TEMPERATURE DEPENDENCE OF $E$ AND $\tan \delta$ FOR POLYMETHYL METHACRYLATE AND POLYSTYRENE WITH DIFFERENT KAOLIN CONTENTS

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The temperature dependence of the dynamic modulus of elasticity $E$ and the loss tangent $\tan \delta$ has been investigated for polymethylmethacrylate (PMMA) and polystyrene (PS) with different contents of kaolin filler ($K$), in the glassy state and in the region of incipient devitrification. It is concluded that supramolecular reinforcing structures appear in filled polymers in which the intermolecular forces are sufficiently strong.

Fillers may have a very important influence on glass-transition temperatures and certain mechanical properties of thermoplastics [1-3]. This is attributed to the orienting effect of the filler surface [1], which leads to a change in supramolecular structure in a layer adjacent to that surface [4]. The influence of the filler extends over distances not greater than 0.15 $\mu$ [5,6], which satisfactorily explains the properties of heavily filled systems but leaves the nature of the effect of low filler concentrations unclear. The strong dependence of the properties of a polymer on its supramolecular structure [7] and the sensitivity of the latter to external influences [8] suggest that low filler concentrations modify the structure of the polymer lying outside the immediate sphere of influence of the filler surface.

As structure-sensitive characteristics we used the dynamic modulus of elasticity $E$ and the loss tangent $\tan \delta$ of the polymers. The resonance method developed in [9] and perfected in [10] was employed. The instrument error consists of the frequency error of the GZ-34 power generator, the error in measuring the length and thickness of the specimen, and the inaccuracy in measuring the amplitude of the vibrations of the clamped and free ends of the specimen. The total error is 5-7% for $E$, and 5-10% for $\tan \delta$. The temperature was maintained constant correct to ±0.5 ° using a contact thermometer. The data presented are the means of 4-5 parallel measurements, the scatter of the points being not more than 3% of the measured value for $E$ and 5% for $\tan \delta$.

The vibration frequency of the specimen varied in the range 100–200 Hz, the principal change of frequency falling in the region of the glassy state, when the frequency of the investigated properties depends only slightly on the frequency interval in question. This is apparent from Fig. 1, which presents the frequency dependence of $E$ for pure polymethylmethacrylate under isothermal conditions. Over the entire range of temperatures investigated the variation of $E$ with frequency from 100 to 200 Hz does not exceed 7%, i.e., the experimental error. This applies, in particular, to the region of incipient devitrification of the polymer, the more so in that in practice the frequency in that region varied only between 100 and 110 Hz. Under the experimental conditions the frequency dependence of $\tan \delta$ likewise did not exceed the experimental error.

A similar law is also observed for polystyrene, which is in full agreement with the published data [11] for these polymers in the glassy state.

In our case the investigated properties of the two filled polymers also proved to be independent of the frequency.

Similarly, a change in frequency from 100 to 200 Hz cannot lead to a significant change in the glass-transition temperature, since changing the time scale of the experiment by a factor of 10 causes a temperature change of only 3 degrees [11].

The temperature at which devitrification begins $T_e$ was determined from the position of the point of inflection on the property-temperature curve along the temperature axis. Since in the glassy state the tempera-

![Fig. 1. Frequency dependence of the dynamic modulus of elasticity of polymethylmethacrylate at various temperatures. The figures next to the curves denote the temperature in °C.](image)

![Fig. 2. Temperature dependence of the loss tangent of polystyrene (a) and polymethylmethacrylate (b) at kaolin contents of: O) 0, A) 1, D) 3, and V) 10 vol-%.](image)
region of devitrification, finding the point of inflection does not present special difficulties. The difference in \( T_e \) for one specimen in 4–5 parallel experiments did not exceed 2°.

As materials for investigation we took polystyrene (PS) and polymethylmethacrylate (PMMA) with molecular masses of \( 8 \cdot 10^4 \) and \( 4 \cdot 10^5 \), respectively, and refined kaolin, particle size 1–3 μ. The components were mixed in an ED-2 rotary extruder and specimens were molded from the mixture at a temperature exceeding the flow temperature by 15–20° with subsequent slow cooling under pressure.

The E and \( \tan \delta \) of the PS specimens do not depend on the amount of kaolin introduced over the entire region of temperatures and kaolin concentrations investigated (Figs. 2 and 3). The temperature \( T_e \) determined from the point of inflection of the \( \tan \delta \)-vs.-T curve was 79–80° C for all the specimens investigated, whereas when determined from the E-T relation it was found to be equal to 93–94° C.

The difference in the \( T_e \) of PS, found from the temperature variations of \( \tan \delta \) and E, is attributable to the fact that these parameters obviously characterize different molecular processes. The loss tangent cannot yet be given a direct molecular interpretation [11]; therefore, it can only be assumed that in PS a temperature sufficient to produce a significant change in the loss tangent is still not enough to change the rigidity of the system, i.e., the quantity E. Both these temperatures are, of course, strictly conditional, characterizing the mechanical vitrification of the polymer with respect to different properties.

The loss tangent for PMMA specimens in the glassy state is approximately three times higher than for PS (Fig. 2) and does not depend on the amount of filler introduced. A sharp difference in the curves is observed in the region of devitrification: for filler contents of 0, 1, 3, and 10 vol-%, devitrification begins at temperatures of about 89, 103, 113, and 116° C, respectively. The \( T_e \) for PMMA, determined from the \( \tan \delta \)-T curve, almost coincides with that found from the E-T curves. When 3 vol-% kaolin is introduced, the E modulus of glassy PMMA increases by 20–25% and remains almost unchanged as more kaolin is added (Fig. 4, curve 1). The concentration dependence of \( T_e \) (Fig. 4, curve 2) also has a tendency to saturation as the kaolin content increases, which is in agreement with the thermomechanical data [2].

This dependence can be described by the equation of a hyperbola,

\[
T_e - T_e^0 = \Delta T_e^{\text{max}} \frac{BC}{1 + BC},
\]

where \( T_e \) and \( T_e^0 \) are the temperatures at which devitrification of the pure and filled polymer begins; \( C \) is the volume filler content; \( \Delta T_e^{\text{max}} \) and B are constants; \( \Delta T_e^{\text{max}} \) is the maximum increase in \( T_e \) for the given polymer-filler system (in our case 30°). Obviously, the constant B characterizes the intensity of the effect of the filler on \( T_e \).

The considerable change in the properties of PMMA when small amounts of filler are introduced indicates profound changes in the supermolecular structure at large distances from the filler surface. In [12] it was shown that the surface of the filler particles considerably reduces the mobility of the bundles in contact with it. It is possible that the presence of sufficiently strong intermolecular forces in PMMA due to the polar side substituents leads to the appearance of elements of the supermolecular structure possessing an enhanced rigidity at considerable distances from the surface of the filler particles. This makes possible a sort of self-reinforcing of the polymer [7] and a corresponding change in the properties of the material outside the immediate sphere of influence of the filler surface.

At a low filler content (in our case up to 3 vol-%) the number of these elements is still small for an appreciable change in E, though sufficient to prevent the development of the free volume of the polymer as the temperature rises, which leads to a sharp increase in \( T_e \).

An elementary calculation shows that the number of reinforcing elements, and hence the effectiveness of the filler, is proportional to the distance from the surface of the particles. This is indicated by the linear correlation between the derivatives of \( T_e \) and the interparticle distance with respect to filler content.

The low polarity of the PS macromolecules excludes the possibility of the polymer whose properties have been modified by the filler surface affecting the entire volume; accordingly, introducing a dispersed filler does not change the properties of this polymer.

Thus, under certain conditions introducing a filler may lead to an important modification of the properties of the polymer as a result of the appearance of reinforcing elements of the supermolecular structure.

Fig. 3. Temperature dependence of the dynamic modulus of elasticity of the polymers at different kaolin contents (notation same as in Fig. 2).