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PROPERTIES OF GRAPHITE-FILLED PLASTICS AND THE EFFECT OF HIGH FILLING*

As is known, the properties of various materials based on high-molecular compounds can be substantially improved by introducing active fillers. The action of active fillers is caused by the influence of the surface of their particles on the development of structure in the filled organic medium. A number of studies have shown (1–5) that in those cases where a spatial structure (a coagulation network) can develop in this medium, the particles of the active filler serve as centers for the development of such a structure, causing an increase in its strength (reinforcement). This also determines the strengthening action of active fillers in such systems as rubbers, filled bitumens, and others.

We investigated the influence of graphite as an active filler in a number of systems, in greatest detail in the systems graphite—Bakelite resin and graphite—polyvinyl chloride. Systems of this kind are of great practical importance in connection with the problem of obtaining stable heat-conducting materials for the manufacture of heat-exchange chemical apparatus. Previously known plastic materials filled with graphite (of the "grafolit" and "faolit T" type), containing 50-60 wt. % filler, do not possess sufficient mechanical strength, and their thermal conductivity does not exceed $3\text{-}5 \cdot 10^{-3}$ cal/cm · sec · deg (6).

In studying the nature of the change in the properties of graphite-filled materials over the widest possible range of compositions, we proceeded from the assumption that on approaching the limiting resin capacity, when practically all the resin passes into the state of extremely structured films on the surface of the filler particles and an extremely strong coagulation network of these particles is formed, interacting through thin residual interlayers of the filled medium, a sharp increase in the strength of the material, as well as in its other properties, should be observed.

Samples of a specified composition for their subsequent testing were prepared as follows. The calculated amount of graphite powder** was mixed with the corresponding amount of resin solution: in the case of phenol-formaldehyde resin the solvent used was ethyl alcohol (Bakelite varnish No. 21 was taken), and in the case of polyvinyl chloride—dichloroethane. The resulting paste was dried until the solvent was completely removed. From the press powders prepared in this way, the required samples were pressed in closed electrically heated press

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

molds under conditions identical for each system.

Mechanical strength, heat resistance, and thermal conductivity were studied, i.e., the properties most important from the standpoint of the practical problem posed. In the case of graphite-Bakelite systems, mechanical strength was evaluated by tests in uniaxial compression of 10 × 10 × 3 mm specimens at 20 and 120°; in the case of systems with polyvinyl chloride the strength was estimated from tests involving indentation by a small-diameter cylinder (2 mm). In this case, the conditional value of the strength was taken to be the stress at which either chipping occurs—in the case of highly filled brittle specimens—or noticeable plastic flow occurs—in the case of relatively low-filled plastic specimens. The relative heat resistance was estimated from thermomechanical curves (7) by determining the temperature at which the deformation of a specimen, under a specified load acting continuously during the experiment, reached a certain conventional value; the thermomechanical curves were recorded with the aid of an apparatus (8) at a constant heating rate of 50 deg/hour;

Fig. 1. Effect of composition on the properties of specimens of the graphite-bakelite system: **1** and **2**—mechanical strength at 20° (**1**) and at 120° (**2**), **3**—thermal conductivity, **4**—heat resistance

Fig. 2. Effect of composition on the properties of specimens of the graphite-polyvinyl chloride system: **1**—mechanical strength at 20°, **2**—thermal conductivity, **3**—heat resistance

the deformation regime corresponded to the conditions of indentation by a small-diameter cylinder; in the case of graphite-bakelite compositions the cylinder diameter was 0.9 mm at a load of 7 kg, and in the case of graphite-polyvinyl chloride compositions the diameter was 5 mm at a load of 5 kg. The thermal conductivity of most specimens was studied by the comparative method of Christiansen; the thermal conductivity of highly filled graphite-bakelite specimens was measured by an absolute method*; for specimens of intermediate composition, the two methods yielded satisfactorily coincident data.

The results of the investigation are presented in Figs. 1 and 2 as curves showing the dependence of the properties of the specimens obtained on their filler content.

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* The work was carried out at the Institute of Physical Chemistry of the Academy of Sciences of the USSR in 1949-1950; its results are presented in Institute Reports No. 191 (June 1950) and No. 454 (July 1951).

** In the experiments described here, graphite from the Botogol deposit was used, employed as a raw material in pencil manufacture.

Consideration of these results shows that all the properties studied do indeed exhibit a sharp increase in the transition from specimens with relatively low filling (containing less than 70 wt. %, i.e., approximately less than 60 vol. %) to highly filled specimens. Thus, the thermal— conductivity, while showing a continuous increase over the entire range of compositions, upon transition to specimens containing 75–80 wt.% filler undergoes a sharp rise, reaching, at a content of 80–85 wt.% graphite, a value of about 0.1 cal/cm • sec • deg, which approximately corresponds to the thermal conductivity of lead.

Of particular interest is a new regularity expressed in the special course of the mechanical-strength curves; moreover, there is some difference here between the two systems studied. In the case of graphite–Bakelite specimens, when up to 50–60 wt.% graphite is introduced, the strength of the material decreases, but upon transition to specimens containing 75–80 wt.% graphite, a noticeable strengthening of the material is observed, especially large when tests are carried out at elevated temperature; a further increase in filler content (to 90–95 wt.%) again leads to a rapid drop in strength. In the case of the graphite-polyvinyl chloride system, however, with increasing filler content the strength of the material rises over the entire range of compositions, although here too, upon transition to highly filled specimens, a stepwise strengthening is observed, and after passing through a maximum in the region of about 80 wt.% graphite content, the strength, as in the first case, rapidly falls. Heat resistance in both cases exhibits the same course: with a relatively slow increase in the region of low-filled specimens, its value gives a very sharp jump upon transition to highly filled specimens.

Thus, the experimental data obtained show that a narrow region of compositions, evidently close to the limiting miscibility (i.e., for the systems studied, at a content of about 80 wt.% graphite (or 70 vol.%)), is characterized by an optimum of the most important properties of the material. We have called this phenomenon the "effect of high filling." The sharp increase in thermal conductivity upon transition to highly filled specimens is evidently caused by the disappearance, in the narrow region of limiting miscibility, of thick interlayers of organic binder separating the particles of the highly thermally conductive filler. The maximum on the mechanical-strength curves is determined by the fact that, in the optimal region of highly filled compositions, all the resin present in the composition is extremely structured by the action of the surface of the graphite grains.* The decrease in strength of specimens of the graphite–Bakelite system when relatively small amounts of graphite are introduced is probably caused by the appearance of inhomogeneities in the material and, along with them, the appearance of additional dangerous sites of stress concentration and "embryos" of fracture. Structuring of the resin under the influence of the filler does not yet

* These determinations were carried out at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR in the laboratory of N. N. Sirota, to whom the authors express their gratitude.

play a noticeable role, since the resin interlayers separating the filler particles have a large thickness, and a coagulation structure of filler particles has not yet formed; moreover, the strength of Bakelite resin at ordinary temperature is too high for even a small amount of its structured regions to affect the strength of the material as a whole. The continuous increase in strength in the region of low-filled graphite-polyvinyl chloride specimens indicates that more homogeneous systems are obtained here, in connection with which the structuring effect, which in itself is of great importance in the case of a polymer resin of linear structure, immediately acquires a greater role; possibly, traces of solvent, which are difficult to remove during drying, also play some role.

From the standpoint of the developed concepts, the course of the heat-resistance curves is also understandable; examination of these curves shows that at high temperatures the strengthening effect is expressed more strongly.

* From the relaxation character of the process of fracture of polymeric materials it follows that their structuring under the action of an active filler will not be reflected in strength with respect to rapidly applied (impact) loads; therefore highly filled compositions possess comparatively low impact strength.

It should, of course, be borne in mind that the properties of highly filled systems must, to a large extent, be determined not only by the adsorption-structuring action of the filler, but also by the "bulk" properties of the initial components—resin and graphite. In particular, the nature and dispersity of the graphite may affect the character of the high-filling effect. It is possible that, in this effect, a definite role is played by friction between filler particles in contact with one another.

Investigations carried out in our laboratory on graphite-filled systems based on polystyrene and polyethylene confirmed that the high-filling effect is of general significance for such systems.

Technological investigations carried out on the basis of the present work led to the production of highly graphite-filled materials—graphite plastics—which are already being used in the chemical industry as heat-conducting plastics.

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