Water resistance of polymer compounds

Водостойкость полимерных компаундов

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Abstract. Composite materials have high physical and mechanical properties, but their widespread use is hampered by a lack of tightness (impermeability to moisture and gases). Mainly this is due to the stress-strain state of the composite structure at the micro level as a result of a comprehensive extension of the polymer owing to the adhesion of the matrix to the fiber. The development of cracks and epoxy binder swelling causes its shrinkage and thus, may change the size of distribution and the internal stress patterns in glass fiber wool and lead to a partial disruption of adhesive bonds at the interface, formation of pores, cracks and other defects in the boundary polymer layer. Finally, it can be the reason of its partial detachment from the fibers’ surface. It should be noted that such changes depend mostly on the chemical structure and composition of the polymer binder. Watertight composite material development increases the possibilities of its using in many industries, including aerospace, shipbuilding, etc. In this paper the water resistance of polymer compounds was investigated by comparing the properties of the samples with modifying compounds based on epoxy resin. As a part of the study water saturation curves were determined for various compounds and curing agents, the optimal concentration of additives were measured. The results demonstrate the possibility of using of polysulfone as an additive in epoxy resin, improving the water resistance of fiber reinforced plastic.

Introduction

Currently, the most promising materials with their strength, elastic and other properties are polymer materials [1–3]. They are used in almost all sectors of the national economy, and especially in the construction [4, 5], the automotive industry [6, 7], the chemical industry, the energy sector [8]. Polymeric materials have high physical and mechanical properties, but their widespread use is hampered by a lack of tightness (impermeability to moisture and gases). Mainly this is due to the stress-strain state of the composite structure at the micro level as a result of a comprehensive extension of the polymer owing to the adhesion of the matrix to the fiber. The development of cracks and epoxy binder swelling causes its shrinkage and thus, may change the size of distribution and the internal stress patterns in glass fiber wool and lead to a partial disruption of adhesive bonds at the interface, formation of pores, cracks and other defects in the boundary polymer layer. Finally, it can be the reason of its partial detachment from the fibers’ surface. It should be noted that such changes depend mostly on the chemical structure and composition of the polymer binder. Watertight composite material development increases the possibilities of its using in many industries, including aerospace, shipbuilding, etc. In this paper the water resistance of polymer compounds was investigated by comparing the properties of the samples with modifying compounds based on epoxy resin. As a part of the study water saturation curves were determined for various compounds and curing agents, the optimal concentration of additives were measured. The results demonstrate the possibility of using of polysulfone as an additive in epoxy resin, improving the water resistance of fiber reinforced plastic.

materials are widely used in modern construction as a coverings of floors (linoleum, polyvinylchloride tiles, etc.), walls and ceilings, waterproofing materials, as well as in the manufacture of heat and sound insulation materials (porous plastics, foams), window blocks and doors, structural and finishing elements of buildings, varnishes, paints, enamels, adhesives, mastics (based on polymer binder) and for many other purposes.

The term “polymer materials” combines three large groups of synthetic materials: polymers [9], plastics [10] and their morphological variety – polymer composite materials (PCM) or, as they are also called, reinforced plastics [2, 11–13].

The binder (matrix) of the polymer composite material (PCM) performs the following functions: provides a material wholeness and promotes the uniform distribution of loads between the reinforcing elements that leads to inhibition of cracks growing, as well as transmission and distribution of stresses. It is matrix that determines the heat, moisture, fire and chemical resistance of PCM [14–16].

Ideal binder should have a high modulus of elasticity, relatively low elongation and high adhesion strength. One of the main requirements to the binder is to match the magnitude of its elongation in the solid state analogous to the deformation characteristics of the filler [17]. Elongation of polymer binder should be a little bit higher than one of the fiber [18]. When using carbon and glass fibers of large diameter (15–20 microns), the elongation is usually not more than 1.5–2%. The thin fibers (diameter is less than 10 microns) have considerably higher magnitude of elongation, which are 3–5%. Thus, the magnitude of the elongation of the binder should be in the range of 1.5–5% [16, 19].

The epoxy binders are widely used in the manufacture of structural parts from composite materials [20]. PCM on their basis are 15 times more durable than silicone ones and several times stronger than phenol based. The epoxy binders are slightly inferior to the epoxy phenolic ones in heat resistance [15]. The main advantage of epoxy resins is high adhesive strength, good manufacturability, low swelling and others [21]. However, epoxy resins are quite brittle, the magnitude of their elongation are typically less than 1% and therefore, it is very important to find effective ways to modify them to increase their deformation properties. Typical plasticizers, such as rubbers, can only a few improve toughness and crack resistance, however modulus and glass transition temperature are reduced by adding to material. One of the methods to significantly increase the deformation characteristics of epoxy resins, which do not cause their performance degradation, is the using of thermoplastics [22], they are added into the epoxy oligomer at its preparation stage and before injection of the herdening agent [23]. The most widely used thermoplastics are polyetherketones, polyetherimides [24–30] and polysulfones [31].

Polysulfone has a low degree of branching and stereoregular structure of macromolecules, but due to the high chain rigidity it is an amorphous transparent polymer. Polysulfone density is about 1240–1250 kg/m³, the glass transition temperature is 190–195 °C. The temperature of destruction is 420°C. Polysulfone is strong heat-resistant engineering thermoplastic with high toughness. Properties and sizes of products do not change in a wide temperature range; frost-resistance can be about 100 °C. This is chemical, water and petrol-resistant polymer. It has good anti-friction and dielectric properties; is non-toxic, and is sterilized by boiling. It is used in electrical engineering, mechanical engineering and medicine [10], and also in instrument making, machine-tool, diesel and automotive industry for the manufacture of structural, sealing and anti-friction parts operating at temperatures up to 150 °C [32, 33]. However, the possibility of polysulfone application to reduce the water permeability of material is poorly investigated [34].

Polyetherimide is an amorphous transparent (amber-transparent) polymer with high rigidity and strength even if continuously used at the temperature up to 170 °C. It has improved mechanical, electrical insulating and thermal properties in comparison with other transparent amorphous plastics, rigidity at high temperatures is higher than this one of many semi-crystalline high-temperature polymers (glass transition point is +216 °C in short-term operating temperature 200 °C). Polyetherimide has high inherent flame resistance without the addition of flame retardants and low smoke generation. Due to the excellent electrical characteristics and flame resistance it is often used for the manufacture of electrical and electronic insulators, contact strips, distributor hoods and other parts that require high strength and stability at elevated temperatures, and is also used in the manufacturing of the aircraft industry parts. Polyetherimide is physiologically inert. Good hydrolysis resistance and dimensional stability permit the use of polyetherimide not only in electrical engineering, but also in medical devices, for example, in analytical devices. Its density is 1270 kg/m³. Polyetherimide is chemically resistant to gasoline, oils, alcohols, weak acids. It has limited resistance to strong acids and is not resistant to alkalis.

Polyetherketone is a high-temperature thermoplastic polymer of taupe or brown-black colour. It differs by amount of ether and ketone groups. The main differences are the glass transition temperature and melting point due to increasing number of ketone groups of the polymer. The glass transition point is 160 °C, melting point is 335 °C, long-term operation temperature is 243 °C, short-term is up to 315 °C. In addition to resistance to high temperature and mechanical stress, polyether ketone has a very good chemical resistance, responds well to machining, has low water absorption and shows high dimensional stability. It is resistant to hydrolysis and hot steam. Polyetherketone density is about 1310–1320 kg/m³.

Epoxy resins (ER) take place in various industries as a basis for adhesives, mastics, coatings, compounds and reinforced plastics [21, 24]. Recently investigations are conducted, they relate to the high penetrating abilities of epoxy oligomers in porous materials with subsequent structuring with the influence of different hardeners and giving of unique compositional properties to the final composite [4, 6, 35].

In this paper the possibilities of polysulfone additives to modify ER in order to improve the operating properties of the final product in high humidity environments or in direct contact with water were investigated. Adding polysulfone in material is justified by its very low shrinkage, resistance to high temperatures, chemical resistance in comparison with other thermoplastics, and also high resistance to hydrolysis. Currently, using of the binder epoxy resin-thermoplastic for the manufacture of composite materials has not been systematically investigated, data on the physical and mechanical properties, as well as the effect of polysulfone on the water resistance of polymer compounds, are practically absent both in foreign and domestic literature.

Methods (Experimental part)

Epoxy resin ED-20 is a viscous light yellow liquid [36, 37]. After hardening, the products based on ER can be subjected to the appearance of cracks due to its low elasticity. So additives are required to modify the properties of ER [38-41]. Polyetherimide (PEI) and polysulfone (PSK-1) were selected as modified additives, which are added to the composition of the polymer compounds with different mass fractions, but not more than 20%. The introduction of modifiers into the polymer compound composition with a concentration more than 20% leads to a marked increase in viscosity and complicates the production process of creating composite materials. Also, the concentration limit of 20% was determined as the most effective for increasing the impact strength and fracture impact strength properties of composites [42], which may be an indirect indicator of the water resistance increase. These polymer compounds are produced with the addition of various hardeners: trietanolaminotitonate (TEAT) and diaminodifinilsulfone (DADFS).

The samples were prepared using the following technologies and the following composition (for example, sample №1):

1) 100g of resin Aradlite LY 556 containing 5 wt % of the PSK-1 (from the final weight of the polymer compound).
2) 90g of hardener Aradur 917.
3) 0.3g (6 drops) of accelerator Accelerator DY 070.
Curing took place in two stages in special silicone forms in the temperature cabinet SNOL 58/350:
Stage 1. Incubation for 3 hours at 90 °C.
Stage 2. Incubation for 12 hours at a temperature of 120 °C.

By similar techniques 13 samples were made of the resins of various compositions. All samples have dimensions of 18mm x 7.5mm x 5mm.

Thus, 14 samples were obtained:
1. 5 wt % PSK-1 TEAT; 6. 5 wt % PSK-1 DADFS;
2. 10 wt % PSK-1 TEAT; 7. 10 wt % PSK-1 DADFS;
3. 15 wt % PSK-1 TEAT; 8. 15 wt % PSK-1 DADFS;
4. 20 wt % PSK-1 TEAT; 9. 20 wt % PSK-1 DADFS;
5. Test ED-20 TEAT; 10. Test ED-20 DADFS;
11. 5 wt % PEI DADFS;
12. 10 wt % PEI DADFS;
13. 15 wt % PEI DADFS;
14. 20 wt % PEI DADFS;

After hardening each sample was placed in a sealed flask with distilled water and with index number corresponding to one of the above. During the 3 months before the full water saturation the weight of samples was measured. On the basis of the increase in weight, water saturation weight was determined for each sample.
As a result of the experimental work water saturation values (ΔM/M) in time (T) were measured for each sample, the time of full water saturation of samples (T1) was determined. At the time of full water saturation of the samples the optimal additives concentration (C) for different hardeners was determined.

The experimental data was summarized in the tables and graphs were constructed on their basis (Figs. 2–5).

Figure 2. Water saturation of 14 samples - time graph
For each sample, water saturation – time graphs; water saturation - time logarithm graphs; water saturation – concentration (mass content) of additives in polymer compounds were constructed. As the examples of these graphs the data of 4, 5, 6, 10 and 12 samples are considered.

Figure 3. Water saturation of 4, 5, 6, 10, 12 samples - time graph

After analyzing water saturation-time data of the samples the most water resistant compounds were identified. As a result of water saturation – time logarithm graphs analysis, the moment of total water saturation was determined for all samples, which was 69-76 days (of 90 days), depending on composition. For total water saturation time the full water saturation – concentration (mass content) of polysulfone and polyetherimide graphs (Fig. 5) was plotted.

**Results and Discussion (Analysis of the experimental data)**

The program of the investigation includes 14 samples. The basis of all the samples was the epoxy resin ED-20 with the addition of two hardeners TEAT and DADFS. As modified additives PSK-1 and were added to the polymer compounds at various concentrations from 5w% to 20w%.

As a result of this experiment the total water saturation data of the samples (Table 1) was gathered. The standard deviation is 0.00001.

**Table 1. The experimental data. The full water saturation of samples**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Water Saturation (ΔM/M)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.176</td>
<td>1.840</td>
<td>1.262</td>
<td>0.907</td>
<td>1.102</td>
<td>1.237</td>
<td>1.417</td>
<td>1.351</td>
<td>1.439</td>
<td>1.017</td>
<td>1.534</td>
<td>1.457</td>
<td>1.558</td>
<td>1.563</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 shows the samples No. 5, No. 10 have sufficiently good water resistance despite the thermoplastics were not being injected in their composition. Among the samples with the addition of polysulfone (PSK-1) and trietanolaminotitonate (TEAT) №4 composition, which contained 20 % of polysulphone, had the highest water impermeability (Table. 1, Fig. 5). Among the samples with the addition of the polysulfone and diaminodifinilsulfone (DADFS) №6 composition, which contained 5 % of polysulfone, had the highest water impermeability (Table. 1, Fig. 5). Among the samples with the addition of polyetherimide (PEI) and diaminodifinilsulfone (DADFS) №12 composition, which contained 10 % of polyetherimide, had the highest water impermeability (Table. 1, Fig. 5).

Analyzing the graph of water saturation - concentrations of additives in the polymer (Fig. 5) we can notice that the water impermeability of the samples with added DADFS hardener is reduced by increasing weight content of polysulfone and polyetherimide additives. At the same time, the water resistance of the samples with added TEAT hardener is increased by increasing of polysulfone weight content. It is important that when we add TEAT hardener the water saturation – polysulfone concentration curve is at extreme if the polysulfone contents is 10 %, and is the least water resistant composition of the test samples.

In the paper [39] the problem of fracture strength of epoxy binders, modified with polysulfone and furfuralacetone resin, was considered. In the article [40], the influence of modifiers (polysulfone and / or carbon nanotubes (CNTs)) on the properties of organoplastics was investigated. The fracture strength and impact strength of reinforced plastics were considered. The article [41] presents data of the PEI and PSC-1 effects on the properties (fracture strength and impact strength) of epoxy binder based on ED-20. Thus, in the above studies [39–41] it was shown that the introduction of thermoplastic modifiers, such as PSC-1, PEI in epoxy resins, increases the fracture strength and impact strength of polymer compositions, that can be considered as an indirect indicator of increasing water resistance. In these studies, the water resistance of the polymers was not directly researched.

Conclusions

The result of this investigation is the determination of the water resistant composition and optimum concentration (weight content) of thermoplastic in polymer compound in order to increase the water resistance of reinforced plastics. The most water resistant sample No. 4 was identified with such composition: “20 %wt of the PSK-1 TEAT.” Thus, the resulting effect of polysulfone 20 %wt application as the additive in epoxy resin permits the use of this thermoplastic material for the manufacture of composites and its application in high-humid conditions.

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