Reports of the Academy of Sciences of the USSR

1963

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 152, No. 2

PHYSICAL CHEMISTRY

E. D. Yakhnin, A. B. Taubman

ADSORPTION MODIFICATION OF DISPERSE QUARTZ AND STRUCTURE FORMATION IN RUBBER SOLUTIONS

(Presented by Academician P. A. Rebinder on 29 IV 1963)

Structure formation in filled polymer systems and the influence of surface-active substances (SAS) on it have been studied in a number of works (^{1}-^{3}). In work (^{4}) it was shown that, by means of adsorption modification, it is possible to increase the molecular compatibility of the solid phase with the polymer binder and to improve the structural-mechanical properties of filled polymer materials —rubbers, paints, etc. In this case, the greatest strength of the systems studied arose with partial coverage of the surface of the solid phase by SAS and chemical anchoring of the modifier molecules, the reasons for which remained not entirely clear.

The purpose of the present work was a detailed study of the relation between adsorption modification of the solid phase and structure formation in filled polymer solutions, based on direct measurement of the adsorption values of SAS* and comparison of them with the strength of the structures arising in nonaqueous media. We studied the adsorption of octadecylamine (ODA) from *p*-xylene on a quartz sample that had been dispersed and thoroughly washed free of impurities, and, in parallel on the same sample, the strength of sediments of concentrated suspensions in xylene and in a 0.5% xylene solution of a purified fraction of SKS-30 rubber.

The adsorption value (at 23°) was determined from the difference between the initial and final concentrations of ODA in the solution by two independent methods, interferometrically and colorimetrically, with good agreement of the results.**

As is seen from the figure, curve 1, the isotherm $A = f(C)$ has a stepped form, indicating the complex character of adsorption. The initial portion of the isotherm up to point a coincides with the ordinate axis, owing to complete absorption of the amine, which indicates a chemisorption interaction. The subsequent

Figure 1

Figure 1: Figure 1

portions of the isotherm from point *a* to saturation correspond to reversible adsorption. This character of adsorption was confirmed by desorption experiments carried out by diluting the solutions above the adsorbent and holding the system for one and a half hours at 60°. An unambiguous interpretation of the stepped course of the isotherms is difficult. However, it must undoubtedly be connected with the energetic heterogeneity of the surface of the disperse quartz particles. Energetic heterogeneity may be caused by amorphization of quartz during grinding (5), by differences in the surface energy of different cleavage planes (6–8), by unequal activity of the silicon atoms and hydroxyl groups located on the surface (9,11), and by other effects. Heterogeneities, apparently of the same kind, also explain the multistep character of isotherms in the adsorption of gases on other solid sorbents (12–14). The different character of ODA adsorption on quartz at the initial and final stages of surface coverage indicates two qualitatively different types of its interaction with the amine. In accordance with the numerous literature data on the adsorption of amines on silicon-containing mineral bodies (15), it may be assumed that the qualitative difference between the areas of the quartz surface on which chemical or physical adsorption of amines occurs is based on the difference in the properties of Si and O atoms. These differences are manifested in the fact that, on the quartz surface during its grinding, regions arise whose properties are determined predominantly by the action of the Si atom, and regions in which the principal role is played by the O atom, existing on the quartz surface in the form of OH groups. Under this assumption, the chemical adsorption of the amine could be due to interaction between Si and N atoms through a coordination-type bond (11), while physical, reversible adsorption could be due to weak hydrogen bonds.

Fig. 1. Dependence of adsorption (A) and limiting shear stress, (P_m), g/cm^2, on the equilibrium concentration (C, mmol/l) of octadecylamine in xylene suspensions of quartz: 1–$A = f(C)$; 2–$P_m = f(C)$ in xylene; 3–$P_m = f(C)$ in a 0.5% xylene solution of SKS-30 rubber.

---

* In (4) the degree of coverage of the surface of the solid phase was estimated by indirect methods.

** For the colorimetric measurements a special procedure was developed, based on the interaction of dinitrofluorobenzene with an amine in an acid-citrate medium, as a result of which a compound with an orange-red color is formed. Despite the small surface area of the sorbent, the accuracy of the procedure developed, with a large number of points taken, made it possible to estimate the adsorption values at different concentrations with sufficient rigor.

The adsorption values at point a and at surface saturation make it possible to estimate the areas occupied by adsorbing regions of each type. At limiting saturation of the surface, the adsorbed molecules are oriented vertically, which is confirmed by the coincidence of the maximum adsorption values for ODA and octylamine (data not given). As can be seen from the figure, the adsorption values at point a and at saturation are respectively equal to $A_a = 1.9$ μmol/g and $A_{\max} = 4.1$ μmol/g. If the area occupied by an amine molecule in the adsorption layer with vertical orientation is taken as 20 Å^2, then the total area of the adsorbent is $S_{\text{tot}} \simeq 0.5$ m^2/g, and the fraction of the surface irreversibly binding the amine accounts for

$$S_{\text{chem}} = \frac{1.9}{4.1} \cdot S_{\text{tot}} \simeq 0.25 \text{ m}^2/\text{g}.$$

Consequently, the area of that part of the surface on which weak hydrogen bonds arise and reversible adsorption occurs will be $S_{\text{OH}} \simeq 0.50 - 0.25 \simeq 0.25$ m^2/g.

It should be noted that the surface of the quartz sample used, determined from low-temperature nitrogen adsorption, proved to be equal to 1.1 m^2/g. The reason for such a significant discrepancy is evidently the peculiar "welding" of quartz particles, firmly established at present (^{16}), which arises during its dispersion. The internal surface of aggregates is to some extent accessible to nitrogen molecules and inaccessible to large amine molecules. Thus, the effective surface of fillers and pigments, especially those obtained by dispersion, must be estimated not only from the adsorption of gases (nitrogen), but also from the adsorption of the corresponding surface-active substances from the liquid medium under study.

The strength of the sediments of suspensions was characterized by the limiting shear stress (P_m), determined by the plate-pulling method (^{1}). The results are presented in Fig. 1 (curves 2 and 3). As can be seen, these curves $P_m = f(C)$ have the general form characteristic also of other systems (^{4})—

with a sharply pronounced maximum of strengthening. The fraction of physical adsorption on the first step of the isotherm is very small; therefore, approximately, its level may be taken as corresponding to the magnitude of chemisorption. The maximum values of both curves fall on this first step; consequently, the strongest structures arise when the chemisorption-active regions of the surface are saturated.

The positions of the maxima (P_m) for coagulation structures of quartz particles in the pure solvent (curve 2) and for combined structures formed by particles and rubber in its solutions (curve 3) coincide. This position of the maximum, in accordance with (^{4}), is also preserved for block specimens. Thus, there is a direct connection between the degree of modification of the solid phase, its ability to form a strong coagulation structure, and its structure-forming action in the polymer system. This connection can be understood only on the basis of definite ideas about the topography of the modified surface, to which the results of the experiments cited above point.

The energetic heterogeneity of the surface, arising in the process of grinding solid bodies, as was noted, leads to differences in adsorption activity and to selective filling of individual regions of the surface. The first step of the isotherm corresponds to a certain optimum degree of surface coverage $\alpha \approx 0.5$ and, in accordance with its initial heterogeneity, to a definite distribution of lyophilized and remaining lyophobic macroregions. Thus a lyophobic-lyophilic macromosaic arises, determining the structure-forming action of the solid phase. It is important to emphasize that only macromosaicity, and not the "mosaicity" of the molecular-statistical distribution of the adsorbate on the particle surface, can influence the nature of the structures formed, in which the areas of contacts between the elements exceed molecular dimensions by many orders of magnitude, which was not taken into account previously. It should be noted that the macromosaic distribution of flotation reagents during adsorption on mineral particles was established experimentally by autoradiographic methods ([17]). The need for sufficient stability of lyophilized regions, without which the macromosaic itself cannot exist, is the probable reason why, in all cases of modification studied so far, strengthening was achieved only with chemical fixation of the modifier molecules. An analogous strengthening of structures of solid emulsifiers in emulsions was investigated in ([18]).

The strength of the relatively small coagulation structure of particles in the solvent is determined by the number and strength of contacts per unit volume. The greatest strength (curve 2) arises with partial lyophilization of the surface. Lyophilization allows the particles, during free sedimentation, to pack most densely. However, since the contacts are made not through the lyophilized but through the remaining lyophobic regions, such a compacted structure proves stronger. The maximum strength, in accordance with the course of the curves $P_m = f(C)$ and $A = f(C)$, arises with the optimal development of the lyophobic-lyophilic macromosaic.

When 0.5% rubber is added to the system, the strength increases sharply; however, as already noted, the character of the curve and the position of the maximum are preserved. Consequently, the polymer structure that arises through the interaction of the polymer with the filler and develops in parallel with its modification is responsible for this increase in strength. In accordance with ([3]), the resulting structure may be regarded as the structure of a polymer that has passed into an oriented state ([20]) on the lyophilized surface of the filler. Since the greatest development of such an induced structure is associated with the greatest development of the inducing coagulation structure of the filler, the optimum conditions for their occurrence coincide. The optimal and, probably, necessary condition for the emergence of a chain coagulation structure developed throughout the entire volume of the specimen

of the filler, detected in (18, 19), is also the presence on the particle surface of a lyophobic-lyophilic macromosaic.

The decrease in the strength of the structures considered upon further modification, as was explained earlier (4), is due to the increasingly complete lyophilization of the surface of the solid phase. Lyophilization leads to weakening and disappearance of the macromosaic, to destruction of the coagulation framework and of the entire structure of the filled polymer as a whole.

The concept of lyophobic-lyophilic macromosaicity as the determining factor in the formation of branched chain structures in filled polymer systems is in good agreement with the established (21) increased washability of active silicon dioxide from rubber in comparison with inactive silicon dioxide, since an aqueous alkali solution will act first of all on the unprotected, apparently lyophobic, macroregions.

It is also interesting to note that macromosaicity makes it possible to represent the formation of a weakening network, developed throughout the entire volume of the filled system and arising under a definite combination of the properties of the medium, the filler, and the modified regions, as a consequence of the "reverse" orientation of particles, in which they face one another with modified regions. It is possible that precisely such a case was observed in work (4).

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
12 IV 1963

REFERENCES

1. P. A. Rebinder, G. A. Ab, S. Ya. Veiler, DAN, **31**, No. 5, 444 (1941).
2. R. Chomikowsky, P. Rehbinder, Acta Physicochimica, U. R. S. S., **8**, No. 3, 290 (1938); Ya. B. Aron, P. A. Rebinder, DAN, **52**, No. 3, 235 (1946).
3. A. S. Kolbanovskaya, P. A. Rebinder, O. I. Lukyanova, *Koll. zhurn.*, **12**, 208 (1950).
4. A. B. Taubman, S. N. Tolstaya, et al., DAN, **142**, No. 2, 407 (1962).
5. G. S. Khodakov, P. A. Rebinder, DAN, **131**, No. 6, 1316 (1960).
6. B. D. Saksena, L. Pant, J. Chem. Phys., **18**, No. 9, 1304 (1950).
7. R. C. Langille, P. E. Braid, F. B. Kenrick, Canad. J. Res., **23B**, 31 (1945).
8. C. Orr, J. M. Dallavalle, *Fine Particle Measurement*, N. Y., 1959, p. 222.

9. V. M. Chertov, R. Yu. Sheinfain, et al., *Ukr. khim. zhurn.*, **27**, No. 2, 190 (1961).

10. A. V. Kiselev, V. I. Lygin, *Koll. zhurn.*, **21**, No. 5, 581 (1959); S. P. Zhdanov, A. V. Kiselev, ZhFKh, **31**, issue 10, 2213 (1957).

11. T. S. Egorova, Yu. A. Zarifyants, et al., ZhFKh, **36**, No. 7, 1458 (1962).

12. N. K. Adam, *Fizika i khimiya poverkhnosti* [Physics and Chemistry of the Surface], IL, 1947, p. 349.

13. G. Jura, D. Griddle, J. Phys. Chem., **55**, 163 (1951).

14. S. Ross, W. Winkler, J. Am. Chem. Soc., **76**, 2637 (1954).

15. R. K. Iler, *Colloid Chemistry of Silica and Silicates*, 1959.

16. G. S. Khodakov, P. A. Rebinder, DAN, **127**, No. 5, 1070 (1959).

17. V. I. Klassen, V. A. Mokrousov, *Introduction to the Theory of Flotation*, 2nd ed., Moscow, 1959, p. 238.

18. A. F. Koretskii, A. B. Taubman, DAN, **124**, No. 2, 258 (1959).

19. A. A. Trapeznikov, DAN, **22**, 2, 84 (1939).

20. B. Dogadkin, K. Pechkovskaya, L. Chernichkina, *Koll. zhurn.*, **8**, 1-2, 31 (1946).

21. B. Dogadkin, R. Uzina, *Koll. zhurn.*, No. 2, 97 (1947).

22. B. Dogadkin, K. Pechkovskaya, E. Goldman, DAN, **119**, No. 6, 1170 (1958).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.