

DETERMINATION OF ADHESIVE STRENGTH IN A THERMOPLASTIC-RESIN-
THIN-FIBER SYSTEM

V. A. Dovgyalo, S. F. Zhandarov,
and E. V. Pisanova

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The properties of fibrous polymer composites depend to a considerable extent on the strength of the bond between the components at the interface. Methods were proposed in [1] for determining the adhesive strength of joints between fibers and thermosetting plastics and results were presented from studies of a large number of specific systems. At the same time, the adhesion of thermoplastic materials to thin (7-40 μm) fibers has been studied very little and is purposely assumed to be low [2]. Despite this, heat-resistant thermoplastic materials reinforced by thin, high-strength and high modulus fibers are finding increasingly wide use in modern technology as structural materials. The methods of producing them, involving combination of the components in a melt of the thermoplastic material, have several ecological and technical-economic advantages over the method of combining the components in a polymer solution. In connection with this, a necessary stage in the development of fibrous polymer composites is study of the wetting and impregnation of the fibrous filler by the molten binder. Also vital is determination of the bond strength between the components. In the present investigation, we propose a variant of the "three-fiber" method [1] that we developed to determine adhesive strength in thermoplastic-resin-thin-fiber systems. This variant takes into account the specifics of dispersed polymers, the use of which is the basis of one of the most promising and flexible methods for the production of polymeric fiber composites without the use of solutions - the powder method [3, 4].

We studied monofilaments based on poly-n-amidobenzimidazol (SHP), poly-n-phenylenterephthalamide (Terlon), and poly-m-phenylenisophthalamide (Phenylone), as well as dispersed (particle size about 100 μm) thermoplastic materials: polycarbonate (PC) with a molecular weight (MW) of $3.4 \cdot 10^4$ and polysulfone (PSF) with an MW = $2.6 \cdot 10^4$. The fibers were washed with hexane and acetone to remove the lubricant and were dried. A thin fiber was placed between two thick (100 μm diameter) glass fibers (Fig. 1). Frames measuring 35 x 20 mm were cut from aluminum foil and the monofilament was fixed in place with PVA adhesive, as shown in Fig. 1 (we used a single frame, in contrast to the double frame used in [1]). The series of prepared frames was placed vertically in a special aluminum holder and was positioned at the point of intersection of the fibers by several particles of the thermoplastic material. This operation was performed with a needle. The particles were held sufficiently tightly to the fibers due to electrostatic attraction. The holder with the frames was kept in a furnace for 15 min at the prescribed temperature. The length of the resulting adhesive joint l and the diameter of the fiber d were measured under a microscope. The frame was then secured in the clamps of an FO-1S tensile testing machine. It was cut as shown in Fig. 1 and subjected to an increasing load. Here, we recorded the force F at which the fiber shifted relative to the matrix. All of the fibers used had a circular cross section, so that the area of contact $S = \pi dl$. The adhesive strength of each specimen was calculated from the formula $\tau = F/S$. The algorithm proposed in [1] was used to calculate the correction $\Delta\tau$ connected with the presence of specimens which failed cohesively and to analyze the errors.

Table 1 shows the results of determination of the adhesive strength of the specimens. It is known [1] that the adhesion of thermosetting plastics to fibers depends to a considerable extent on the contact area. Thus, the measurements of adhesive strength τ were obtained within a fairly narrow interval of contact areas: $S = (3.80 \pm 0.35) \cdot 10^{-3} \text{ mm}^2$. In working with thermoplastic materials, it is difficult to obtain joints of a specified length. Due to the high viscosity of the melt, an excessively large or small drop, several drops, or a drop which wets the fiber on one side may be formed at the point of intersection with the fibers. On the average, in each series only 30% of the specimens had the necessary contact geometry. Moreover, tests of selected specimens showed that the scatter of the experimental

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TABLE 1. Adhesive Strength of Joints* Between Thermoplastic Materials and Organic Fibers

Fiber	d_{av} μm	$S_{av} \times 10^3$ mm ²	n_{τ}	n_{σ}	n_{of}	$\bar{\tau}$ MPa	$\Delta\tau$ MPa	$\frac{\Delta\tau}{\bar{\tau}}$ %	τ_0 MPa	D_{τ} MPa	d_{τ} MPa	$\frac{\sqrt{D_{\tau}}}{\bar{\tau}}$	$\frac{\sqrt{d_{\tau}}}{\tau_0}$
Polysulfone													
Terlon	11,2	3,85	40	—	40	38,1	0,0	0,0	38,1	30,0	30,0	0,144	0,144
SHP	11,5	3,72	46	5	51	43,4	0,5	1,1	43,9	20,0	19,0	0,103	0,099
SHP†	11,5	3,80	45	7	52	37,3	1,5	3,9	38,8	16,5	68,7	0,109	0,214
Phenylone	13,4	3,91	14	39	53	29,6	3,2	10,8	32,8	9,1	14,8	0,102	0,116
Polycarbonate													
Terlon	11,2	3,79	48	—	48	39,4	0,0	0,0	39,4	21,2	21,2	0,117	0,117
SHP	11,5	3,84	41	5	46	45,2	0,5	1,1	45,7	21,6	22,2	0,103	0,103
Phenylone	13,4	3,97	11	45	56	30,0	4,1	13,7	34,1	5,9	10,4	0,081	0,095

*The adhesive joints were formed at 300°C over 15 min.

†The fiber was in the condition received (unwashed).

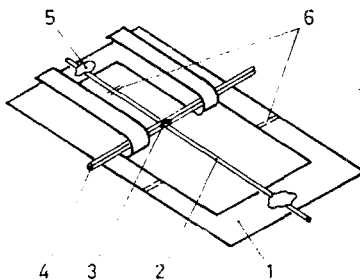


Fig. 1. Test specimen: 1) frame of aluminum foil; 2) thin fiber; 3) thermoplastic material; 4) glass fibers; 5) PVA adhesive; 6) cut line.

values of τ was considerably smaller than in the case of thermosetting plastics [1]. In our opinion, this makes it possible to reliably determine the true mean adhesive strength τ_0 with a total number of tested specimens $n = 40-50$. We connect the reduction in the dispersion of the experimental values of $\tau-D_{\tau}$ and the true dispersion of d_{τ} for thermoplastic materials with the unchangeability of their chemical makeup during the formation of the contact. The curing of thermosetting plastics in the presence of fibers is characterized by selective adsorption of one of the components of the mixture by the surface [5]. Here, the component adsorbed may be an epoxy oligomer [6], an amine curing agent [7], or other material, depending on the type of fiber. This adsorption destroys the stoichiometry of the composition and results in incomplete curing in the surface layers. The nonuniform structuring of the boundary layers and the creation of randomly-located micropores [7] lead in this case to large scatter of the experimental values of τ .

The use of a microscope to study fibers extracted from the matrix showed that the failure of the joints was adhesive in character in each case: no traces of polymer were found on the surface. Also, a certain number n_{σ} of the specimens failed cohesively — through the fibers. With $S = \text{const}$, the value of n_{σ} is determined by the ratio of the adhesive strength of the joint to the strength of the fiber. Whereas $n_{\sigma} = 0$ for Terlon, in the case of SHP several percent of the specimens failed through the fibers. The number of specimens that failed adhesively n_{τ} was considerably less than n_{τ} with the changeover to the weaker Phenylone fibers. Thus, the true mean adhesive strength for Phenylone and SHP was calculated with the following correction [1]: $\tau_0 = \bar{\tau} + \Delta\tau$.

It can be seen from the table that the investigated thermoplastic materials adhere sufficiently strongly to the aromatic polyamide fibers. Although not as great as the adhesive strength of joints between similar fibers and thermosetting plastics (given a comparable contact geometry), the resulting values of τ_0 (33-46 MPa) are comparable to the bond strength in systems consisting of a thermosetting plastic and a carbon (glass) fiber [1]. The bonds of both thermoplastic materials with the SHP fibers turned out to be the strongest, while

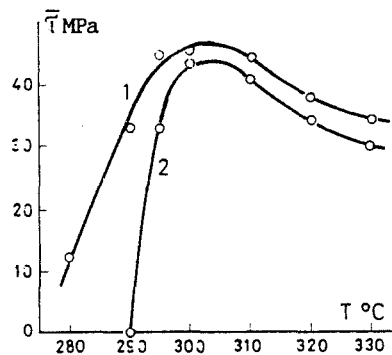


Fig. 2.

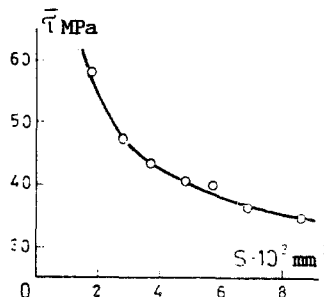


Fig. 3

Fig. 2. Effect of the temperature of formation of joints between a thermoplastic material and SHP fibers on the adhesive strength of the joint: 1) PC; 2) PSF ($S_{av} = 3.8 \cdot 10^{-3} \text{ mm}^2$).

Fig. 3. Dependence of adhesive strength on the area of the joint for a system consisting of PSF and an SHP fiber. $T_f = 300^\circ\text{C}$.

the bonds with Phenylone turned out to be the weakest. It is typical that the values of τ_0 in the joints with PC and PSF differ little for each type of fiber. This is evidently connected with the similar chemical structure of the thermoplastic materials, which are aromatic polyesters. Whereas the reason for the strong adhesion of thermosetting plastics is believed to be their formation of chemical bonds with the surface of fibers [1], in the present case the main role is evidently played by Van der Waals interactions and hydrogen bonds between NH-groups of fibers and ester groups of the thermoplastic materials, i.e., the adhesion is of a physical nature.

The above-cited values of τ_0 characterize the interaction of the binders with a clean fiber surface. However, organic-fiber-reinforced plastics are often made using fibers in the condition received, i.e., when the fibers are coated with a lubricant and other processing substances. The adhesive strength of joints of thermoplastic materials with untreated fibers is somewhat lower than was established above (see Table 1). The greatest reduction in τ_0 (by 12%) is seen for joints between PSF and SHP fibers from a batch containing a large amount of lubricant - 3% of the weight of the fibers. A similar effect was described in [1] for thermosetting fibers and is due to the fact that inert substances inhibit the formation of bonds between the fibers and the matrix.

The formation of an adhesive joint in systems consisting of a thermoplastic material and a fiber is influenced to a considerable extent by the viscosity of the binder melt and, thus, the temperature at which the contact is formed T_f . It turns out that the dependence of τ on T_f is extreme for both polymers (Fig. 2). The ascending part of the curves reflects the increase in adhesive strength due to an increase in the actual contact area resulting from a reduction in the viscosity of the melt. Thus, although PSF forms a drop on the surface of the fiber at 280°C , almost no adhesive joint is formed ($\tau = 0$). The reduction in τ at $T_f > 300^\circ\text{C}$ is evidently attributable to the increase in thermoelastic stresses in the joint accompanying its cooling to room temperature [1]. It can be assumed that adhesive strength will reach the maximum values possible for the given system under the conditions normally present during the manufacture of organic-fiber-reinforced plastics - under pressure at a temperature $T_f < 300^\circ\text{C}$.

Figure 3 shows the dependence of τ on the area of the joint for PSF-SHP-fiber system. As in the case of thermosetting plastics [1], an increase in the contact area S is accompanied by a marked reduction in adhesive strength due to an increase in residual stresses. A similar relationship was established for all of the investigated pairs of thermoplastic materials and fibers, which shows the need to allow for the scale factor for all types of binders - regardless of their type - at $T < T_b$.

Conclusion. A method was developed for determining adhesive strength in thermoplastic-material-thin-fiber systems formed from a melt. Values of τ_0 were determined for joints between PSF and PC On the one hand and high-modulus organic fibers on the other hand. We studied the dependence of the bond strength on the temperature at which the contact is formed,

the area of the contact, and the condition of the surface. The adhesion of PC and PSF to organic polyamide fibers is good enough to make it unnecessary to develop adhesives or specially modify the fiber surfaces for the production of organic-fiber-reinforced plastics. The low shear strength of laminated plastics based on thermoplastic resins is evidently due to the small area of actual contact, which is in turn a consequence of the poor wetting and impregnation of the fiber filler by the melt.

LITERATURE CITED

1. YU. A. Gorbatkina, Adhesive Strength in Polymer-Fiber Systems [in Russian], Moscow (1987).
2. D. Matsui, "Adhesive strength of carbon-fiber-reinforced plastics," *Kyoka Purasuchikkusu*, 31, No. 10, 489-495 (1985).
3. V. A. Dovgyalo, O. R. Yurkevich, S. N. Zinov'ev, and K. P. Pomerantseva, "Production and properties of materials based on a dispersed polymer binder and a reinforcing filler," *Izv. Akad. Nauk BSSR Ser. Fiz. Tekh. Nauk*, No. 4, 28-31 (1985).
4. V. A. Dovgyalo, S. N. Zinov'ev, K. P. Pomerantseva, and O. R. Yurkevich, "Effect of prepreg production practice on the structural properties of carbon-fiber-reinforced plastics," *Dokl. Akad. Nauk BSSR*, 30, No. 3, 237-239 (1986).
5. B. Chabert and G. Nemoz, "Influence of fibre surface and fibre-matrix interface in composite properties," *Proc. Symp. High Performance Fibers, Textiles and Composites*, Manchester (1985), pp. 123-141.
6. Yu. S. Lipatov, A. Yu. Filipovich, and R. A. Veselovskii, "Study of the boundary layers of epoxy adhesives and the potential for controlling them," *Vysokomol. Soedin. Ser. A*, 28, No. 11, 2259-2264 (1986).
7. A. Garton, W. T. K. Stevenson, and S. P. Wang, "The crosslinking of epoxy resins at interfaces. V. Amine-cured resins at carbon and graphite surfaces," *J. Polym. Sci. Polym. Chem. Ed.*, 26, No. 5, 1377-1391 (1988).

EFFECT OF PARAMETERS OF THE DISTRIBUTION OF THE LENGTH AND ORIENTATION OF SHORT FIBERS ON CHARACTERISTICS OF THE DYNAMIC VISCOELASTICITY OF A POLYMER COMPOSITE

Yu. A. Dzenis and R. D. Maksimov

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The study of the dynamic viscoelastic characteristics of filled composites is an important direction being taken in research into polymeric composite materials (CM) [1-3]. It is known that the introduction of short fibers into the polymer matrix leads to a change not only in the elastic properties of the composite, but also its dissipative properties [4]. It was shown in [5] that the length of the reinforcing fibers has a substantial effect on the dynamic characteristics of CM's. The authors of [6-8] established that the component E' of the complex modulus and the loss tangent of the materials are dependent on the ratio of the dynamic loading directions and the orientation of different fillers. Nevertheless, the technology used to make products composed of composites generally leads to crushing of the fibers. As a result, the length l of the reinforcement in a CM is characterized by a broad statistical distribution $f(l)$. The method used to convert the materials into a product may also have a large influence on the distribution of the orientation of short fibers, thus accounting for anisotropy of the material properties. The authors of [9, 10] studied the effect of parameters of the distributions of fiber length and orientation on the elastic characteristics of short-fiber CM's. The goal of the present investigation is to study the effect of the volume content, mean length, length distribution, and orientation distribution of fibers on the complex dynamic characteristics of a polymer composite.

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