PHYSICAL CHEMISTRY

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1962

SovietRxiv

Abstract

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ON THE MECHANISM OF STRUCTURE FORMATION IN HYDROCARBON SUSPENSIONS OF CARBON BLACK IN CONNECTION WITH THE PROBLEM OF ACTIVE RUBBER FILLERS

Despite numerous studies of the reinforcing action of active fillers in rubber compounds ([1,2]), the role of the interaction of filler particles with one another and with the dispersion medium—the polymer macromolecules—and, consequently, the physicochemical mechanism of the action of active rubber fillers, still remains unclear.

We have studied the processes of structure formation in model systems involving carbon black as the principal active filler of rubbers. The investigations were carried out in concentrated suspensions of carbon black in a nonpolar hydrocarbon medium; the influence of filler content, polymer concentration, and surface-active additives, as well as temperature, was studied ([3]).

We used methods for measuring electrical conductivity and recording current-voltage curves over a wide range of potential gradients, as well as for studying the structural-mechanical (thixotropic) properties of the suspensions. The current-voltage curves were recorded with a constant voltage applied in the range from 0.01 to 100 V, which corresponded to changes in the potential gradient by 4 orders of magnitude—from 0.025 to 250 V/cm. Measurements were carried out 3 hours after preparation of the suspension*, when the specific electrical conductivity had already reached its maximum value λ_m and thereafter practically did not change with time, which indicated the practical completion of the process of coagulation structure formation.

Figure 1 gives (on a logarithmic scale) the dependence of the current I on the potential difference V applied to the electrodes. For comparison, dotted straight lines corresponding to Ohm's law are plotted, i.e., to a specific electrical conductivity of the suspension independent of V. In our experiments the specific electrical conductivity of the suspension (10% carbon black, measurements at 20°) (curve 1) increased with increasing V, remaining constant only in the region of sufficiently small and sufficiently large V. At $V < 0.1$ V, $\lambda_m \approx 2 \cdot 10^{-7}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$; further, with increasing V, λ_m rises sharply (by ≈ 30 times), reaching at

Fig. 1

Figure 1: Fig. 1

$V > 60$ V the maximum value $\lambda_m \approx 6 \cdot 10^{-6}\ \Omega^{-1} \cdot \text{cm}^{-1}$. At a higher temperature (40°) (curve 2), the specific electrical conductivity is not only higher, but also increases with increasing potential gradient still more sharply, by ≈ 2 orders of magnitude. The curves $\lg I$–$\lg V$ (Fig. 1) have a characteristic S-shaped form. They obey the equation $I = c \cdot V^n$ (2) only at low and high V, where $n = 1$, and near the inflection point, where $n = \Delta \lg I / \Delta \lg V$ has a maximum value ≈ 2 (at 20°) and ≈ 3 (at 40°).

Earlier in our laboratory (4) it was shown that spatial coagulation structures in suspensions are formed by van der Waals forces of adhesion, which bind particles through thin residual interlayers of the liquid dispersion medium, in particular, the polymer. These thin interlayers provide shear mobility of the particles in the structure, its comparatively low strength, and thixotropic reversibility (restoration after destruction) at sufficiently high dispersity. It is especially important that it is precisely these interlayers that determine the pronounced elastic aftereffect—a kind of high elasticity characteristic of thixotropic coagulation structures with rigid particles, for example, aqueous suspensions of bentonite clays, even in the complete absence of flexible polymer chains (4).

Fig. 1. Current-voltage curves for a 10% suspension of lamp black "B" in nonpolar vaseline oil, taken at 20° (1) and 40° (2)

As E. D. Shchukin showed, the elasticity of such structures is caused by a decrease in entropy upon mutual orientation of the particles as a result of shear deformation, and by a reverse increase in entropy upon their disorientation after the stress is removed. Subsequently, the same elastic aftereffect was established in suspensions of carbon black in a hydrocarbon medium (5).

Our experiments showed that the coagulation structure of carbon-black suspensions in vaseline oil also possesses well-pronounced thixotropic properties. If, after completion of the development of the coagulation structure, the spatial network formed by the carbon-black particles is destroyed by stirring (points A, A', A''), then the electrical conductivity of the suspension drops sharply and then again gradually increases, characterizing the process of restoration of the destroyed structure (Fig. 2). Destruction and restoration of the carbon-black structure are reproduced many times.

With any mechanical action on a structured carbon-black suspension—shaking,

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* Suspensions of lampblack of type A in nonpolar vaseline oil were prepared by a standard method (3), which ensured good reproducibility of the experiments.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

stirring, even light tapping on the beaker containing the suspension—the very initial stage of destruction

Fig. 2. Changes in the electrical conductivity (λ) of a 10% suspension of carbon black in vaseline oil during destruction and restoration of the coagulation structure

Fig. 3. Changes in the electrical conductivity of a 30% carbon-black suspension after its drying and reverse absorption

of the structure causes a sharp decrease in the established (maximum) electrical conductivity. This makes it possible to judge with great accuracy the degree of destruction and restoration of the structure ([3], [6]), and to finely estimate its strength (limiting shear stress) from the sharp drop in electrical conductivity upon deformation in appropriate elastoplastometers, for example, in instruments with coaxial cylinders of the Shvedov type.

Changes in the electrical conductivity of a 30% suspension of carbon black in xylene during evaporation and subsequent reabsorption of the dispersion medium were also studied. The suspension was placed in a recess etched with hydrofluoric acid in a glass plate. Platinum electrodes were located on two sides; the surface of the suspension was carefully leveled by cutting with a razor blade.

The electrical conductivity of the suspension increases sharply as the xylene evaporates (which was carried out at different rates), and then falls again when xylene vapor is absorbed by passing saturated vapor over the suspension. The changes in electrical conductivity during evaporation and condensation of the vapor are reproduced many times (Fig. 3).

The suspensions we studied are sufficiently, but not extremely, lyophilic, since the surface of the carbon-black particles is always heterogeneous—more or less lyophilic (oxidized) regions impart to it a distinctive mosaic structure. In suspensions of this type one cannot assume direct contact of particles with complete displacement of the solvation shells between them. Structure formation occurs when the particles approach one another to a small distance (on the order of several molecular layers), with preservation of a thin layer of the dispersion medium between the particles. This is confirmed by the fact that hydrocarbon suspensions of carbon black, even at high concentrations of the solid phase (30–40%), have a relatively low specific electrical conductivity: $\lambda_0 \sim 10^{-5}\ \mathrm{ohm}^{-1} \cdot \mathrm{cm}^{-1}$, and at the same time possess a spatial structure with noticeable mechanical strength. The presence of interlayers of medium between the particles is also confirmed by the S-shaped form of the current-voltage curves.

The increase in the specific electrical conductivity of a suspension with increasing potential gradient is caused by breakdown of the thin interlayer of medium between particles forming aggregates, which in turn are linked into a loose structure. Since the surface of carbon-black particles is heterogeneous, it is obvious that molecular interaction is greater between the more active regions. As a result, the interlayer of medium between the most polar particles, for example oxidized ones, is squeezed out to a greater extent and has the smallest thickness. When the thickness of such an interlayer is less than $10^{-7} \div 10^{-8}$ cm, electrons pass through it and the specific electrical conductivity of the system is a constant quantity. Contacts with preservation of interlayers of greater thickness are then nonconducting. With increasing potential gradient these interlayers are also broken down—the entire system becomes increasingly electrically conducting (Fig. 1). Such a scheme of structure formation is confirmed by reversible changes in the electrical conductivity of a carbon-black suspension during absorption and evaporation of the dispersion medium.

The proposed scheme also corresponds to the considerable increase in the electrical conductivity of carbon-black suspensions with increasing temperature (3): an increase in temperature first leads to an increase in the electrical conductivity of the suspension, associated with a decrease in the viscosity of the medium, which facilitates the approach of carbon-black particles and increases the number of contacts with a minimal thickness of the interlayer of medium. The intensifying thermal motion disrupts individual contacts and reduces the relative number of contacts with small interlayer thicknesses; this is manifested in a fall in the electrical conductivity of the suspension with further increase in temperature (6,7,8).

The introduction of surface-active substances, even in small amounts (tenths of a percent), sharply lowers the electrical conductivity of the suspension—for 10% carbon black in vaseline oil, addition of 0.05% oleic acid lowers it by a factor of 10. Formation of adsorption layers on the surface of the particles of the dispersed phase leads to stabilization of the system, preventing the development of a coagulation structure, with which the decrease in electrical conductivity, as well as in the mechanical strength of the system, is associated.

Small additions of adsorbing polymers also lower the electrical conductivity and strength of the coagulation structure of carbon black; however, this po-

allows larger amounts of active filler to be introduced into the system, which promotes the development of a spatial structural network of the polymer (rubber) itself.

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Received

10 X 1961

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