ROLE OF ADSORPTION PROCESSES IN FORMATION OF THE STRUCTURE AND PROPERTIES OF POLYMER COMPOSITE MATERIALS

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The characteristics of adsorption of PVC on the surface of fibre and disperse fillers were established: fibre fillers are the best sorbents for PVC since sorption takes place more actively and the magnitude is higher in their presence; as a consequence, a more complete structure of the PCM can be formed and a better set of properties can be realized in these systems; modification of the surface with an increase in its energy and the number of active sites in the filler intensifies sorption; there is a correlation between sorption of the polymer on the filler and the properties of the PCM. Based on an analysis of the physicochemical reaction of the components, the characteristics of formation of a structure which leads to the required properties of the material were established in developing the technology for fabrication of PCM.

Polymer composite materials (PCM) are playing an important role in the development of modern industry by determining the acceleration of scientific and engineering progress in aviation, automobile, machine-building, construction, and other branches of the national economy to a great degree.

The use of fibre or disperse fillers gives PCM a specific set of properties and allows them to compete with scarce traditional materials. In addition, the use of chemical fibre wastes or wastes from other plants assists in solving ecological problems.

The properties of PCM are not only a function of the properties of the starting components, but also, to a great degree, of the surface phenomena which take place on the phase boundary [1, 2]: wetting, adsorption, adhesion, relaxation, and cross-linking in the condition of a hard surface [3].

The published data [3, 4] and our previous studies [5-8] showed that the hard surface of both a fibre and a disperse filler in PCM can have an important effect on the kinetics of cross-linking of polymers on different levels of organization, as well as on the properties of the filled polymer. This can be manifested by an accelerating or slowing effect; the dual effect of fillers in the different stages of formation of the polymer is also possible. The presence of a solid surface alters the mobility of the functional groups, chain segments, and larger structural formations both toward an increase and toward a decrease [3].

However, such an important process as adsorption, which plays a fundamental role in the reaction of the polymer with the filler, has not yet been studied in detail for many PCM systems. Moreover, together with wetting, adsorption is of independent interest. The goal of the studies described below was to investigate adsorption of the polymer on different fibre and disperse fillers and to determine its role in the formation of the structure and properties of PCM.

Brand S-7059-M polyvinyl chloride (PVC) — solution in cyclohexane (CH) and dichloroethane (DCE) — was used as the polymer binder. The fillers for comparison were taken with a different surface energy [4, 6]:

— reinforcing fibre fillers (with surface energy of 30-50 kJ/m², close in value to the surface tension of the binder): hydrated cellulose viscose fibre and the polyacrylonitrile (PAN) fibre Nitron, drawn and undrawn;
— mineral fillers (with a higher surface energy of ~200 kJ/m², which markedly differs from the surface tension of the binder, which can impede formation of the structure of the PCM): chalk, kaolin, talc, slate ash, and some of its modifications.

TABLE 1. Physicochemical Characteristics of Fillers

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density, g/cm³</th>
<th>Specific surface area, m²/g, determined by different methods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>chromographic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pulsed [13]</td>
</tr>
<tr>
<td>Viscose</td>
<td>1.49 — 1.52</td>
<td>2.55</td>
</tr>
<tr>
<td>drawn</td>
<td>1.15 — 1.17</td>
<td>0.54</td>
</tr>
<tr>
<td>undrawn*</td>
<td>1.44 — 1.46</td>
<td>1.97</td>
</tr>
</tbody>
</table>

*The density of the fibre was estimated without washing off the sodium thiocyanate.

A tendency toward an increase in the surface tension of the binding oligomers in going from the liquid to the solid state and a clear effect of the chemical nature of the reinforcing filler on their wettability was previously established in studying wetting of fibres [7]. It was shown that the wettability of fibre fillers can be increased as a function of the different properties of the surface: the orientational order, degree of crystallinity, porosity, defectiveness. The wettability of the fibres can be increased by chemical and physical methods and by combining fibres of different activity in the reinforcing system.

It was expedient to establish the effect of fillers of different activity and some methods of modifying them on adsorption of the polymer. Slate ash was modified by treating it with different substances (stearic acid, trivalent iron sulfate crystal hydrate) capable of causing the appearance of new active sites on the surface of the ash [3] to increase sorption of the polymer; the fibres were modified by orientational drawing.

Adsorption of the polymer on the surface of the fillers was studied on the example of the study of the adsorption equilibria of the polymer—solvent—filler system with the method used in the Adsorption Laboratory at Moscow State University [9].

The change in the concentration of components in the bulk solution was determined in studying adsorption from solutions in static conditions. The change in the concentration was related to the entire volume of the solution used for adsorption and the adsorption values corresponding to adsorption determined according to Gibbs were calculated.

The excess adsorption value in this study was calculated with an equation obtained on the assumption that the volume of the solution \( V \) does not change during adsorption:

\[
\eta^i = \frac{V(C^0_i - C)}{m}
\]

where \( C^0_i \) is the starting concentration of the solution, mM; \( C \) is the equilibrium concentration of the solution after adsorption, mM; \( m \) is the weight of the sorbent, g.

For a complete study of the adsorption phase, the data on adsorption of PVC from solutions were presented in the values of the total concentration of the adsorption volume with the equation

\[
n^i = n^i / (1 - x_i)
\]

where \( x_i \) is the concentration of PVC, mole fractions; \( n^i \) is the total concentration, mmole/g; \( n^i_1 \) is the excess adsorption value, mmole/g.

Knowing the total concentration subsequently required for calculation of the thermodynamic functions of the adsorption solution, the effect of the surface and disperse adsorbents on the adsorption properties of PVC from dilute solutions in CH and DCE was investigated (Figs. 1 and 2). The curves obtained are typical of adsorption of polymers from dilute solutions. The best adsorption of PVC was on fibre sorbents in comparison to mineral sorbents. This is due to the more important specific reaction of the macromolecules of PVC with the surface of the fibre sorbent, which is in agreement with the published data.