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1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ADSORPTION MODIFICATION OF FILLERS AND PIGMENTS AND STRUCTURE FORMATION IN POLYMER SOLUTIONS

(Presented by Academician P. A. Rehbinder on 15 VIII 1961)

When a solid dispersed phase is introduced into a polymer, a necessary condition for its effective action as an active filler is the closeness of the molecular properties of the particle surface and of the polymer. This primarily determines—along with high dispersity—the high effectiveness of various kinds of carbon black, a hydrophobic filler of organic origin. For the same reason, most mineral fillers, usually hydrophilic in character, have a relatively weak capacity for the active filling of polymers, expressed in improvement of the mechanical and other properties of the filled material. In this connection, processes of adsorption modification acquire special importance, i.e., changes in the molecular properties of the surface of particles of hydrophilic fillers by means of oriented adsorption of surface-active substances (surfactants). The resulting hydrophobization of the surface of the filler particles increases their "wettability" by the polymer phase and strengthens their bond with the polymer, as was studied in detail in the works of P. A. Rehbinder and co-workers ([1], [2]). In this case modification leads to activation of the filler; in a number of cases, however, activation does not occur. As models of filled systems one may consider concentrated suspensions of filler particles in polymer solutions containing additions of surface-active substances which, depending on the concentration in solution, as it increases, first peptize the particles, lyophilizing them, and then stabilize them as a result of lyophobization. This causes in the system successively coagulation structure formation and then destruction of the structure that has formed ([2], [3]).

A number of works have been devoted to the study of the influence of fillers and pigments on the properties of polymers in the presence of surfactants—in rubbers ([4]), and in paint-and-varnish materials based on drying oils ([5]); however, the regularities of adsorption modification of mineral disperse phases and its influence on the filling effect in connection with the composition and molecular properties of the components of the complex system: polymer–solvent—filler (pigment)—surfactant, have not been systematically studied. Investigation of this question is the aim of the present work.

The objects of study were: (a) 0.5% solutions of SKS-30 rubber in toluene, filled with kaolin (from the Turbovsk deposit), and (b) 1.2% solutions of perchlorovinyl resin (PVC) in toluene and in dichloroethane, filled with titanium dioxide of the rutile form, with polymer-to-solid-phase ratios of 1 : 80 and 1 : 40, respectively. The dispersity (specific surface area) of particles of both fillers was determined by low-temperature adsorption of nitrogen, and that of kaolin, in addition, in an aqueous suspension—by adsorption of a cation-active dye (methylene blue*) (^{6}).

The study of structure formation in suspensions consisted in determining, by tangential displacement of a plate on a Weiler-Rebinder apparatus, the changes in the magnitude of the limiting static shear stress (P_m) caused by introducing a surfactant modifier into the solution. Limiting structuring of the suspensions was achieved in 48 h. In parallel with these model studies, on a Polanyi-type dynamometer the tensile strength (P_t) was measured for technological rubber specimens based on SKS-30 rubber, filled with activated kaolin (90 parts by weight per 100 parts by weight of rubber) and vulcanized for 60 min at 140° and a pressure of 27 kg/cm^2. Specimens of titanium white films based on PVCS or on linseed oil were evaluated by their resistance, under the action of ultraviolet rays, to "chalking" —the process of destruction of the film and release onto its surface of TiO_2 particles, as a result of disruption of the bond between the pigment and the binder*. For the convenience of comparing the results of both series of measurements, the concentrations of surfactant were assessed not by their equilibrium values in solution, but were dosed (in percent) relative to the amount of solid phase of filler (pigment) in the suspension or in the specimen. Therefore, the degree of surface coverage of the particles—for example, kaolin—by the adsorption layer of amine was determined not by calculations of adsorption of the modifier itself, but indirectly, by photometric measurements of the adsorption of methylene blue on areas of the kaolin surface that remained free after adsorption of the amine.

Fig. 1. Curves of the dependence $P_m = f(C_{\text{p.a.v.}})$ for rubber solutions and $P_t = f(C_{\text{p.a.v.}})$ for rubber specimens filled with kaolin modified with surfactant. 1—0.5% solutions of SKS-30 rubber in toluene, modifier—octadecylamine; 2—the same, modifier—stearic acid (SA); 3—the same, modifiers—ODA+SA (at constant concentration (2%)); 4—rubber specimens based on SKS-30 rubber, modifier—ODA; 5—the same, modifier—SA; 6—the same, modifiers—ODA+SA (at constant concentration (2%)).

Fig. 2. Curves of the dependence $P_m = f(C_{\text{p.a.v.}})$ for perchlorovinyl resin solutions filled with TiO_2, modified with surfactant.
1—1.2% solutions of PVCS in toluene, modifier—ODA; 2—the same, modifier—

* It should be emphasized that estimates of the dispersity (S_1) of fillers are conditional in view of the influence on it of the nature of the dispersion medium, as is evident from the results of our measurements—in air, for kaolin $S_1 = 17.4$ m^2/g, and for TiO_2 (^{7}) m^2/g; while in an aqueous suspension, for kaolin $S_1 = 36$ m^2/g. To this should be added that the specific surface changes during modification, for example increasing as a result of peptization of particle aggregates.

Fig. 1. Curves of the dependence $P_m = f(C_{\text{p.a.v.}})$ for rubber solutions and $P_t = f(C_{\text{p.a.v.}})$ for rubber specimens filled with kaolin modified with surfactant. 1—0.5% solutions of SKS-30 rubber in toluene, modifier—octadecylamine; 2—the same, modifier—stearic acid (SA); 3—the same, modifiers—ODA+SA (at constant concentration (2%)); 4—rubber specimens based on SKS-30 rubber, modifier—ODA; 5—the same, modifier—SA; 6—the same, modifiers—ODA+SA (at constant concentration (2%)).

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Fig. 2. Curves of the dependence $P_m = f(C_{\text{p.a.v.}})$ for perchlorovinyl resin solutions filled with TiO_2 modified with surfactant. 1—1.2% solutions of PVCS in toluene, modifier—ODA; 2—the same, modifier—SA; 3—1.2% solutions of PVCS in dichloroethane, modifier—ODA.

Figure 2: Fig. 2. Curves of the dependence $P_m = f(C_{\text{p.a.v.}})$ for perchlorovinyl resin solutions filled with TiO_2 modified with surfactant. 1—1.2% solutions of PVCS in toluene, modifier—ODA; 2—the same, modifier—SA; 3—1.2% solutions of PVCS in dichloroethane, modifier—ODA.

SA; 3—1.2% solutions of PVCS in dichloroethane, modifier—ODA.

The results of the measurements are presented in Figs. 1 and 2. As can be seen, in accordance with modern concepts concerning the emergence in concentrated in the modified suspensions of spatial coagulation structures (3), which determine the effect of polymer reinforcement, all curves $P_m = f(C_{\text{p.a.s.}})$ are characterized by the presence of a sharply expressed optimum in the action of the p.a.s. The maximum of the curves corresponds to a definite degree of modification (hydrophobization) by adsorption layers of the surface of the filler particles, at which, for example, kaolin activated with octadecylamine (ODA) forms in a toluene solution of SKS-30 rubber a structure with $P_m = 670$ dyn/cm^2 instead of the initial value for it of 170 dyn/cm^2. The position of the maximum corresponds to $C_{\text{p.a.s.}} = 2.0\%$, after which a rapid decrease in strength is observed (Fig. 1, 1). An equally sharp reinforcement effect (from 150 to 330 dyn/cm^2) occurs in a toluene solution of PVC containing TiO_2, also modified with ODA, but the position of the maximum in this case corresponds to a considerably lower (0.2%) content of p.a.s. in the system (Fig. 2, 1).

This form of the curves indicates that the "critical" region of filling of the particle surface by the adsorption layer of p.a.s., in which structuring of the system caused by peptization of the particles ceases and dilution of the structure begins as a result of their stabilization in the polymer medium, is very narrow. On the other hand, it follows from the course of the curves that the greatest reinforcement of the structures occurs at a certain optimal hydrophobization of the solid-phase particles, corresponding to an incompletely saturated adsorption layer. Adsorption measurements with methylene blue on kaolin showed that the surface filling in this case is about 50%; the limiting degree of filling of the layer corresponds to the transition to the horizontal section of the descending branch of the curve. It should be noted here that the position of the horizontal section at the end of the curves $P_m = f(C_{\text{p.a.s.}})$ for kaolin and TiO_2 is different—in the first case the final value $P_m \approx 300$ dyn/cm^2 considerably exceeds its initial value $P_m \approx 175$ dyn/cm^2, while in the second it proves to be lower (curves 1 in Figs. 1 and 2). The reason for this evidently lies in the fact that in the crystal lattice of kaolin the "landing area" for one adsorbed amine ion is $S_n \approx 80$ Å^2 (7), which limits the possibility of complete surface coverage when the exchange complex of the clay is replaced, even with a horizontal arrangement of long-chain organic ions on the internal surfaces of the kaolin lattice. As a result, the coagulation structure of kaolin retains considerable strength even at high ODA concentrations, in contrast to TiO_2, for which the indicated restrictions of a steric nature are absent and, consequently, greater hydrophobization and

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* To evaluate chalking, a method was used involving photometry of white prints on black paper, obtained from irradiated lacquer-paint films in a gloss meter developed at GIPI-4. For carrying out these measurements the authors express their gratitude to S. V. Yakubovich and V. A. Zubchuk.

stabilization of the particles are achieved.

Further, the effect of active filling arises only with chemisorption modification of the particle surface. For rubber filled with kaolin, this occurs with ODA (Fig. 1, 1), which, like other cation-active compounds, is adsorbed irreversibly on quartz and quartz-containing minerals (^{8}). This was established by us in direct experiments from the absence of desorption of cation-active dyes from kaolin when it was treated with electrolyte solutions, in accordance with the data of other authors (^{9}). With reversible adsorption, for example of stearic acid (SA), activation of the filler is not observed—the curve 2 runs parallel to the abscissa axis. It is interesting to note here that the joint presence of ODA and SA sharply reduces the activation effect: P_m at the maximum falls from 670 to 280 dyn/cm^2, although the position of the maximum remains unchanged (curve 3). The action of both additives on TiO_2, which has an amphoteric character, manifests itself differently; in this case a sharply expressed activation effect is given not only by ODA but also by SA (Fig. 2, 1 and 2). At the same time, in accordance with the stronger chemisorption interaction compared with ODA, leading to surface soap formation, SA gives a sharply expressed maximum ($P_m \approx 350$ dyn/cm^2) at a much lower $C_{\text{p.a.s.}}$ (0.080%).

An influence of a quite special character on the structuring of the system

The TiO_2—PVKhS—ODA system is influenced by the nature of the polymer solvent. If, all other conditions being equal, dichloroethane rather than toluene is used as the solvent for PVKhS, the effect of the modifier is reversed. From a comparison of curves 1 and 3 in Fig. 2 it is seen that, for the unmodified pigment in dichloroethane, P_m, which has a somewhat higher value than in toluene (280 instead of 150 dyn/cm^2), does not increase as hydrophobization proceeds, but decreases, revealing a minimum whose position corresponds to the same value of $C_{...}$ ($\sim 0.2\%$) that is characteristic of the position of the maximum P_m for the system in toluene.

It is important to emphasize that the indicated regularities of adsorption activation and structure formation in concentrated suspensions formed by fillers in polymer solutions strictly model the properties of real systems—rubbers and paints. Measurements of the strength of technological rubber specimens based on SKS-30, filled with kaolin activated by ODA, on the one hand, and investigation of the "milling" process during photochemical aging of titanium white films also containing ODA, on the other, showed complete correspondence in the variation of these properties with modifier concentration. Thus, curve 4 in Fig. 1, repeating the course of curve 1, gives a maximum at the same value $C_{...} = 2.0\%$, while the breaking strength of the rubber specimens increases from 46 to 100 kg/cm^2. Similarly, curves 5 and 6 reproduce the course of curves 2 and 3, which refer to the model system. In exactly the same way, the intensity of milling proves to be the smallest (the strength of the pigment-binder bond proves to be the greatest) at the optimal surfactant concentration corresponding to the maximum value of P_m.

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Received
15 VIII 1961

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Note: Figure translations are in progress. See original paper for figures.