Features of the structure of interfacial layers in polymer composites

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Abstract. Using relaxation spectrometry methods, the features of formation of interfacial layers in polymer composites based on 5-211-BN epoxyanilinophenol formaldehyde binder reinforced with CBM high-modulus aramid fibers are studied. The cases of the initial unmodified and modified neutralization of the surface of the reinforcing filler under loading in various temperature-time regimes are considered. It is shown that the used set of relaxation spectrometry methods allows one to evaluate the features of formation and the structure of interfacial layers in polymer-polymer systems. It is established that the morphological structure of the interfacial layer is strongly dependent on the chemical nature of the components and on the intensity of their interaction.

1. Introduction

The researchers’ interest in polymer composites is due primarily to their inherent complex of physical, mechanical and operational properties and to the features that distinguish them from traditional structural materials. The main distinguishing features of organoplastics are their low density (1000-1400 kg/m³), high stability of properties, low porosity, increased ductility and toughness, low thermal conductivity. The study of the properties of organoplastics and the possibility of their practical application was carried out by many authors, for example, [1-15].

The properties of polymer composites, which are a polymer-polymer system, depend, first of all, on the properties of the composite’s components, which are block polymers. In addition, the combination of components gives a synergistic effect, which consists in the fact that the polymer composite in the process of its formation acquires properties that are not characteristic of isolated components. According to the existing data, this is due to the interphase boundary layer, which is formed because of interaction of the composite’s components and can, under certain conditions, be considered as the third phase of a two-component composite [1]. Therefore, it is the interfacial layer that plays an important role in the formation of the physicomechanical and operational properties of polymer composites.

2. Formulation of the problem

One of the significant problems in creating polymer composite materials is the problem of obtaining information about the interfacial interaction of the binder with the filler surface, as well as the degree of influence of this interaction on the mechanical characteristics of polymer composite materials in general.
Therefore, the study of the features of the interfacial layers structure formation and their effect on the physicomechanical and operational properties of polymer composites is an important and urgent task.

To assess the intensity of interaction between the components of organoplastics and the structural features of their interphase layers, by methods of relaxation spectrometry (the method of bending resonance vibrations, the method of free torsional vibrations (GOST 20812-75) and the method of thermoelectronic analysis (GOST 25209-82)), the relaxation properties of organoplastics were studied based on 5-211-BN epoxyanilinophenol formaldehyde binder, reinforced with CBM high-modulus aramid fibers with an initial unmodified and modified neutralization surface.

The use of these methods for the study of organoplastics enables one to determine their properties due to relaxation processes occurring in organoplastics under loading in various temperature-time regimes. The molecular mobility in organoplastics is determined by the chemical nature of their components and the intensity of their interaction. This makes it possible to evaluate individually the contribution of the components and the interfacial layer to the properties of organoplastics. On the other hand, the surface modification of the reinforcing fiber changes the conditions of interaction at the phase boundary, and this makes it possible to evaluate the contribution of the interaction intensity of the components [4].

3. The results obtained and their discussion

An analysis of the results of studying the viscoelastic properties of organoplastics based on the initial and modified surfaces of the reinforcing filler shows that four relaxation processes due to different levels of molecular organization in organoplastics appear on the temperature dependence of the mechanical loss tangent $\tan \delta$ (Figure 1). Here, $\alpha_1$ is the relaxation process (responsible for defrosting molecular mobility in the polymer matrix), and $\alpha_2$ is the process responsible for the molecular mobility in the reinforcing filler [5,6]. The structure of the interfacial layer in reinforced polymer-polymer systems is determined by the nature of the components of this system and may be associated with the formation of joint supramolecular structures.

![Figure 1](image)

**Figure 1.** Dependence of the tangent of the mechanical loss angle of organoplastics with unmodified (1) and modified filler surface (2) on temperature.

Apparently, $\alpha'_1$, $\alpha'_2$ — are relaxation processes responsible for molecular mobility in the interfacial layer formed during formation of organoplastics with the initial reinforcing filler. The presence of two relaxation regions in the interfacial layer indicates the heterogeneity of the structure of this layer. It can be assumed that in this case, along with the adsorption and diffusion interaction, a chemical interaction
is also realized, as a result of which, the boundary surfaces of the components of organoplastics are modified. Therefore, $\alpha_2' - \alpha_1'$ is the relaxation process due to molecular mobility in the modified near-boundary region of the binder, and $\alpha_2'$ is the relaxation process due to molecular mobility in the modified surface of the reinforcing filler. Thus, organoplastics in this case can be represented as a four-phase polymer-polymer system consisting of a polymer binder block, a polymer block of a reinforcing fiber, and a two-phase transition layer.

Let us pay attention to the peculiarity of defrosting of molecular mobility in the reinforcing filler in both studied organoplastics. A specimen with an initial reinforcing filler exhibits a wide peak of mechanical losses of $\alpha_2$ relaxation process (half-width is approximately 50 degrees). The width of this peak for organoplastics with a modified fiber surface is much smaller. The fact that in organoplastics with a modified filler surface, the defrosting of molecular mobility occurs in a narrow temperature range indicates that diffusion-chemical treatment leads to a redistribution of the spectrum of relaxation times of this process and to a high degree of corporativity of this relaxation process due to the transition of amorphous regions of the fiber from glassy to highly elastic state.

Such a high degree of corporativity can be achieved with sufficiently tight packing of chains in an amorphous layer of fiber. This may be due to the diffusion penetration of the matrix components into the fiber sheath, which leads to its fluxing. Apparently, this explains the fact that the temperature of $\alpha_2$ process of relaxation of organoplastics based on a modified fiber is shifted toward lower temperatures. When a fiber surface is modified by diffusion-chemical treatment, the interfacial layer appears as an $\alpha'$ of the relaxation process, which indicates a homogeneous structure of the interfacial layer. It can be assumed that the interfacial layer in this case is caused, along with the diffusion interaction, as well as the adsorption of the polymer matrix of organoplastics on the fiber surface, and the fluxing of the fiber surface prevents their chemical interaction.

It is known that as a result of adsorption interaction with the surface, the number of possible confirmations of macromolecules on the surface is limited, as a result of which the relaxation behavior of the polymer matrix and its packing density change, which, in turn, is accompanied by a mixing of the maximum peak of $\alpha_1$ relaxation process towards high temperatures. This is most likely to be due to the limited mobility of the molecules of the boundary layer of the matrix adsorbed onto the fiber surface. Then organoplastics can be represented as a three-phase polymer-polymer system, which includes the phase of the polymer matrix block, the phase of the polymer fiber block and the interfacial layer due to the diffusion and adsorption interaction of the components of organoplastics.

At a temperature of 393 K, the organoplastics matrix is in a glassy state. To determine the dynamic shear modulus, free torsional vibrations are realized in the sample. Then the dynamic shear modulus $G'$ of organoplastics is determined by the intensity of intermolecular interaction in the matrix and in the interfacial layer. Modification of the fiber surface leads to a decrease in the shear modulus $G'$ due to a decrease in the intensity of intermolecular interaction, primarily at the phase boundary. Young’s modulus $E'$ was calculated by the method of bending resonant vibrations, while its value is mainly determined by the stiffness of the reinforcing filler. The surface modification of the reinforcing filler shows that at a temperature corresponding to the glassy state, the matrix $E'$ of organoplastics increases by about 50% (Table 1).

**Table 1.** Viscoelastic properties of organoplastics with the initial and modified surface of CBM reinforcing filler.

| Filler surface | $E \cdot 10^{-9}$, Pa | $G \cdot 10^{-8}$, Pa | $G_{h,k}$ | $T_{\alpha_1}$, K | $T_{\alpha_2}$, K |
|----------------|---------------------|---------------------|---------|-----------------|-----------------|
| Initial        | 11.5                | 0.0213              | 9.5     | 2.7             | 408             | 523             |
| Modified       | 17.9                | 0.0172              | 8.9     | 2.45            | 415             | 518             |
All this once again confirms the fact that the modification of the fiber surface leads to a denser packing of chains in the amorphous layer of the fiber. In the region of high elasticity (at a temperature above the glass transition temperature), the physical intermolecular bonds of the van der Waals nature are mainly destroyed, therefore, the magnitude of the dynamic shear modulus in the region of the high elasticity plateau is determined by the possible chemical interaction between the components of organoplastics, which affects the degree of their adhesive interaction.

A comparison of the dynamic elastic moduli in the plateau region of high elasticity shows that it decreases with modification of the fiber surface, which implies that the modification of the fiber surface prevents the formation of chemical bonds between the matrix and the reinforcing fiber. The results obtained are in good agreement with the data obtained using the method of thermally stimulated depolarization (TSD). On the thermogram of the current of thermally stimulated depolarization of organoplastics based on the initial reinforcing fiber in the temperature range 373-523 K, three relaxation processes due to different levels of molecular mobility (Figure 2) are observed.

Moreover, $\alpha_1$ relaxation process is responsible for the dipole-segmental mobility in the polymer matrix $\alpha_1$; $\alpha'_2$ relaxation processes, apparently, are responsible for molecular mobility in the developed interfacial transition layer.

It is known that the phase boundary is an electrically active region of polymer-polymer systems [7]; therefore, with polarization of organoplastics, this layer plays the role of a deep trap of free charges. When organoplastics are polarized, free charges are injected from the surface of the electrodes. These charges are localized in the electrically active interfacial region, in this case, a double electric layer is formed in the volume of the electret, and the polarity of the bulk layer will be opposite to the polarity of the outer layer.

Depolarization of the injected free charge determines the inverse $\alpha'_1$ relaxation process. Judging by the temperature position of the inverse maximum, it can be assumed that the electrically active region in organoplastics is a cross-border region modified during chemical interaction. The layer of the polymer matrix of $\alpha'_2$ relaxation process, is apparently responsible for the dipole-group relaxation in the modified surface of the reinforcing filler.

On the thermogram of organoplastics with a modified diffusion-chemical treatment of the fiber surface, an inverse maximum is not observed. This confirms the fact that the neutralization of the fiber
surface prevents the chemical interaction of the components of organoplastics even in this case, when the molecular mobility in the interfacial layer manifests itself in the form of the $\alpha'$ relaxation process.

4. Conclusions
Thus, the complex of the considered relaxation spectrometry methods allows one to evaluate the features of the formation and structure of interfacial layers in polymer-polymer systems. It also shows that the morphological structure of the interfacial layer is strongly dependent on the chemical nature of the components and on the intensity of their interaction. The interfacial layer in organoplastics can be formed both as a result of conformational transformations and adsorption interactions characteristic of composite materials, and as a result of mutual diffusion of components and the formation of chemical bonds between the matrix and the reinforcing fiber. Depending on the nature of the interaction of the components of polymer composites, both three-phase and four-phase models can be used to predict and calculate their physical, mechanical and operational properties.

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