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Adhesive Strength of Fullerene-Doped Epoxyamine Compositions

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Abstract—Dependence of adhesive strength of model gluing epoxide compositions glass–binder–glass hardened with aliphatic and aromatic amine hardeners on the fullerene additive content is studied. When aromatic amine is used as a hardener of epoxy-diane resin, addition of fullerenes does not affect the adhesive strength. On the contrary, when aliphatic amine hardener is used, the increase of adhesive strength as compared to nondoped composition was 400%. Use of a mixture of aliphatic and aromatic hardener leads to substantial synergism of their effect on strength properties of the fullerene-doped compositions.

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Strength properties of glass-reinforced plastics are known to be strongly dependent on the value of adhesion on the boundary of the surface of reinforced glass fibers and polymer matrix [1]. It was suggested [2] to measure the value of adhesion as a tensile stress for pulling apart two glass plates glued crosswise together with epoxy-amine binder. A specific feature of this procedure is its high sensitivity to defects of gluing and residual stress at the phase boundary, which upon loading causes fast propagation of the main crack. At the same time, it is known [3–6] that addition of doping nanomaterials such as fullerenes, shingites, “astralenes,” nanotubes, montmorillonite and other compounds of carbon or silicate nature with developed surface may act as stoppers of the main crack by dissipating its energy as a result of formation of large number of microcracks. An increase in dissipative properties (viscosity of destruction) of binders and composites on their bases is an important factor of strengthening these materials [7, 8].

In the present work, the effect of fullerene additives on the adhesive properties of epoxy-amine binders has been studied.

Earlier [3–6] it was reported on the use of fullerenes for improving physicomechanical and thermophysical characteristics of polymer materials. Due to the presence of highly active C=C double bonds in the molecules of fullerenes their interaction with functional groups present in the gluing composition is possible. When epoxy-amine compositions are used, these functional groups are the amino groups of the hardener and epoxy groups of the resin. Therefore fullerenes may participate in the process of hardening forming chemical bonds with the polymer matrix and, thus, imparting the glue with enhanced adhesive strength and affecting the other physicochemical properties.

Investigation of the strength properties of the composites was performed on a model glue joint (MGJ) glass–binder–glass. In Fig. 1 the dependence of adhesive strength of MGJ (σ_{gl}) on the fullerene additive content for thermoreactive epoxy-amine composition with aliphatic and aromatic hardeners is shown. As can be seen from the plot, hardening of the epoxide resin ED-20 with aromatic amine, 4,4'-diaminodiphenylmethane (DDM), provides much higher initial strength of gluing (8 MPa) as compared to the aliphatic amine polyethylenepolyamine (PEPA) 1.87 MPa. However, addition of either fullerene C_{60} (F, curve *1*) or the mixture of fullerenes C_{60}/C_{70} (MF, curve *2*) into the gluing composition with DDM does not increase the strength of gluing. These results can be due to several reasons: firstly, to poor stability of the dispersed medium and sedimentation of fullerenes during the process of hardening because of a slow increase of viscosity; secondly, to low reactivity of aromatic amine with respect to double bonds of fullerene (the Michael reaction).

At the same time, when PEPA was used as a hardener the adhesive strength substantially increased

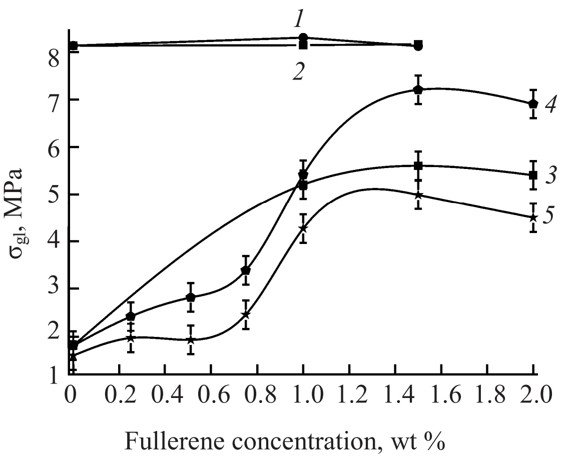

Fig. 1. Dependence of adhesive strength of MGJ (σ_{gl}) on the fullerene additive concentration, type of hardener and regime of hardening: (*1*) hardener DDM, additive C_{60}; (*2*) hardener DDM, additive C_{60}/C_{70}; (*3*) hardener PEPA, additive C_{60}, hardening at 80°C; (*4*) hardener PEPA, additive C_{60}/C_{70}, hardening at 80°C; (*5*) hardener PEPA, additive C_{60}/C_{70}, hardening at 20°C.

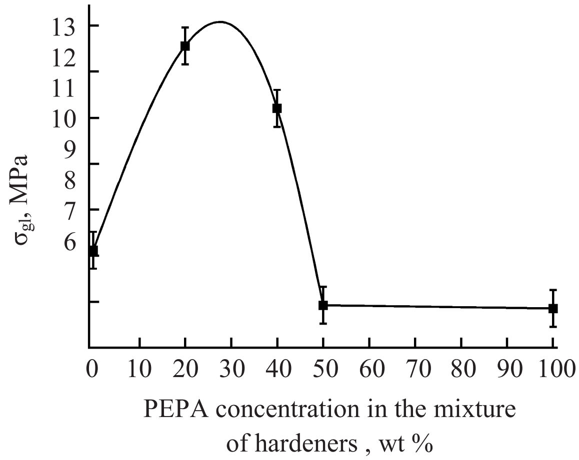

Fig. 2. Dependence of adhesive strength of MGJ on the PEPA content in the mixture of hardeners DDM–PEPA for the fullerenes mixture content of 1.5 wt %.

with the fullerene concentration passing through maximum for the fullerene content in the composition of 1.5 wt % (curves *3* and *4*). The use of fullerene C_{60} as an additive increases the adhesive strength of MGJ as compared to the nondoped composition by 300% (to 5.6 MPa), and the use of the mixture C_{60}/C_{70}, by 400% (to 7.2 MPa). Such a difference may be caused by the presence of a more active fullerene C_{70} in the mixture C_{60}/C_{70}. It should be mentioned that the mixture of fullerenes C_{60}/C_{70} is two-three times cheaper than fullerene C_{60} of 99.5% purity. The fullerene effect on the adhesive strength of epoxy–amine compositions hardened with PEPA may be due to a fast increase of initial viscosity at room temperature as well as to the ability of the fullerene double bonds to react with highly reactive amino groups of the aliphatic hardener PEPA.

The temperature regime also strongly affects the adhesive strength. Hardening of ED-20 with PEPA in the presence of MF at room temperature led to a decrease in the strength by a factor of 1.4 (to 5 MPa) as compared to the composition hardened at 80°C.

Therefore, the obtained results demonstrate that the use of aromatic amines as hardeners leads to a high-strength gluing but without any positive modifying effect in the presence of fullerene. And, vice versa, the use of aliphatic amines provides lower initial adhesive strength but it is markedly increased in the presence of fullerenes. That is why, to achieve higher adhesive strength, we tried to obtain the optimum combination of aliphatic and aromatic amines for the composition doped with 1.5wt % of MF (Fig. 2).

When using a mixture of hardeners PEPA and DDM as a hardener for the fullerene-doped epoxy-diane resin ED-20 a growth of the maximum of adhesive strebgth of MGJ (to 13 MPa) for the PEPA content of 20–40 wt %, that is, a substantial synergism in mutual action of hardeners of different type on the strength properties of the fullerene-doped compositions was achieved. Further increase of the PEPA content in the hardening composition (above 50%) led to a decrease in the adhesive strength, which reaches the values close to the adhesive strength of the composition ED-20 + PEPA + MF. Hence, doping of the glue composition by the mixture of fullerenes increases the initial adhesive strength of MGJ from 1.8 MPa for the system ED-20 + PEPA to 13 MPa for the system ED-20 + (DDM+PEPA) + MF, that is, a 620% growth in the adhesive strength is observed. These results can be used for purposeful modification of glass-reinforced plastics with fullerenes.

EXRERIMENTAL

Two glass plates of 60×25×6 mm size were used for MGJ. Between the crosswise arranged plates a fluoroplastic gasket was placed to regulate the thickness of the glue joint (~120 μm). In the gasket an opening of 6 mm diameter was cut out regulating the square of gluing. The binder was poured into the opening in the gasket, the plates were pressed with the load of 250 g and placed into a special unit and then to a heating cabinet. The surface of the glass plates was not chemically or mechanically treated.

The tensile strength of the glue joint (σ_{gl}) was determined at 20°C by stretching of MGJ by cross claws with the rate 3 mm min^{-1}. The average value of σ_{gl} was taken from the results obtained on 9 specimens.

Fullerene C_{60} and a mixture of fullerenes C_{60}/C_{70} as a dry toluene extract of the fullerene-containing soot prepared by electric arc method was used [9].

Introduction of fullerenes into the gluing composition was performed by ultrasound dispersion of the extract in the epoxy-diane resin ED-20 with subsequent mixing with the hardener PEPA or DDM. Hardening with PEPA (mass ratio 9:1) was performed starting from room temperature for 24 h and then at 80°C during 3 h. Hardening with DDM (mass ratio 4:1) was performed at 80°C for 5 h and then at 120°C for 3 h. For combined use of hardeners PEPA and DDM the hardening was performed similar to that with DDM.

The possibility of effective modification of epoxyamine compositions by doping with fullerene C_{60} and a mixture of fullerenes C_{60}/C_{70} is demonstrated. The effect is achieved due to formation of chemical bonds between the modifier and the polymer matrix. It is found that the modifying ability of fullerenes depends on the activity of the double bonds in their molecules and on the reactivity of amino groups of the hardener determining the extent of the Michael reaction. The regime of hardening and the components of the gluing composition also play an important role. Therefore, the use of fullerenes capable of chemical binding with the polymer matrix favors the increase of crack resistance of glue joints thus increasing the adhesive strength of the final nanocomposites.

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