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Fig. 1

Figure 1: Fig. 1

## Abstract

## Full Text

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# MONOLAYERS OF POLYDIMETHYLSILOXANE POLYMERS. RHEOLOGICAL PROPERTIES AND MICROSTRUCTURE OF FILLED PASTES

*(Presented by Academician S. I. Volʹ fkovich, May 21, 1964)*

The complex combination of physicochemical properties (adsorption, rheological) of organosilicon and organoelement liquids and polymers (linear, branched), and their interactions with fillers, is of interest for studying the structure of lubricants, crude rubbers, and coatings. In the present work, polydimethylsiloxanes (PMS) of different molecular weight, from 2000 and higher, were studied as model systems; the lower of these are flowable liquids, while the higher are viscous systems, elastic under rapid compression and also flowing under prolonged action. Liquid polymers are often called melts. As the filler, white carbon black BS-280* was studied. It was of interest to study: 1) adsorption of the polymer from the liquid phase on the filler; 2) properties of polymer monolayers on the surface of water in order to assess its packing and changes of state upon compression on a smooth surface, and comparison with the properties of adsorption layers on a solid surface; 3) the process of dispersing the filler in the PMS medium and the application of the electron-microscopic method for evaluating the size of its particles; 4) rheological properties of polymers and pastes based on them; 5) the effect of additives of low-molecular-weight surface-active substances (surfactants) and of PMS itself as a surfactant on the properties of pastes.

**Fig. 1.** Dependence of the two-dimensional pressure $F$ on the area $a$ per siloxane unit $SiO(CH_3)_2$ for PMS with $M = 2000$ (a), 37,000 (b), 95,000 (c), 400,000 (d), 600,000 (e)

Fig. 1 shows curves of the dependence of the two-dimensional pressure $F$ on the

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* Obtained from the Scientific Research Institute of the Tire Industry.

Fig. 2. Adsorption isotherm $x$ from hexane for PMS ($M = 2000$) on two BS-280 samples (1, 2) and BS-280 preliminarily treated with trimethylchlorosilane (3); $t = 30°$.

Figure 2: Fig. 2. Adsorption isotherm $x$ from hexane for PMS ($M = 2000$) on two BS-280 samples (1, 2) and BS-280 preliminarily treated with trimethylchlorosilane (3); $t = 30°$.

area $a$ per siloxane unit $SiO(CH_3)_2$ for PMS monolayers with molecular weight $M$ from 2000 to 600 000. In all cases the values of $F$ at $a > 20$ $\text{Å}^2$ are small and evidently correspond to compression of an island-type monolayer. Beginning with $a = 18.6$—$20.3$ $\text{Å}^2$ per unit (this interval contains the extrapolated values of the curves for polymers both of a single value of $M$ and of different values), $F$ rapidly increases to the value 8.5 dyn/cm, approximately constant and the same for different $M$, which is reached at $a = 15$—$16$ $\text{Å}^2$. Further, down to $a \approx 9$ $\text{Å}^2$, $F$ remains constant and then in all cases begins to increase somewhat. Thus, on the curves in this interval of values of $a$ there are several characteristic points $ABCDE$. This general course of the curves agrees with that found in work ($^1$) for PMS with low $M$, but the values of $a$ at the indicated points for our polymers prove to be smaller than in work ($^1$). For example, at point $A$ the average area per unit from Fig. 1 corresponds to 19 $\text{Å}^2$, whereas in work ($^1$) 22.5 $\text{Å}^2$ was obtained. In this connection we regard the structure of the monolayer somewhat differently than in ($^1$). An area of 22.5 $\text{Å}^2$ would correspond to linearly extended molecules in the form of straight rods with completely symmetrically arranged bonds –SiO–. Such a structure seems unlikely because of the flexibility of the siloxane chain. It is easier to admit a state of the chains of individual molecules in the form of flat disks built from coiled chains; in this case inclinations of some units relative to the plane of the water surface are possible, and, on average, somewhat smaller areas per unit. Such areas may be 19 $\text{Å}^2$ under weak compression and 15.5 $\text{Å}^2$ under stronger compression (at point $B$). At point $C$, spirals of 6–8 units are formed. The area at this point, $a = 9$ $\text{Å}^2$ (as also 11 $\text{Å}^2$ in ($^1$)), may be attributed to one turn of the spiral. In this case, the subsequent increase in $F$ is evidently already connected with the squeezing out of spirals from the monolayer.

**Fig. 2.** Adsorption isotherm $x$ from hexane for PMS ($M = 2000$) on two BS-280 samples (1, 2) and BS-280 preliminarily treated with trimethylchlorosilane (3); $t = 30°$.

Nor is it excluded that the polymers studied by us are to some extent branched, which should give, on average, a smaller area per unit even when the molecule is linearly extended. It is of interest that the curves $F(a)$ prove to be similar for polymers with very greatly differing molecular weights, despite the fact that not all the polymers obtained by us were synthesized in one laboratory. If the supposition concerning the influence of molecular branching on the area of the monolayer is confirmed, this method may be used to estimate the average degree of branching of polydimethylsiloxanes.

Adsorption curves of PMS ($M = 2000$) from hexane on BS-280 at 30°, expressed as the dependence $x = f(C_p)$, obtained with a liquid interferometer, are shown in Fig. 2. It follows from them that the measured adsorption $x$ passes through a maximum, and its maximum value corresponds to $x_{\max} = 155$ mg per 1 g of BS (at $C_p = 45$ mg PMS per 1 g of hexane). This value, when calculated for the total surface of BS-280 in m$^2$/g, gives an area per siloxane unit of 22.2 Å$^2$, which corresponds approximately to point $A$.

on the curve in Fig. 1. However, it is more likely that the surface available to PMS is smaller than that obtained from nitrogen adsorption, for example 170-200 m$^2$/g, which is close to the area calculated from the mean particle sizes of 200 Å found by electron microscopy. In this case, the area per unit will be 13.5-15.8 Å$^2$, which corresponds to section $BC$ of the curve in Fig. 1, i.e., to a densely compressed monolayer. Further, if it is assumed that the surface available to the polymer is 150 m$^2$/g, the area per unit will be 11 Å$^2$, i.e., also within section $BC$ of the curve in Fig. 1.

The adsorption curves of PMS presented here are similar in shape to the adsorption curves of low-molecular substances from solutions ($^2$); however, adsorption curves with maxima for polymers apparently have not yet been described in the literature. The decrease in adsorption $x$ for PMS beyond the maximum, as

**Table 1**

**Dependence of the structural strength $P_r$ (g/cm$^2$) of pastes and of the mean sizes of soot particles on the number $n$ of times it is passed through the rolls**

| | $n =$ 1;$P_r = 1.6$ | $n =$ 5;$P_r = 8.0$ | $n =$ 10;$P_r =$ 13.9 | $n =$ 20;$P_r =$ 95.1 | $n =$ 25;$P_r =$ 100.0 |
|---|---|---|---|---|---|
| Character of the pasteMean particle size, $\mu$ | Heterogeneous dispersion$\sim 50$ | Heterogeneous dispersion$\sim 50$ | Heterogeneous dispersion$\sim 50$ | Homogeneous dispersion0.02 | Homogeneous dispersion0.02 |

in the case of low-molecular substances, may be connected with a number of causes: filling of the adsorption volume by a concentrated solution, competitive adsorption of both components of the solution, and, finally, the influence of the porosity of the adsorbent BS-280. The adsorption value found allows one to consider that the adsorption layer is monomolecular, and that the PMS molecules present in it are probably in a coiled state. The adsorption value $x = 155$ mg

Fig. 3. Electron-microscopic photographs of BS-280 pastes in PMS M-37 000 (30:100) (parts by weight) at different numbers of passes $n$ through paint-grinder rolls: A $-n=1$; $-n=5$; $-n=25$; , —with addition of decanol 0.011 $M$ at $n=1.25$, respectively; —with addition of decanol 0.055 $M$ at $n=1$.

Figure 3: Fig. 3. Electron-microscopic photographs of BS-280 pastes in PMS M-37 000 (30:100) (parts by weight) at different numbers of passes $n$ through paint-grinder rolls: A $-n=1$; $-n=5$; $-n=25$; , —with addition of decanol 0.011 $M$ at $n=1.25$, respectively; —with addition of decanol 0.055 $M$ at $n=1$.

per 1 g of BS is close to the value found ($^3$) for the adsorption of polydimethylsiloxane rubbers, i.e., high-molecular PMS, on quartz, for which the curves have no maximum.

Both the adsorption and the mechanical properties of filler pastes in PMS depend on the process of dispersing the filler and on the influence of surfactant additives. The process of dispersing white soot in PMS with $M = 37{,}000$ is accompanied by an increase in the structural strength of the pastes (30 parts by weight of BS per 100 parts by weight of PMS) to a constant value $P_r \approx 100$ g/cm$^2$ (Table 1)*.

To study the microstructure of the pastes, a method of single-stage carbon replicas directly from the pastes was developed. The photographs were taken with a Tesla electron microscope. The BS particles are comminuted in PMS comparatively slowly and only at $n$ = 20–25 reach ≈ 200 Å (Fig. 3, *A*, *B*, *V*). The introduction of low-molecular alcohols, for example decyl alcohol, at a concentration of 0.011 $M$ per 100 g of solution only slightly accelerates the dispersion process (Fig. 3, *G*, *D*), whereas at 0.055 $M$ (Fig. 3, *E*) the particle size already reaches 200 Å at $n=1$. A study of the effect of alcohols from $C_4$ to $C_{10}$ as surfactants on the structural strength of pastes, measured in an instrument with tangential displacement of a plate ($^4$), showed that, adsorbing from the PMS medium, the alcohols strongly lower the structural strength, blocking the bonds between the white-soot particles and weakening their interaction. With lengthening of the alcohol molecule the effect is intensified; however, with butanol, the most polar of the alcohols used, strengthening of the structure is observed after the curve $P_r(C_{90}$ ) passes through a minimum. This strengthening of the structure is evidently connected with flocculation of particles, which gradually weakens, since with time a decrease in strength is observed in the pastes.

Of great interest is the behavior of the polymer itself as a

* Dispersion was carried out on a three-roll laboratory paint mill.

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Fig. 3. Electron-microscopic photographs of BS-280 pastes in PMS $M$-37 000

Fig. 4. Dependence of the shear strength of pastes on the PMS content ($M = 37\,000$) in petroleum jelly oil (solid : liquid = 20 : 80) (wt.). Aging time of the paste $\tau$: 1—0, 2—5 days.

Figure 4: Fig. 4. Dependence of the shear strength of pastes on the PMS content ($M = 37\,000$) in petroleum jelly oil (solid : liquid = 20 : 80) (wt.). Aging time of the paste $\tau$: 1—0, 2—5 days.

(30:100) (parts by weight) at different numbers of passes $n$ through paint-grinder rolls: A $-n = 1$; $-n = 5$; $-n = 25$; , —with addition of decanol $0.011\,M$ at $n = 1.25$, respectively; —with addition of decanol $0.055\,M$ at $n = 1$.

surface-active peptizer or structure-forming agent with respect to the filler in a nonpolar liquid, for example in white petroleum jelly oil. Figure 4 shows the dependence of the structural strength of pastes on the concentration of PMS ($M = 37\,000$) in the liquid phase over the interval from 0 to 100% at a solid : liquid ratio of 20 : 80 (wt.). The complex curve has two minima and two maxima (for a paste aged for 5 days). This indicates the complex character of the regularities in the change of the interaction of filler particles over a broad concentration range of the two (liquid) components—weakly polar and nonpolar. The first minimum apparently pertains to the stabilizing action of the adsorption monolayer of PMS, which disrupts the blocking of white carbon-black particles in the oil; the subsequent increase in $P$ is due to additional peptization of large aggregates into smaller ones and to their interaction at as-yet unprotected sites. In the region of the second maximum, effects of selective wetting of the filler by one of the liquids and stratification of the system with separation of the second liquid are possible.

**Fig. 4.** Dependence of the shear strength of pastes on the PMS content ($M = 37\,000$) in petroleum jelly oil (solid : liquid = 20 : 80) (wt.). Aging time of the paste $\tau$: 1—0, 2—5 days.

From the standpoint of the structure and rheological properties of polymer pastes with filler, the rheological properties of the organosilicon polymers themselves are also of interest. Polymers with $M$ from 2000 to 97 000 were investigated in an elastorelaxometer ($^5$). It was established that they possess extremely small elastic deformations, entirely incomparable in magnitude with the deformations in ordinary rubbers; this is explained by the excessively high flexibility of the PMS molecules, which coil into isolated coils, almost not interlacing with one another and interacting only very weakly with one another. Such polymers behave as Newtonian liquids up to a sufficiently high velocity gradient, and only polymers with $M \geqslant 97\,000$ show signs of strength properties, expressed in a weak maximum $P_r$ on the stress-strain curve $P(\varepsilon)$ at $\dot{\varepsilon} \geqslant 100$ s$^{-1}$ and in deviation from Newtonian flow at smaller velocity gradients. Weak deviations from Newtonian behavior are also observed in pastes of the same polymers at not very high degrees of filling (< 20 parts by weight BC per 100 parts by weight polymer), whereas at fillings above the indicated ratio the systems acquire the properties of a plastic-solid body.

The set of properties considered reveals interesting features of polydimethylsiloxane polymers and of their interaction with filler, and also establishes the commonality of the properties of such systems with other polymers and colloidal systems.

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