PHYSICOCHEMICAL MEASUREMENTS

MODEL REPRESENTATION OF FILLED POLYMERS

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We have investigated the mechanical properties and dielectric relaxation in polyamide-6 composites with fiber glass and mica. We propose a new model for filled polymers, assuming that the material consists of two interpenetrating continuous phases. The first phase is the polymer sorbed on the surface of the filler particles, mechanically stronger and having a higher modulus of elasticity. The second phase is the unsorbed polymer. The calculated mechanical characteristics of the composites (tensile strength and modulus of elasticity) agree well with experimental data.

The widespread use of plastics for engineering and technical purposes in construction of machinery and instrumentation requires introduction of reinforcing fillers into the original polymers. Such fillers considerably improve the physicomechanical properties of the plastics: mechanical strength, hardness, modulus of elasticity, impact toughness. They also improve the service properties (creep is reduced) and the engineering properties (shrinkage during molding is reduced).

Presently a large number of models have been proposed for predicting the characteristics of filled polymers from the parameters of the original components [1, 2]. These models describe the systems reasonably well when inert fillers with low reinforcing capability are introduced: metallic or glass spheres, clay particles, chalk. But systems filled with reinforcing fillers whose particles have an extended surface (flakes, fibers) and are capable of sorbing a large number of polymer macromolecules are unsatisfactorily described by these models.

In this work, we have prepared composites based on the polymer which is most widely used for engineering purposes and which is able to function under load at elevated temperatures: polyamide PA-6 (Capron). We used fiber glass and mica (Flagopit) as the fillers.

To monitor the change in relaxation properties of the polymer during filling, we used the dielectric method: measurement of the dielectric constant $\varepsilon$ and the tangent of the dielectric loss angle $\tan \delta$ in the frequency range 200 Hz to 1 MHz and the temperature range 20-140°C. We also determined the volume and surface resistivity at room temperature and humidity, for 100% humidity, and in the temperature range 20-140°C.

As we know, the electrical and mechanical relaxation characteristics are correlated. So because of the high accuracy and throughput possible when using electrical elements, the indicated method is often used (rather than the dynamic mechanical methods in [3, 4]) to determine the relaxation time, transition temperatures, and to estimate the molecular mobility. The error in measuring $\tan \delta$ by the dielectric method was no greater than 5%; the error in measuring the dielectric constant $\varepsilon$ was no greater than 1%.

The results of the investigations are presented in Fig. 1 and in Table 1. The experimental results are considered more fully in [5].

On the temperature dependence of $\tan \delta$ (see Fig. 1), we see two maxima: in the 40-80°C region and in the 120-140°C region. We know [3, 6] that the first maximum is associated with the glass transition: thawing of the mobility of segments of the macromolecules found in the amorphous phase. The second maximum is probably [3] also due to the glass transition, but involves segments of macromolecules found at boundaries with crystalline regions. In this case, the selection of conformations is limited, which leads to a rise in the glass transition temperature $T_{eq}$ compared with the glass transition temperature $T_{eq}$ inside the amorphous phase. The effect of crystallization on the rise in the glass transition temperature and the multiplicity (splitting...
TABLE 1. Mechanical, Relaxation, and Engineering Characteristics of Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Filler</th>
<th>Filler content, mass %</th>
<th>( \sigma_c ), MPa</th>
<th>( E_y ), GPa</th>
<th>( s ), kJ m(^{-2} )</th>
<th>( t_{\ell_1} ), °C</th>
<th>( t_{\ell_2} ), °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-6</td>
<td>—</td>
<td>—</td>
<td>60</td>
<td>2</td>
<td>—</td>
<td>1.5</td>
<td>46.5</td>
</tr>
<tr>
<td>SV-20</td>
<td>Fiber glass</td>
<td>20</td>
<td>140</td>
<td>7</td>
<td>45</td>
<td>0.7</td>
<td>18.8</td>
</tr>
<tr>
<td>SV-30</td>
<td>Fiber glass</td>
<td>30</td>
<td>170</td>
<td>9</td>
<td>55</td>
<td>0.5</td>
<td>32.3</td>
</tr>
<tr>
<td>SM-15</td>
<td>Mica</td>
<td>15</td>
<td>80</td>
<td>3.5</td>
<td>40</td>
<td>0.85</td>
<td>43</td>
</tr>
<tr>
<td>SM-25</td>
<td>Mica</td>
<td>25</td>
<td>55</td>
<td>4.5</td>
<td>55</td>
<td>0.6</td>
<td>33.7</td>
</tr>
</tbody>
</table>

Note: \( \sigma_c \) tensile breaking stress; \( E_y \) modulus of elasticity; \( s \) impact toughness; \( s \) shrinkage.

of the tan \( \delta \) maximum) has been discussed in detail in [7]. We must note that the second high-temperature maximum often is ascribed to \( \alpha_\ell \) relaxation, molecular mobility on the surface of crystallites [8].

The glass transition temperatures \( T_{c1} \) and \( T_{c2} \) were determined by extrapolation of the logarithm of the frequency of the dielectric loss maximum \( \log f_m \) vs. the reciprocal absolute temperature \( 1/T_m \) curve to \( \log f_m = 0 \), i.e., to a frequency of 1 Hz, according to the procedure in [9]. It has been experimentally established that \( T_c \) (both \( T_{c1} \) and \( T_{c2} \)) decreases with an increase in filling (see Table 1). According to available literature data [4], such a phenomenon is due to loosening up of the polymer matrix due to hindrance when crystallization occurs because of the presence of the fillers, which are nuclei for crystallization. So the layer adjacent to the filter is more dense, and the polymer between the dense regions is looser than before filling.

Loosening of the polymer matrix causes a reduction in the viscosity of the melt during molding. This has a beneficial effect in molding of articles, since the presence of fillers increases the viscosity. Experiments have shown that when up to 30% (by mass) filler is introduced, molding proceeds as normally, but above this value molding is drastically hindered.

We have attempted to calculate the expected values of the modulus of elasticity and the mechanical strength after introduction of fillers and to analyze the suitability of existing models for describing the observed experimental dependences.

According to Nilsen [1, 2], the modulus of elasticity for a composite material \( E_y \) when disperse fillers are introduced depends on the following factors: the volume fraction of filler \( V_f \), the modulus of elasticity of the filler \( E_{y_f} \), and the polymer \( E_{y_p} \):

\[
E_y = E_{y_p} (1 + AB V_f) / (1 - B V_f),
\]

where \( A = k_E - 1; B = (E_{y_p}/E_{y_f} - 1)/(E_{y_p}/E_{y_f} + A); \psi = 1 + (1 - V_{\text{max}}) V_f V_{\text{max}}^{-2}; k_E \) is the Einstein coefficient; \( V_{\text{max}} \) is the maximum volume content of filler, depending on the geometric shape of the filler particles: for spherical particles \( V_{\text{max}} = 0.6, k_E = 2.5; \) for flakes when \( L/D = 6 \) to 10 (ratio of the diameter to the thickness), \( V_{\text{max}} = 0.5 \) and \( k_E = 5 \). Since Poisson’s ratio for Capron is equal to approximately 0.35, the value of \( k_E \) is multiplied by the correction factor 0.87.

After rescaling the mass content \( m, \% \) to the volume content \( V_f \) using the formula \( V_f = d_p [d_f - d_p]^{-1} \), taking into account the relation \( V_f + V_p = 1 \), the density of the material is \( d = d_f V_f + d_p V_p \), where \( d_f \) and \( d_p \) are the densities of respectively the filler and the polymer. The mass content of the filler is \( m_f = d_f V_f / d \).

The influence of the filler is enhanced when anisotropic particles are introduced (flakes (Flagopit mica) or fibers (fiber glass)) compared with a filler with spherical particles (kaolin). The calculations using Eq. (1) for mica are presented in Fig. 2 and in Table 2. Equation (1) is not suitable for fiber glass, so for the calculations when fiber glass was introduced, we used the formula

\[
E_y = E_{y_f} V_f (1 - L_{\ell_2}/2L) + E_{y_p} (1 - V_f),
\]

where \( L \) is the average length of the fibers and \( L_{\ell_2} \) is the critical length above which adhesion between fiber and binder exceeds the strength of the filler. For glass fibers in polymers, \( L_{\ell_2} = 0.26 \) mm [1]. The calculation results for glass fiber filler are also presented in Fig. 2. In the calculations, we used the characteristics of the polymer and the filler taken from handbooks. The density \( d \) is 1130 kg/m\(^3\) for Capron, 2850 kg/m\(^3\) for Flagopit, and 2500 kg/m\(^3\) for fiber glass. The modulus of elasticity \( M \) is 2000 MPa for Capron, 172,000 MPa for Flagopit, and 67,500 MPa for fiber glass.