

Physical Structure of Phenolaniline-Formaldehyde Resol Resin and its Kaolin-Filled Phenoplasts

L. G. BOZVELIEV, *Research Institute of Plastics Processing, Sofia, Bulgaria* and M. G. MIHAJLOV, *Institute of Physics at the Bulgarian Academy of Sciences, Sofia, Bulgaria*

Synopsis

An investigation of the physical structure of samples of phenoaniline-formaldehyde resol resin in uncured and cured state, and of its phenoplasts containing different ratios of kaolin filler, was made with the aid of electron microscope pictures. The uncured and cured resin consists of microglobules of a size of 40–80 Å, which agglomerate to form larger-sized globules of various dimensions. After a mathematical elaboration of the results of a large number of measurements, it was established that the diameters of the globules are casual values distributed in accordance with the normal (Gaussian) law. Both in the resin and in the kaolin-filled phenoplasts (at a rate of 25 to 47 vol-%), after curing at 170°–180°C and a pressure of 300 kg/sq cm, the mean diameter of the observed globules was of a rather steady value and remained within the limits of 230–240 Å (with a standard deviation of 30–40 Å). A method was elaborated of determining the mean thickness of the adsorption coating of the resin on the filler particles. Calculations show that in the filling interval we have chosen, the thickness of the absorption coating is not below 1.8–0.6 times the mean thickness of the globules.

INTRODUCTION

Electron microscope investigations show that the physical structure of thermosetting crosslinked polymers does not constitute a stereocrosslinked monolithic block, but is an agglomerate of colloid particles immersed during the polymerization process in a substrate of a lower molecular weight.^{1–4}

A similar structure of phenol-formaldehyde resin is assumed in Houwink's isogel⁵ and Stäger's spherocolloidal theory.⁶ Barkhuff and Karswell⁷ examine the individual stages of the formation of spherocolloidal particles in phenoplasts and relate their size to conditions of reaction and other conditions. Kargin and Slonimskij⁸ believe the basic type of structure arising in polycondensation-produced polymers to be the globular one. In it monomolecular globules are initially obtained, which subsequently, depending on the character of the molecular chain, combine into polymolecular globules or form aggregates. In the filled polymers, according to Lipatov,⁹ it is not the individual macromolecules, but the supramolecular structures of the packet and globule type, that enter into an adhesion interaction with the filler's surface. In the filler-binder system, a part of the binding agent forms adsorption coatings around the filler particles, while the remainder

fills up the voids between them and forms the solvation coatings. The ratio between these coatings depends on the particle size and the packing characteristics of the filler.¹⁰ A practical measure in this respect is the filler's oil adsorption number, which is directly related to its resin number and the properties of the filled plastics.¹¹ Bessey and Lammiman¹² introduce the concept of "true" oil adsorption of pigments (TOA), which is "the proportion of oil required just to fill the voids in the close packed powder."

EXPERIMENTAL

The phenolaniline-formaldehyde resol resin (PAFRR) we have investigated is obtained by the joint condensation of phenol and aniline with formaldehyde, in a 4:1:7 molar ratio and the utilization of a MgO catalyst. The kaolin filler we utilized has the following rated granulometric composition (determined by the Andreasen¹³ sedimentation method, for a longer sedimentation time): particles of a size of up to 0.2 μ , 23%; 0.2 to 0.5 μ , 20%; 0.5 to 1.0 μ , 16%; and above 1.0 μ , 41%. The minimum size of kaolin particles measured on the electron microscope photos is about 0.05 μ . Its specific surface, determined by the method of the low-temperature adsorption of nitrogen,¹⁴ is 17.7 ± 0.4 sq m/g.

Three compounds of the resin were prepared by the hot mills method, with 25.42%, 39.92%, 47.64% kaolin, 3% calcium stearate, and 0.8% montan wax volumetric content. The mixing was done on laboratory mills at a temperature of 85°–95°C of the front (work) roll, and of 120°–130°C of the back roll, during a total mixing time of 8–10 min. Under these conditions, the compounds are well milled and homogenized to a maximum kaolin content of about 50 vol-%. Samples were cured at 170°–180°C, a pressure of 300 kg/sq cm, and a cure time of 1.2 min per 1 mm thickness.

Fragments were broken off the individual test specimens thus produced, and the kaolin moldings were prepared at a pressure of 1000 kg/sq cm, and single-stage platinum-carbon replicas of their surface were provided. These were investigated with the aid of a Hitachi type 11-A electron microscope with a direct magnification of 40,000 times that could be increased up to 100,000 or 200,000 times through photographic enlarging. In order to avoid possible errors in the measurement of the sizes of individual globules,² their diameters were determined along the linear chains consisting of 3 to 10 globules in contact with one another. The data on the diameters of a large number of globules for every sample were processed by statistical methods, and thereafter histograms were built.^{15,16}

RESULTS AND DISCUSSION

The results of the electron microscope investigations are given in Figures 1 through 8. According to the observation data, the structure of the uncured (Fig. 1) and the cured (Fig. 2) PAFRR consists of microglobules of a minimum size of 40–80 Å and an estimated molecular weight of 30,000 to

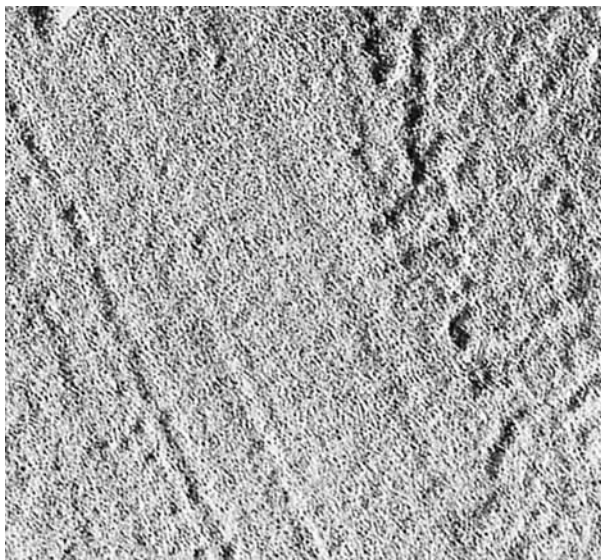


Fig. 1. Electron microscope picture (magnification $104,000\times$) of uncured PAFRR.



Fig. 2. Electron microscope picture (magnification $104,000\times$) of cured PAFRR.

200,000, which is of the order of the molecular weight of a number of other polymers. These microglobules for the most part tend to aggregate to larger globules of various sizes. Both types of globules manifest a tendency to form chaotically disposed short linear chains.² The physical structure we observed may have a more general character since it has been found in other stereocrosslinked polymers as well.^{17,18}

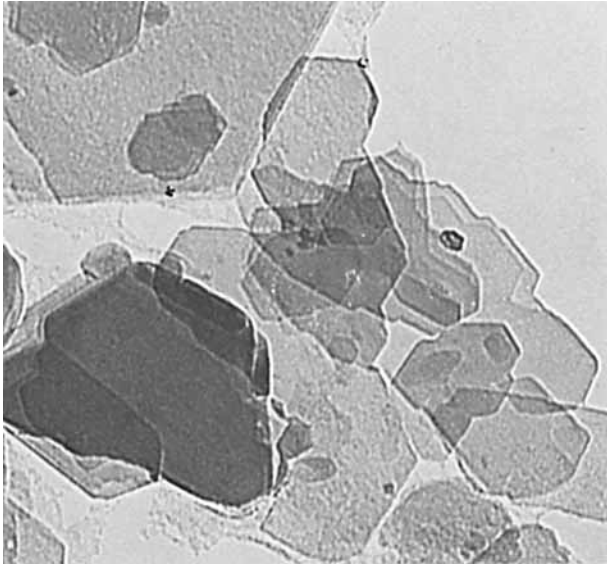


Fig. 3. Electron microscope picture (magnification 104,000 \times) of kaolin.

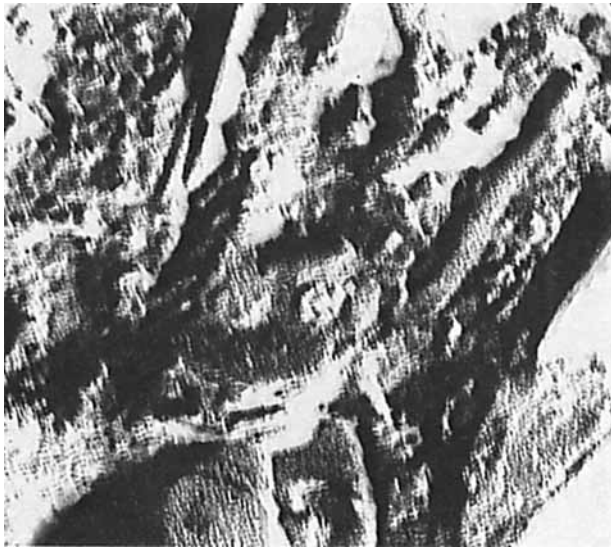


Fig. 4. Electron microscope picture (magnification 104,000 \times) of phenoplast (1-5) with 25.42 vol-% kaolin filler.

After comparing the experimental and theoretical distribution density of globule diameters with the Pearson criterion,¹⁵ it may be said that the observation data corroborate the supposition that these diameters are casual values, distributed by the normal (Gaussian) law. The kaolin particles constitute broken plate-like forms of the hexagonal system with a granular

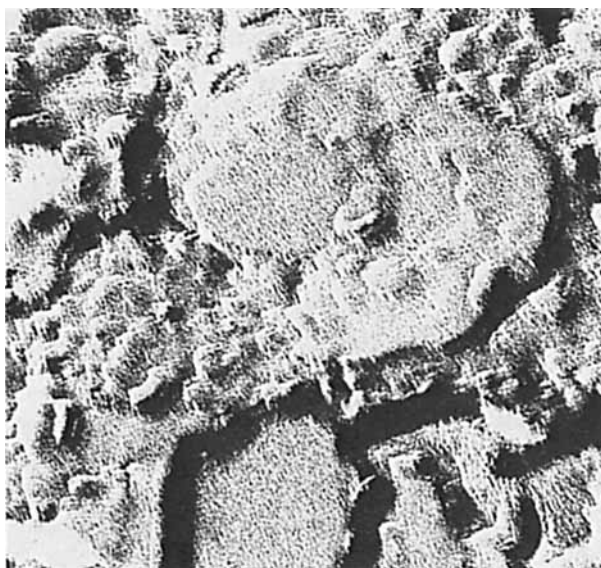


Fig. 5. Electron microscope picture (magnification $104,000\times$) of phenoplast (1-1) with 32.92 vol-% kaolin filler.



Fig. 6. Electron microscope picture (magnification $104,000\times$) of phenoplast (1-1) with 32.92 vol-% kaolin filler.

surface with 98 \AA grains and a $\sigma = \pm 6 \text{ \AA}$ standard deviation (Fig. 3). According to the electron microscope observations with filler containing phenoplasts, the breaking of the samples occurs mainly in the direction of the plate plane of the kaolin particles (Figs. 4, 5, 7, and 8). Figure 6 shows a microphotography of a single observation object, in which a mul-

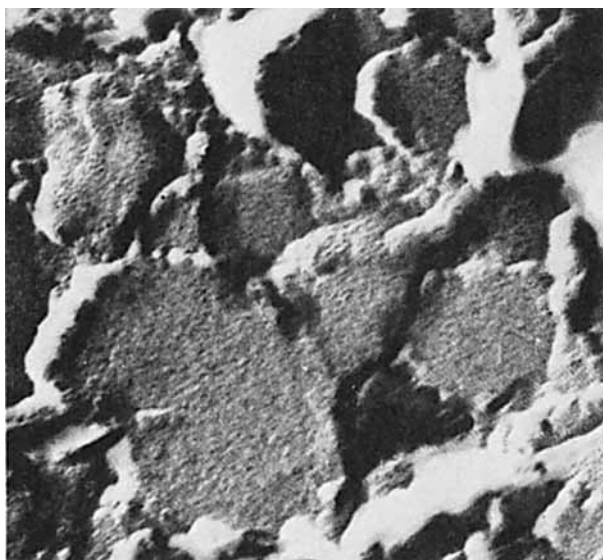


Fig. 7. Electron microscope picture (magnification 104,000 \times) of phenoplast (1-3) with 47.64 vol-% kaolin filler.

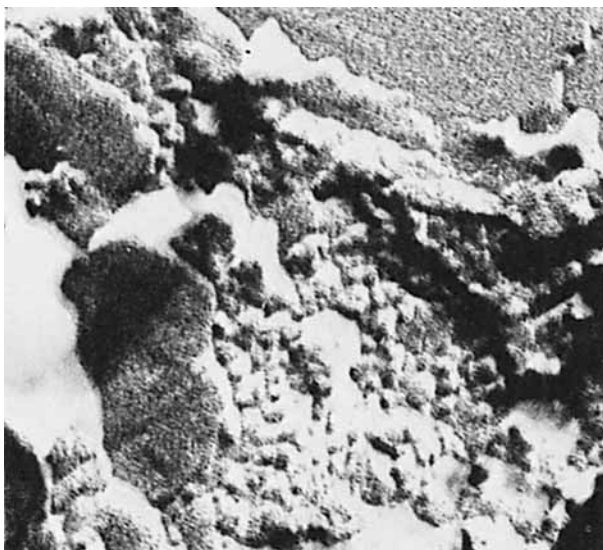


Fig. 8. Electron microscope picture (magnification 104,000 \times) of phenoplast (1-3) with 47.64 vol-% kaolin filler.

titude of small side walls are seen of arranged kaolin plates, and it is difficult to decide whether what is seen is structures comprising resin globules or an aggregation of filler.

The plate-like structure of the filler, with the microglobules, is clearly visible (Figs. 7 and 8), although the globules are less frequent on the kaolin

surface (Figs. 4, 7, and 8). It is possible that the fission of the resin-made adsorption coatings between two filler plates is done through the globules and not along the zones between the globules.¹ Another explanation of the observed phenomenon is also possible. In the presence of the lubricant, the interaction of the globules of the resin with the surface of the filler will decrease as a result of the interaction of the surface of the filler with the molecules of the lubricant. The adsorption speed of the smaller molecules, which is determined by the diffusion, is higher than that of the larger-sized molecules.⁹ Because of this, it can be assumed that the surface of the kaolin particles is coated with molecules of the lubricant. Such a selective adsorption and coating of the surface of pigments with linseed fatty acids in paint films is assumed also by Asbeck and Van Loo.¹⁹ It is possible that in our case the breaking of the samples is taking place along the layer of

TABLE I
Statistical Data of Globule Diameter Measured in the Various Investigated Substances

No.	Type of substance	VCF (Volumetric concentration of the filler) %	Number of counted globules	Statistical globule mean diameter and 99.9% confidence interval $\bar{m} \pm \epsilon_{\beta}, \text{Å}$	Statistical standard deviation and 99.9% confidence interval $\sigma_m(I\beta)$
1	Uncured PAFRR	0	714	269.41 ± 5.78	46.92(42.64 ÷ 50.84)
2	Cured PAFRR	0	1147	245.02 ± 3.66	37.65(35.01 ÷ 40.12)
3	Phenoplast 1-5	25.42	300	232.27 ± 5.51	29.03(24.81 ÷ 32.71)
4	Phenoplast 1-1	32.92	242	244.29 ± 5.63	26.61(22.27 ÷ 30.34)
5	Phenoplast 1-3	47.64	541	237.95 ± 4.06	28.68(25.65 ÷ 31.42)

lubricant between the kaolin surface and the globule resin coating. Globules are observed mainly in the adsorption coatings along the edge of the plates and in the solvation coatings which are not linked with the filler (Figs. 4, 5, 7, and 8). Measurement results are given in Table I.

When comparing the statistical totalities of the diameters of the globules of the individual substances with the Student criterion¹⁶ in a more precise way, these totalities show a difference, but the diameters of the most likely globules in the individual substances, with the exception of the diameter in the uncured PAFRR, are very similar in size (Table I). On the basis of the data obtained, it can be assumed that in the production of filler-containing phenoplasts on the mills, a blending occurs between the filler particles and the globules existing already in the uncured resin, which form the adsorption and solvation coatings preserved after the cure.

DETERMINATION OF THE MEAN THICKNESS OF THE RESIN ADSORPTION COATING ON THE PARTICLES OF THE FILLER

Certain authors consider the individual dispersed particles of the filler-binder system not only as filler particles, but also as particles consisting of the filler substance plus its adsorption coating of binding agent joined with the surface of the filler by the effect of the forces of adhesion.¹⁰ For the calculation of the thickness of the adsorption coatings, by analogy with reference 10, we assume that the physical structure of filler containing phenoplasts consists of particles in contact with one another, which are composed of the kaolin particle proper enveloped in an N -number of adsorption globule coatings. The voids between these close-packed particles are filled with globule solvation coatings. Figure 9 shows a determination by methods¹² of the curves of the void volume in 100 g kaolin depending on the volume of the added linseed oil at the various experimental pressures.

The "true" oil adsorption (TOA), comprising the adsorption and solvation oil coatings for every pressure (p), can be determined by the curves of Figure 9 at the points where the void volume disappears, and is given by the equation

$$TOA = 53.03 - 14.74 \lg p. \quad (1)$$

According to the data of Figure 9 and the calculations we made to the bend of the curves, which occurs at 4.8 ml of linseed oil per 100 g kaolin, particles of a monomolecular layer of a 24 Å thickness¹⁰ are formed. This is the adsorption coating building oil. The oil subsequently added is almost proportional to the decrease in the voids and is used for the formation of solvation coatings. The volume of the latter can be calculated by deducing the TOA of 4.8 ml oil/100 g kaolin, and after a recalculation it can be given in vol-% of the compound, with the aid of the following equation:

$$V_{\text{solv}} = \frac{48.23 - 14.74 \lg p}{90.48 - 14.74 \lg p} \times 100 \text{ vol.}\% \quad (2)$$

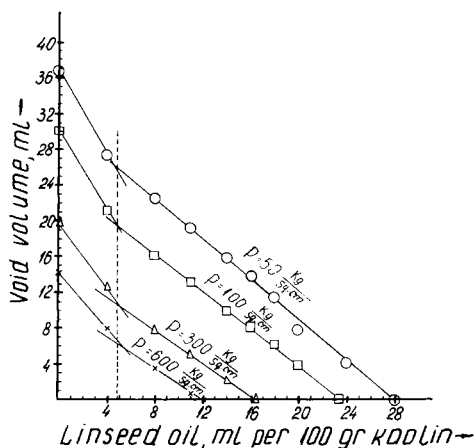


Fig. 9. Volume of voids in pressed kaolin-linseed oil blends depending on pressure.

Assuming that the ratio between the volume of the solvation coatings and the total volume, both with the close-packed particles wrapped in a monomolecular oil coating and with such particles wrapped in a N -number of globule coatings, is kept constant (while only the scale factor is changing), we will be able to apply eq. (2) for filled phenoplasts as well. Under a pressure of 300 kg/sq cm, which is the pressure of their molding, solvation coatings account for an estimated 21.8 vol-% of the total volume. The mean thickness of the adsorption coating could in that case be derived from the equation

$$\bar{d}_{ad} = \frac{(100 - VCF) - 0.218 \times 100}{VCF \times D_k \times K \times F} \times 10^4 = \frac{78.2 - VCF}{47.26 \times VCF \times K} \times 10^4 \text{ (\AA)} \quad (3)$$

where VCF = the volumetric concentration of the filler (vol-%); D_k = the specific weight of kaolin (2.67 g/ml); F = the specific surface of kaolin particles, determined by low-temperature nitrogen adsorption (17.7 ± 0.4 sq m/g); K = a coefficient accounting the degree of covering of the specific surface of particles by the structural units of the resin ($K \leq 1$).

In the interval chosen for kaolin filling by the hot mills method, which starts at 25.42 vol-% and reaches a possible maximum at 47.64 vol-%, the mean thickness of adsorption coating shall vary between $439/K_1$ Å and $135.7/K_2$ Å. If we assume $K = 1$ and the mean diameter of the globules to be 240 Å, then the mean thickness of the adsorption coating shall be $1.8 \div 0.6$ times the mean thickness of the globule. This also means that in this interval the filling occurs by the formation of an average of $3.6 \div 1.2$ adsorption layers of globules between the particles of the filler. In actual reality, however, and with higher filler ratios in particular, the number of the thus determined adsorption layers should be greater, because in that case an aggregation of the filler intervenes and the coefficient accounting the degree of coating of the specific surface of the filler is $K < 1$.

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