

Investigation of the Dependence of the Properties of the Phenoplasts of Phenolaniline-Formaldehyde Resol Resin on the Degree of Kaolin Filling and on Their Physical Structure

L. G. BOZVELIEV, *Research Institute of Plastics Processing, Sofia Bulgaria* and V. S. KABAIVANOV, *Higher Chemical and Technological Institute, Chair of Plastics Technology, Sofia 56, Bulgaria*

Synopsis

An investigation was made of the dependence of 13 types of standard physical and mechanical and electric insulation properties of phenoplasts of phenolaniline-formaldehyde resol resin on their filler content in a broad range of 14 to 47 vol-%. It is found that the respective curves have more than one maximum and periodically pass through several maximums and minimums. The periodicity is more clearly seen in the curves reflecting the dependences of the properties on the calculated mean thickness of the resin adsorption coating on the filler particles. With these curves the extremal values appear over more or less even intervals of the adsorption coating thickness. The periodicity relating to the change in this thickness is explained by the periodic formation of particles of a new type of filler in the points of a whole number of monoglobular adsorption coatings, and of a maximum amount of globules oriented toward them in the points of a whole number and a half monoglobular adsorption layer. The periodical appearance of an oriented (regarding the particles) globular layer determines the appearance of periodical positive and negative orientation effects in the properties of the phenoplasts. The diagram we propose is confirmed by the regular periodical change in the various properties as well as by the measured ratios of the mean thicknesses of the adsorption coating in the points of the extremums of the various types of curves, determined by the differential curves method.

INTRODUCTION

With phenoplasts for molding, blends of a phenolic resin, a filler, and some lubricating substance are usually utilized. Depending on the type and amount of the filler, the properties of molded goods can greatly vary. Lipatov¹ believes that the adhesion of the polymer to the surface of the filler is one of the basic factors determining the physical and mechanical properties of filled systems. In his view, the influence of the filler on the properties is due to the basic causes as follows. With filled polymers, an adhesion interaction does not intervene between the surface of the filler and individual macromolecules, but between it and supramolecular structures of the packet and globule type, and thus only a portion of the segments

of the polymer molecules participating in these structures interact directly with the surface.

In respect of the secondary structures, the adsorption of polymers on the surface of a solid can be considered as monomolecular. The mobility of the chains in the adsorption layer is limited for two reasons:¹ (a) because there is an energy interaction, an adsorption interaction of the supramolecular structures with the surface; and (b) because it has an entropic character, as the configuration set of the macromolecules must be poorer as compared with the one of the volume for purely geometric reasons, because on the surface they are unable to assume the same number of conformations as in their volume. The changes in the properties of the polymer comprise not only the latter's layers which are in contact with the filler's surface, but also the more remote ones. The binding of the supramolecular structures and their orientation in the surface layer makes impossible the obtention of a closely packed structure. Consequently, the surface layers of the polymer must possess properties differing from those of the volume, in the sense that they are formed of less resilient and therefore less closely packed macromolecules. Owing to the less close packing of the surface macromolecules, an increase may be expected in the mobility of the side groups which are not bound with the filler and a decrease in the relaxation time. But the increase in the glassification temperature of filled polymers tells of an increase in the mean relaxation time and an extension of its spectrum toward an increase in that time for the slowest processes of regroupment of the supramolecular structures. As the investigations of the dielectric relaxation in filled polymers have shown, the interaction with the surface exerts an influence mainly to the effect of limiting the mobility of the larger structural elements. Simultaneously, the mobility of the segments is changed insignificantly, while the mobility of the side groups may even be increased because of the diminished density of the packing.¹

According to Stel,² the properties of blends of a phenolic resin and a filler, (the water absorption, for instance) sometimes change in proportion to the filler content. According to the above literature data on the mechanical properties, a maximum is registered, because the resin, which serves as a binder, achieves but a weak binding when its ratio is insufficient.

Barg³ believes that the filler disperses the resin into a continuous system of oriented membranes the strength of which, according to the statistic theory of the distribution of microcracks, increases in proportion to the decrease in the thickness and can be brought down to the theoretical one at an extremely small thickness (1μ).

The strength of plastics must grow in a linear way with the growth in the filler's active surface to the maximum corresponding to a finitely oriented bimolecular layer of the binder. From the experimental data, however, it results that a direct dependence of the strength on the amount of the filler is observed only to a definite limit, after which a sharp decline in the strength is usually observed. This fact is explained by the technical difficulty of an even distribution of the small volume of binding substance

over the huge surface of the filler.³ Such a limit of a sharp change in the indicators, considered as the critical pigment volumetric concentration (CPVC), is accepted by Asbeck and Van Loo⁴ as the basic physical point of transition to a system of pigment and binder of the paint coating type.⁴ It is influenced by such factors as the basic packing characteristics of the pigment, the type of the utilized binding agent, the type and amount of the available special additives, the fineness of the grinding of the system, and the dispersion or agglomeration degree of the pigment. According to the same authors, in that critical point there is a precisely sufficient amount of binding agent required to fill the voids between the pigment particles, and it constitutes the densest degree of their packing.

In another work,⁵ we established that the physical structure of phenolaniline-formaldehyde resin is an agglomerate of globules of various diameters close to the Gaussian distribution. In cured phenoplasts based on this resin and containing a kaolin filler, the physical structure of the resin is preserved. Within the selected range of filling of 25.4 to 47.6 vol-% kaolin, according to the experimental data and the calculations, the orientative mean thickness of the adsorption resin coating will be equal to between 0.6 and 1.8 times the mean diameter of the globules. The purpose of this work, proceeding from the above concepts of this type of phenoplasts, is to investigate the dependencies of the values of the various indicators on the filler's volumetric concentration and on the relating mean thickness and structure of the adsorption resin coating on the kaolin particles.

EXPERIMENTAL

Materials

The materials and the kaolin-filled phenoplasts described in our previous work⁵ are utilized, although further phenoplasts with a kaolin content increasing by 3.5–4.0 vol-%, up to a 14 vol-% kaolin filling (a total series of nine compounds) were also produced.

Testing of the Phenoplasts

A total of 13 different physical and mechanical and electric insulation indicators were determined for the phenoplasts of a different kaolin content. The tests of the samples was carried out in accordance with the methods described in Section 4 on Test Methods of BDS (Bulgarian State Standard) 10-68, on Bakelite molding powder. In addition, on the standard samples for the electric insulation indicators the dielectric loss tangent ($\tan \delta$) and the permittivity (ϵ') were determined with a P-525 bridge,⁶ at a frequency of 50 Hz and a voltage of 1000 V. The dielectric loss coefficient (ϵ'') is obtained⁷ from the expression

$$\epsilon'' = \tan \delta \times \epsilon'$$

The Brinell hardness of the samples was determined with the aid of an AS-111 Budapest hardness meter.

Calculation of the Sensitivity H of the Standard Tests

The sensitivity of a given type of standard test to the change in the value of the indicator in the investigated series of nine compounds, or the H value, was determined by the formula

$$H = \frac{N_{\max} - N_{\min}}{9} \frac{2 \sum_{i=1}^9 \frac{\sigma_i}{\sqrt{n_i - 1}}}{9}$$

where N_{\max} and N_{\min} = the maximum and minimum value, respectively, of the indicator for a given test of the compounds of the series; σ_i = the standard deviation of the indicator in the compound i ; and n_i = the number of the tested samples of the compound i .

Under the conditions of the standard tests (five to eight tested samples) the denominator of the above expression⁸ gives us the mean 90% confidence interval of all the measured values of the series. For a greater security in the changes of the indicator, it is necessary that $H \gg 1$. In our tests, H moved between 3 (in the determination of the percentage of the voids) up to 11 (in the determination of the dielectric loss $\tan \delta$ and the dielectric permittivity ϵ'). In Figures 1, 2, 3, and 4, the difference in the ordinates of the maximum and minimum values of a given indicator for the investigated nine compounds is proportional to the value of the sensitivity H .

Mapping Out Differential Curves

In order to determine the points of the extrema more precisely, we mapped out along the curves expressing the dependence of the indicators on the mean thickness of the adsorption coating the respective differential curves by graphic point differentiation with a mechanical mirror differentiator.⁹

RESULTS AND DISCUSSION

Dependence of Properties from Volumetric Concentration of Filler

In the determination of the influence of the volumetric⁴ concentration of the filler on the indicators, three basic types of curves, given on Figure 1 by characteristic representatives, are outlined. As can be gathered from Figure 1, the change in the indicators of the individual curves and their passing through a maximum and a minimum have a periodical character. For definite filler concentrations (given in dotted lines), the type 3 curves as compared with the type 2 and type 1 curves have opposite main extrema (minimums and maximums). If we accept that the critical limit of volumetric filling (CPVC) is the point of the sharpest change in the indicators when changing the degree of filling⁴, then the place of these

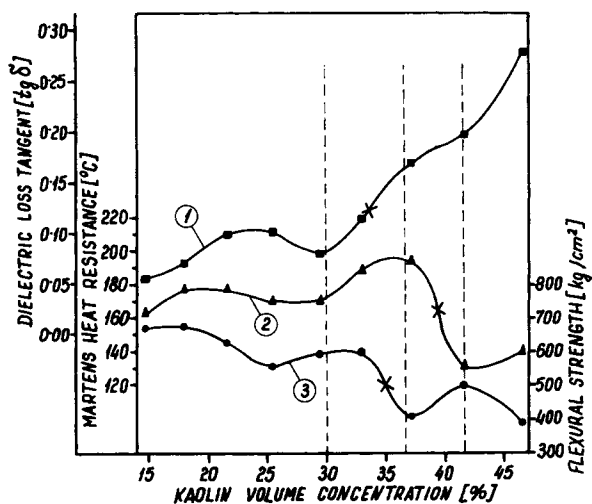


Fig. 1. Dependence of (1) dielectric loss tangent ($\tan \delta$), (2) Martens heat resistance, and (3) flexural strength of phenoplasts on their kaolin content.

points will coincide for two types of curves only (the ones indicated by (x) inflex points, Fig. 1).

Dependence of Properties on Mean Thickness of the Resin Adsorption Coatings and Approximation of Curves

In another work,⁵ we established the dependence, for this type of phenoplasts, relating to the mean thickness of the resin adsorption coating on the kaolin particles of the volume concentration of the filler. The curves of the value of the 13 types of indicators which we have determined depending on the thus calculated mean thickness of the resin adsorption coating are grouped in three basic kinds of curves by coinciding main extrema and critical limits of filling (Figs. 2, 3, and 4).

For the explanation of the periodicity of the above curves, we adopted the diagram of the periodical change in the structure of the adsorption coating in the course of the filling. It is related to the periodical formation of a whole number of monoglobular adsorption coatings on the particles of the kaolin, because of which they can be considered as particles of a new type of filler¹⁰ (Fig. 5).

With the gradual increase in the volumetric concentration of kaolin, the number of filler particles will increase in proportion, while the mean thickness of the adsorption coating of resin will smoothly decrease.⁵ At that, as is indicated in Figure 5, it will be passed periodically from a whole number of monoglobular coatings in A (29.8 vol-% kaolin) to a whole number and a half of globular coatings in B (36.0 vol-% kaolin), and again to a whole number of purely globular coating in C (42.6 vol-% kaolin). In that case, two new filler particle types (shaded on Fig. 5) will form, in A with a biglobular coating, and in B and C with monoglobular resin coating. The

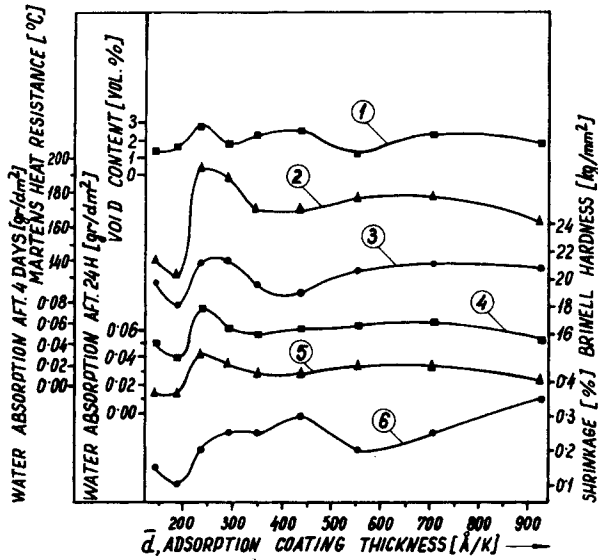


Fig. 2. Dependence of (1) void content, (2) Martens heat resistance, (3) Brinell hardness, (4) water absorption after four days, (5) water absorption after 24 hr, and (6) shrinkage of phenoplasts on mean thickness of resin adsorption coating.

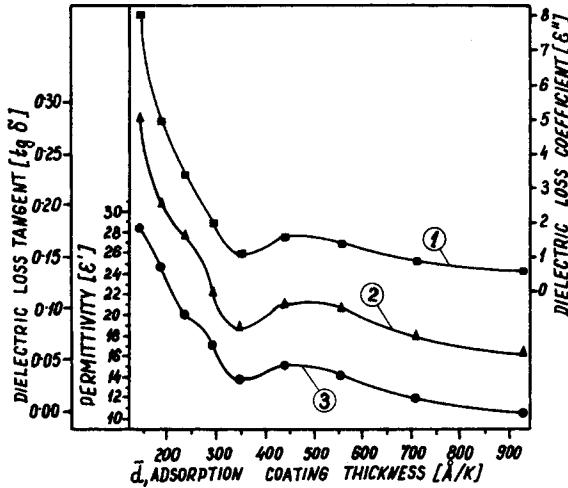


Fig. 3. Dependence of (1) dielectric loss coefficient (ϵ''), (2) dielectric loss tangent ($\tan \delta$), and (3) permittivity (ϵ') of phenoplasts on mean thickness of resin adsorption coating.

amount of oriented globules as to the new particles in the adsorption coatings will reach a maximum in B (\sim one third of the volume of the adsorption coating), and a minimum in A and C (Fig. 5). The intermediary layer of oriented globules will determine periodical orientation effects, the maximums of which will have to increase with the growth of the kaolin con-

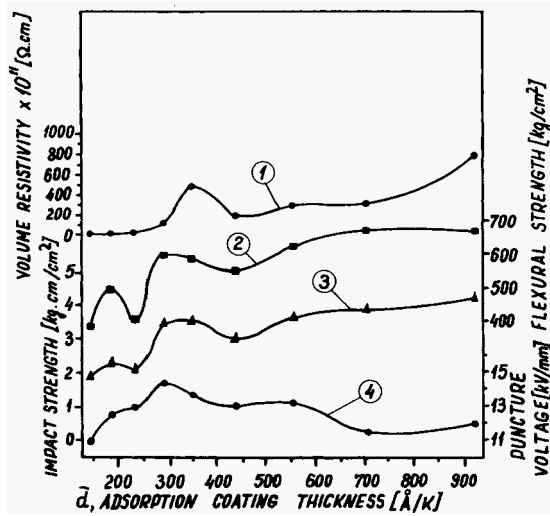


Fig. 4. Dependence of (1) volume resistivity (ρ_v), (2) flexural strength, (3) impact strength, and (4) puncture voltage of phenoplasts on mean thickness of resin adsorption coating.

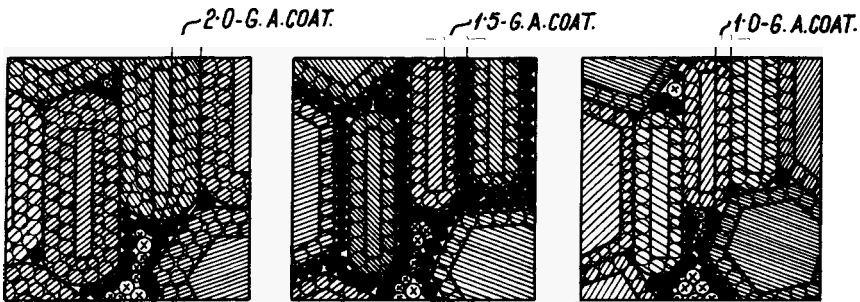


Fig. 5. Diagram of change in physical structure of the investigated phenoplasts depending on degree of filling: ⊗ globules forming new particles); ● globules oriented toward the particles; ⊙ globules in solvation coatings⁵.

tent, because the relative volume of the oriented layer in the total adsorption revetment will be up.

The curves of Figures 2, 3, and 4 may be approximated with a basic smooth curve, which is rapidly changing until it reaches the formation of a biglobular adsorption coating and to which orientation effects passing periodically through a maximum (positive (+0 ef), or negative (-0 ef) orientation effects) are added or subtracted. With the increase in the mean thickness of the adsorption coatings, the maximum of the orientation effects will decrease (Fig. 6).

The proposed diagram is also confirmed by the character of the change in the curves of Figures 2, 3, and 4. The periodical increase in the percentage of the voids of curve 1 in Figure 2 tells of a periodical increase in the amount

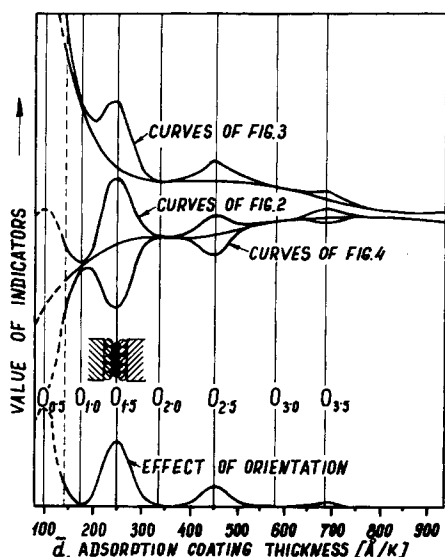


Fig. 6. Diagram of influence of orientation effects on various indicators.

of the oriented globules in the adsorption layer. There is a periodical increase also in the water absorption, the Brinell hardness, and the Martens heat resistance (+0 ef, Fig. 2). Because of the periodical decline in the density of the packing of the globules, the mobility of the side groups is periodically increased, and simultaneously the $\tan \delta$, ϵ' , and ϵ'' all up (+0 ef, Fig. 3). With the growth of the amount of the oriented layer, the strength indicators will decrease because of the increase in the quantity of the microcracks owing to the decreased density of the packing (-0 ef, Fig. 4). In the points of maximum orientation of the intermediary monoglobular layer, the curves of Figures 2 and 3 will reach a maximum (+0 ef), while the curves of Figure 4 will show a minimum (-0 ef). In standard low sensitivity H tests, with a greater mean thickness of the adsorption coating certain unevennesses in the curves are smoothed out, because the orientation effects are relatively small.

Determination of Mean Thickness and Buildup of Adsorption Coatings in the Points of the Orientation Extrema

For a more precise determination of the thicknesses of the adsorption coating, with which the orientation effects show extremal values, along the curves of Figures 2, 3, and 4 we have mapped out graphically the respective differential curves up to a mean thickness of the adsorption coating of 720 Å/K (Figs. 7, 8, and 9).

Assuming that the orientation effects have a symmetrical character in respect of this thickness, we have determined their extremum (minimum and maximum) values for each curve in points of an equal distance from two clearly expressed bends of the differential curve (inflexions of the normal

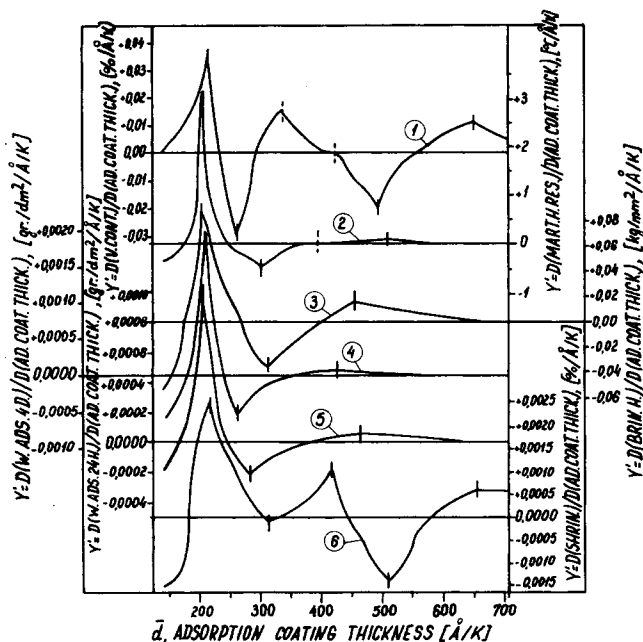


Fig. 7. Dependence of differential curves of (1) void content, (2) Martens heat resistance, (3) Brinell hardness, (4) water absorption after four days, (5) water absorption after 24 hr, and (6) shrinkage of phenoplasts on mean thickness of resin adsorption coating.

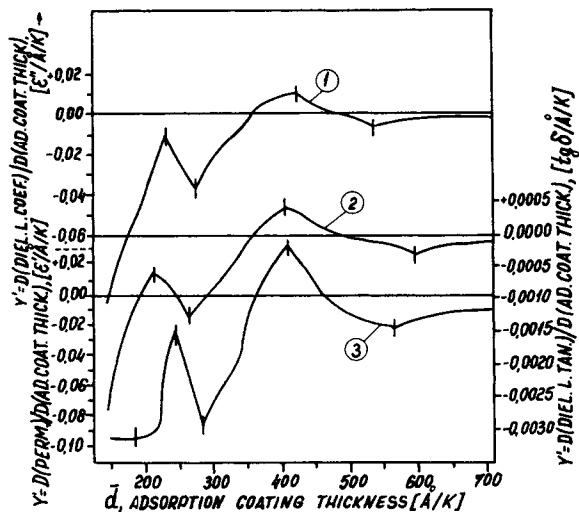


Fig. 8. Dependence of differential curves of (1) dielectric loss coefficient (ϵ''), (2) dielectric loss tangent ($\tan \delta$), and (3) permittivity (ϵ') of phenoplasts on mean thickness of resin adsorption coating.

curves) which are indicated by vertical lines of Figures 7, 8, and 9. In that way, the mean thicknesses are determined for points $O_{1.5 \text{ max}}$, $O_{2.0 \text{ min}}$, $O_{2.5 \text{ max}}$, and $O_{3.0 \text{ min}}$, indicated on Figure 6. The value of this thickness in the point $O_{1.0 \text{ min}}$ is not well expressed by two bends of the differential curves and is taken in the points where the value of the differential curve is equal to 0. In Table I, the calculated mean values of the mean thicknesses of the adsorption coating are given for the thus determined extrema values of the orientation effects of all curves.

As can be seen from Table I, the determined mean thicknesses of the adsorption coating in $\text{\AA}/K$ in the points of the minimum and maximum

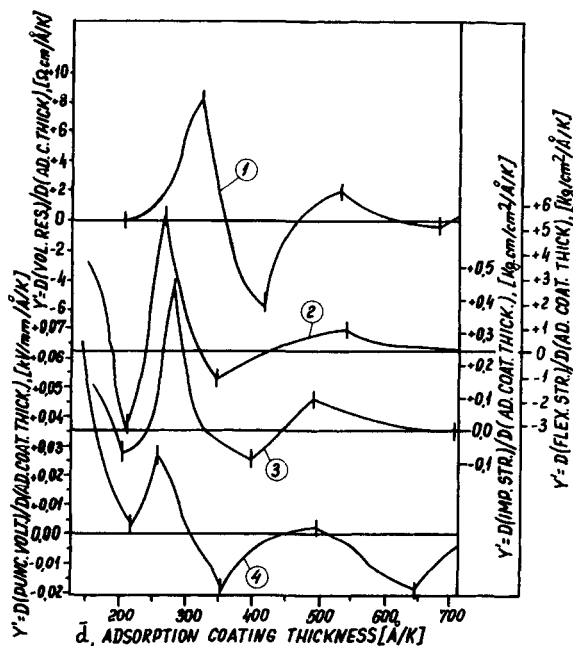


Fig. 9. Dependence of differential curves of (1) volume resistivity (ρ_v), (2) flexural strength, (3) impact strength, and (4) puncture voltage of phenoplasts on mean thickness of resin adsorption coating.

values of the orientation effects for the different curves in accordance with the proposed diagram show a good coincidence, and the 95% confidence interval, with the exception of the one for $O_{1.0 \text{ min}}$, varies within relatively narrow limits. If we accept that the mean thickness of the adsorption coating in $O_{1.0 \text{ min}}$ is 1.0 (monoglobular layer), then in every following point this thickness is increased by about half a monoglobular layer, with a tendency to increase with the lower fillings ($\Delta =$ from 0.41 to 0.73). In our previous work,⁵ we have established that the mean diameter of the resin globules in the cured samples and in the kaolin-containing phenoplasts of this resin is 240 \AA . But the precise way of mutual arrangement of the

TABLE I
Mean Thicknesses of the Adsorption Coating
in Orientation Minimums and Maximums

Points of orientation min. and max. (Fig. 6)	0 _{1.0 min}	0 _{1.5 max}	0 _{2.0 min}	0 _{2.5 max}	0 _{3.0 min}
Thickness of adsorption coating \bar{d}_{ad} , in Å/K, and 95% conf. interv., %	177.2 ± 7.6%	249.3 ± 2.8%	342.4 ± 4.9%	456.5 ± 5.1%	584.4 ± 3.7%
\bar{d}_{ad} at 0 _{1.0 min-1}	1.00	1.41	1.93	2.57	3.3
Increase in the adsorption coating, Δ	—	0.41	0.53	0.64	0.73
K_t with a tetragonal arrange- ment of globules in adsorption coating	0.74	0.69	0.71	0.76	0.81
K_h with a hexagonal arrange- ment of globules in adsorption coating	0.79	0.76	0.79	0.85	0.92

globules, filling up the low molecular part of the resin and the lubricating substances, is not clear. In the arrangement of the globules in the tetragonal system, the mean thickness of the n -monoglobular adsorption coating will be equal to n times the mean diameter of the globule, or

$$\bar{d}_{tetr} = 240 \times n \text{ (Å)}$$

For the more compact packing with the hexagonal system, for geometrical reasons the thickness of the mean n -monoglobular adsorption coating (in Å), with a mean diameter of the globules $D = 240$ Å, will be

$$\bar{d}_{hex} = \frac{D + (2n - 1) \cdot \sqrt{3}/2 \cdot D}{2} = 16.06 + 207.8.n \text{ (Å)}.$$

If we accept that in the points of the orientation minimums and maximums the mean thicknesses of the adsorption coatings are precisely 1.0:1.5:-2.0:2.5:3.0 globular layers, and that the mean diameter of the globule is 240 Å, then, in Table I, the coefficients of the degree of coating of the specific surface of kaolin are calculated by the structural units of the resin⁵ K_t and K_h for both types of packings. From the data of Table I it appears that these coefficients vary from 0.70 to 0.79, for the highest filling to as high as 0.81 to 0.92 for the lowest filling. The change in the coefficients K_t and K_h depending on the filling can be explained by the fact that at higher filler concentrations, an interaction between its particles sets in, as a result of which a part of the filler's surface is prevented from interacting with the polymer.¹ The data of Table I show that an increase in the filler content from 14 to 47 vol-% (Fig. 1) prevents about 20% of the surface of the kaolin particles from interacting with the globules of the resin because of the resulting aggregation of kaolin particles into larger structures.

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