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THERMAL AND CHEMICAL STABILITY OF GLASS FIBERS WITH A BORON POLYMER PROTECTIVE COATING

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A new protective coating comprised of polymethylene-*n*-triphenyl boric acid ester, which increases the heat and chemical resistance as well as the strength of glass fibers used in the manufacture of fiberglass for different applications, is proposed.

Key words: glass fibers, protective coating, boron polymer, heat resistance, corrosive medium, unit tenacity.

The main problem of the development of new composite construction materials based on thermosetting matrices and reinforcing fillers is organizing an efficient interphase adhesion interaction between the components at an interface. As elementary fibers are formed their surface is coated with lubricants based on mineral oils, fatty acids, polyvinyl alcohol, and so on in order to improve the textile properties. However, lubricants sharply degrade the adhesion properties of fibers. For this reason, in the fabrication of composite materials, before the fibers are permeated with a binder, the lubricants are removed by washing in a solvent or by heat-treatment at temperature above the decomposition temperature of the material from which the lubricant is manufactured. For mineral fibers, such as glass fibers, preference is given to heat-treatment, where 0.05 – 0.10% of the solvent remains on the surface, while washing can reduce its content to only 0.3 – 0.6%. As a result of an increase of the surface energy the wettability of the heat-treated fibers increases sharply but in the process the residual stresses, arising at the fiber – binder interface because of the large difference in the thermoelastic properties between fiber and binder, increase considerably in the polymer composite material (PCM) fabricated from such fibers. To reduce these stresses and increase the adhesion strength of the components of the PCM the fibers are covered with protective coatings, viz., multifunctional compounds capable of interacting with the surface of the fibers and binder thereby forming chemical bridges which increase the strength of the composite [1].

A patent search showed that universal protective coatings for different types of reinforcing fibers do not exist. Each one as well as the form of the polymer matrix make their own contribution to the energy balance of the interaction of the components at phase interfaces and, correspondingly, to the energy balance of the decomposition of the corresponding composite material. For this reason, the search for new protective-coating additives capable of increasing the complex physical and chemical interconnectedness of the components at phase interfaces and, correspondingly, the strength of the manufactured plastics is unquestionably of great interest. In addition, since articles manufactured from them are often used in corrosive media and at high temperatures (drawing setups for vapors of non-oxidizing acids, measuring tanks, storage reservoirs for chemicals, piping for transporting vapors, petroleum products, and so on) preference should be given to protective coatings that increase the heat and chemical resistance of the treated fibers.

In the present work a boron polymer (polymethylene-*n*-triphenyl boric acid ester) synthesized at the Biisk Technological Institute was investigated for the protective coating of glass fibers. The results of [2], where this boron polymer was used to modify an epoxy anhydride binder in order to increase the physical and mechanical characteristics of construction-grade fiberglass, served as the justification for this. The protective effect was studied on roving comprised of RVMPN 10-420-80 grade glass fibers (elementary fiber diameter 9 – 10 μm, linearity 400 – 420 tex, unit tenacity 430 mN/tex). The lubricant was removed by heat-treating the fibers at 250°C for 1 h, after which its content was about 0.08%.[2]

For the investigations the roving was treated with a 1% solution of the boron polymer in ethanol and then dried to constant mass.

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[2] Here and below the content by weight, wt.%, unless stipulated otherwise.

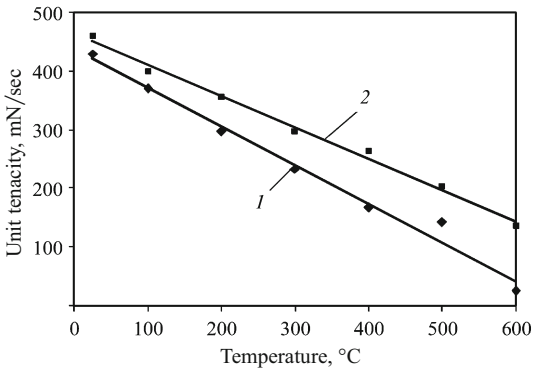

Fig. 1. Temperature dependence of the strength of the initial (*1*) and finish-coated (*2*) roving.

The effect of the protective coating on the heat resistance of the glass fibers was evaluated according to the change in their mass and unit tenacity in the temperature interval 100 – 600°C after soaking for 20 min at each set temperature.

The chemical resistance of the fibers was evaluated according to the mass and strength losses after exposure to distilled water and different corrosive media, viz., 2 N HCl and 2 N NaOH. The fiber mass giving total fiber surface area 5000 cm^2 was taken for the investigations. The weighed amount m in grams was calculated according to the relation

$$m = \pi d^2 l \rho / 4,$$

where d and l are the diameter and length of the fiber, cm, and ρ is the density of the glass, g/cm^3, measured by means of hydrostatic weighing.

The fibers were processed by boiling for 3 h in an appropriate reagent (250 ml) in a flask connected with a reflux condenser, after which the fibers were transferred onto a filter, washed with distilled water, and dried at temperature 110°C to constant mass and the percentage mass loss Δm was calculated. The chemical resistance U, %, was determined from the relation

$$U = \frac{m - m_1}{m} \times 100\%,$$

where m_1 is the mass of the sample after treatment in a corrosive medium, kg.

The R-0.05 rupture machine was used to measure the strength of the roving. The reinforcing material was prepared for the rupture tests as follows: the fibers were glued with spacing 10 mm from one another to millimeter paper; flat millimeter paper of height 20 mm was glued over the edges of the samples on both sides so that the working part of a sample was 70 mm long. The grips were set and supports were used to regulate the initial distance between them.

The tests were conducted with the lower grip moving at a constant velocity, which with the sample in tension must permit measuring the load to within no more than 1% of the measured quantity. The distance between the grips was set at 70 mm, which corresponded to the working length of the sample. The rupture load was taken as the arithmetic mean value of all the test results. The unit tenacity P_0, N/tex, was found from the relation

$$P_0 = P/T,$$

where P is the rupture load, N, and T is the linear density, tex.

It is evident in Table 1 that the glass fibers, losing up to 4.4% with increasing temperature, acquire after the protective coating is applied heat resistance comparable to that of the initial roving before heat-treatment.

The results of the strength tests also show the positive effect of the protective coat on the heat resistance of glass fibers (Fig. 1).

The strength loss of the glass fibers after heating is due to the fact that at elevated temperatures crystallization processes start to occur in the fibers [3]. According to the current understanding of the kinetics of crystallization this process occurs mainly on the surface of the fibers.

The strength of the coated roving is greater than that of initial roving in the entire experimental temperature range, and the difference in strength between them increases with increasing temperature (see Fig. 1).

The results of the determination of the chemical resistance U of glass roving on the basis of the mass loss after boiling in different corrosive media are presented in Table 2. It is evident that the chemical resistance increases after application of the protective coating.

The results of the strength tests presented in Table 3 confirm the data on the chemical resistance of glass roving.

The application of a protective coating to the glass roving, which significantly decreased the damage to the surface of the fibers, also decreases the effect of corrosive media on them.

TABLE 1. Heat-Resistance of Glass Fibers U, Determined from the Mass Change

Roving	Mass change, %, after heat-treatment as temperature, °C						
	25	100	200	300	400	500	600
Initial	100	99.90	99.83	97.73	97.70	95.87	95.65
Coated	100	99.98	99.90	99.30	99.39	99.29	99.32

TABLE 2. Chemical Resistance U of Glass Fibers

Glass roving	Index value after treatment in					
	H_2O		2 N HCl		2 N NaOH	
	Δm, g	U, %	Δm, g	U, %	Δm, g	U, %
Initial	0.0168	96.95	0.1650	66	0.0608	84
Coated	0.0141	98.28	0.1573	70	0.0519	90

TABLE 3. Strength of Glass Roving Before and After Treatment in Corrosive Media

Parameter	Parameter value					
	initial			finishing-coated		
	H_2O	2 N HCl	2 N NaOH	H_2O	2 N HCl	2 N NaOH
P, N	180.0 ± 3.2	96.8 ± 2.7	84.5 ± 2.5	222.7 ± 4.9	118.3 ± 3.3	103.1 ± 4.1
P_0, mN/tex	418.6 ± 7.4	225.1 ± 6.2	196.5 ± 4.8	517.9 ± 9.6	275.1 ± 6.4	239.8 ± 7.2

In summary, it was shown that the heat and chemical resistance and the strength of glass fibers can be increased by appliying the new finishing-coating: polymethylene-*n*-triphenyl boric acid ester.

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