermoplastic polymers was shown. Nevertheless, few studies have been devoted to external friction of polymers under conditions of their transition from the crystalline to the fluid state and from the glassy to the highly elastic and fluid states ([3–6]). The most significant results were obtained by A. I. Elkin ([3]), who established that the transition of polymers from the glassy state to the highly elastic state is accompanied by an increase, and then a decrease, in the friction force. The literature data on the influence of polymer melting on the coefficient of friction are random and contradictory in character ([4–6]).

Fig. 1. Schematic diagram of the Tr-7 tribometer. *1*—hemispherical slider; *2*—disk; *3*—holder; *4*—dynamometric plate; *5*—hinged support; *6*—lever; *7*—load; *8* —electric motor; *9*—reducer; *10*—glass bell jar; *11*—sealing liquid; *12*—plate.

To study external friction of polymers on polymers and of metals on polymers over a wide temperature range, a tribometer (Tr-7) was developed, shown schematically in Fig. 1. In this instrument, contact is made between the hemispherical slider *1* and the flat surface of the polymer disk *2*. The slider is inserted into holder *3*, rigidly connected with dynamometric plate *4*. The other end of the plate is able to rotate freely in the vertical direction in hinged support *5*. Above the dynamometric plate—in the same plane with it—is located lever *6*, along which load *7* moves. The position of the load, fixed by transverse grooves

Fig. 2

Figure 2: Fig. 2

on the lever, determines the magnitude of the load. Sliding in the contact zone of the friction bodies is effected by rotation of the disk specimen. Rotation is imparted to the disk by synchronous motor *8* through multistage gear reducer *9*. To create elevated temperatures on the surface of the disk specimen, a radiation furnace positioned above it is used. The friction bodies are placed in a vacuum chamber. It is divided by a glass bell—

by cap **10** into the preliminary-vacuum cavity (I) and the high-vacuum cavity (II), which is in fact the working chamber of the instrument. These two cavities are separated from one another by a hydraulic seal, which is formed when the lower edge of the glass bell jar, delimiting the high-vacuum cavity, is immersed in the sealing liquid **11** poured into the recesses of plate **12**. As the sealing liquid, petroleum oil with a low vapor pressure (of the order of $1 \cdot 10^{-12}$ torr at 20°) or liquid gallium is used. The rotating shaft entering the preliminary-vacuum cavity is sealed by an oil film in the narrow gap between two metallic lapped surfaces, one of which is attached to the shaft through a bellows. The sealing of the shaft and of the electrical leads at the boundary between the preliminary- and high-vacuum cavities is accomplished by means of hydraulic seals.

Fig. 2. Effect of temperature on the friction of steel against amorphous polymers (load 10 G, sliding speed $5 \cdot 10^{-3}$ cm/sec).
1 —polyvinyl acetate; **2** —polystyrene; **3** —polymethyl methacrylate

Studies of polymers on this tribometer, the results of which are presented in the present work, were carried out in a vacuum of the order of 10^{-6} torr, at constant loads (10 and 10^3 G) and sliding speeds ($5 \cdot 10^{-3}, 1 \cdot 10^{-2}, 1 \cdot 10^{-1}$, and 1 cm/sec). Loads within the indicated limits do not substantially affect the results of the experiments. Therefore, below only the results obtained at a load of 10 G are given. At sliding speeds up to and including 1 cm/sec, the change in temperature in the surface layer of the polymer under the influence of friction may be neglected, and it may be assumed that it is determined only by the radiation heater. The temperature at the friction surface of the polymers was increased continuously in the course of the experiments according to a linear law.

The objects of study were crystalline and amorphous polymers: high-pressure polyethylene (Alkathene 2), low-pressure polyethylene (Hostalen GD), the same polymer with various degrees of radiation crosslinking, polypropylene (Montecatini), polystyrene (GOST 94440–60), polyformaldehyde (experimental sample), polyvinyl acetate (experimental sample), and polymethyl methacrylate (TU MKhP 2368–50). As counterbodies, hemispheres 4 mm in diameter made of hardened steel ShKh-6 were used.

Figure 2 shows the dependence of the friction force (F) on temperature ($t°$) for

Figure 3

Figure 3: Figure 3

a number of amorphous polymers. It is seen from this that the character of the change in friction force during the transition from the glassy to the highly elastic state is, in general, consistent with that described in works (3,5). However, the present work covers a broader range of polymer states, including the fluid state. This makes it possible to evaluate the influence of polymer fluidity on friction in the region of the transition from the glassy to the highly elastic state.

Figure 3 presents data for crystalline polymers. If the temperatures are sufficiently low, then the friction force at constant speed and load does not depend (or depends only weakly) on temperature. In the temperature region close to the melting temperature, the friction force changes sharply with temperature. The ascending branches of the curves $F(t^\circ)$ for highly crystalline polymers are distinguished by considerable steepness. They are due to changes in the parameters of the crystalline lattices (7) and in the mechanical properties (8–10) of polymers in the region of their premelting. The maxima on the curves $F(t^\circ)$ lie in the region of the melting temperatures of the polymers (their values, determined in a polarizing microscope at a heating rate of 0.5 deg/min, are marked on the abscissa axis by arrows). They are much more pronounced

more sharply than during the transition of polymers from the glassy to the high-elastic state. A comparison of the curves $F(t^\circ)$ for high-pressure polyethylene (1) and low-pressure polyethylene (2a—2e) shows that the sharpness with which the maximum is expressed, in particular its height, depends substantially on the regularity of the structure of the crystalline polymer. The descending branches of the curves $F(t^\circ)$ are associated with the development of the process of polymer melting, namely with an increase in the thickness of the melt layer and a decrease in its viscosity. In the region of polymer melting, an inversion of the character of the dependence of the friction force on the sliding velocity is observed (at $t^\circ = \text{const}$). An increase in velocity (at $t^\circ = \text{const}$) in the region of the processes of premelting and melting of polymers causes a decrease in the friction force, while in the melt region it causes an increase (viscous resistance). The combined influence of changes in sliding velocity and temperature is conveniently considered while maintaining the condition $F = \text{const}$. Both on the ascending and on the descending branches of the curves $F(t^\circ)$, this condition is satisfied if, as the temperature increases, the sliding velocity also increases. In all cases, with increasing velocity, the curves $F(t^\circ)$ shift toward higher temperatures. This is evidence that, both on the ascending and on the descending branches of the curves $F(t^\circ)$, a relaxation mechanism of (respectively external and internal) friction is manifested.

Fig. 3. Effect of temperature on the friction of steel against crystalline polymers (load 10 g). 1—high-pressure polyethylene (sliding velocity $5 \cdot 10^{-3}$ cm/sec); 2—low-pressure polyethylene (*a*—*e*—sliding velocities $5 \cdot 10^{-3}$; $1 \cdot 10^{-2}$; $1 \cdot 10^{-1}$; 1

Figure 4

Figure 4: Figure 4

cm/sec); 3—polypropylene (the designations are the same); 4—polyformaldehyde ($5 \cdot 10^{-3}$ cm/sec)

Fig. 4. Effect of temperature on the friction of steel against radiation-crosslinked specimens of low-pressure polyethylene (sliding velocity $5 \cdot 10^{-3}$ cm/sec). 1—irradiation dose $5 \cdot 10^6$; 2—$16 \cdot 10^6$; 3—$50 \cdot 10^6$; 4—$150 \cdot 10^6$ rad

Consequently, in both cases $F(t^\circ)$, increases in velocity and temperature act in opposite directions, compensating one another to some extent.

An increase in the mobility of macromolecular segments with increasing temperature in the region of polymer premelting leads to a stronger manifestation of their high elasticity, to an increase in compliance, in the area of actual contact and in the number of adhesive bonds of the polymer with the counter-surface (with the other friction conditions—velocity and load—unchanged). This corresponds to the ascending branches of the curves $F(t^\circ)$. On the other hand, an increase in sliding velocity should lead to a decrease in the mean lifetime of adhesive bonds between the friction surfaces and to a reduction in the friction force.

As for the descending branches of the curves $F(t^\circ)$, the increase in the friction force in the molten surface layer with increasing velocity is explained simply by the fact that the friction is liquid friction. A certain decrease in the maxima on the curves $F(t^\circ)$ with increasing sliding velocity

is due to a shift of the maxima toward higher temperatures, where the viscosity of polymer melts is lower.

The experimental data presented in Fig. 3 are in good qualitative agreement with the interesting works ([11]), in which the dependence of the friction coefficient of crystalline polymers on sliding velocity was considered, and it was found that within a certain range of velocities, as they increase, the friction coefficient increases, reaches a maximum, and then decreases. In our opinion, these results are due to melting of the polymers at elevated velocities.

For a more detailed clarification of how the flowability of polymers affects their friction in the highly elastic state, the study of cross-linked polymers was of considerable interest. Since flowability is most sharply manifested during the melting of highly crystalline polymers, radiation-cross-linked samples of low-pressure polyethylene were used. The polyethylene was exposed to Co^{60} γ-radiation. The results of experiments with them at a sliding velocity of $5 \cdot 10^{-3}$ cm/sec are presented in Fig. 4, where the data for the initial, non-cross-linked sample are shown by the dotted line. In the cross-linked samples there is no maximum on the $F(t^\circ)$ curves. This is associated with the absence of transition of the polymer into the flowing state and confirms that the descending branches of the $F(t^\circ)$ curves in our experiments are due to the influence of flowability. With an increase in the number of transverse bonds, first, the upper horizontal segment on the $F(t^\circ)$ curves decreases, since the compliance of the polymer decreases; second, the steep rise on the ascending branches of these curves begins at lower temperatures. The reasons for the latter feature in the behavior of cross-linked polymers may be: amorphization of their structure under the action of irradiation and a change in the adhesive characteristics of the samples, since irradiation was carried out in air and was accompanied by surface oxidation.

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Received
4 II 1965

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