The influence of modification on the properties of epoxy anhydride binder and microplastic based on it

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SUMMARY
An investigation was made of the modifying effect of epoxy oligomer and elastifier (rubber) on the properties of epoxy anhydride binder. The boundary values of modifier content that ensure the most satisfactory combination of processing and mechanical characteristics were determined. A positive effect from modification of the binder was realised in microplastic on basalt roving.

Binders based on epoxy oligomers, owing to their valuable combination of processing and service properties, have been widely used in the production of polymer composites. The compositions of the epoxy binders are constantly being improved for the purpose of increasing their elastic strength characteristics and heat, fire, and cracking resistance, reducing their water absorption, and so on.

The properties of epoxy oligomers are chiefly influenced by their molecular weight [1]. A high molecular weight of the oligomer leads to a reduction in the gelation time and shrinkage during curing, and to an increase in the physicomechanical properties, but in this case its viscosity increases. During curing, low-molecular-weight (low-viscosity) oligomers form densely crosslinked rigid polymers with increased brittleness and low cracking resistance. Therefore, in spite of the existence of a wide range of epoxy oligomers of different composition and properties, it is difficult to produce a low-viscosity polymer matrix possessing an elastic structure after curing.

A promising approach to creating binders with prescribed properties for polymer composites is the combined use of reactive oligomers with different molecular weights, and also their blends with monomers and polymers. This approach makes it possible in a wide range to vary the composition of the composites, to change their rheology, and to control the curing process, the shrinkage, and the phase structure.

The rheological properties of the binders have a considerable influence on the choice of regimes for the formation of polymer composites and the organisation of processes for their production. For high-quality impregnation of the reinforcing material, it is very important that the viscosity of the binder is low and hardly changes over the course of the entire time of its processing. According to literature sources [2, 3], the optimum viscosity \( \eta \) of thermosetting binders for the manufacture of articles by the method of ‘wet’ winding, which includes a stage of impregnation of the reinforcing filler, lies in the range 0.1–1 Pa s. The life of the binder \( t_1 \) is characterised by the time of increase in viscosity at processing temperature from its initial value to a value with which its use is still possible.

In this work, in the composition of binders for basalt-fibre-reinforced plastic winding articles, these parameters were adopted as the criteria for assessing the processing characteristics.

To determine the life of the binder, use was made of an RVTs-K90R1 digital rotation viscometer with a measuring cell consisting of a rotating inner cylinder and a stationary outer, thermostat-heated cylinder. During rotation of the inner cylinder placed in the investigated liquid, a moment of resistance arises that is transformed into a numerical value.
The mechanical characteristics were assessed from the tensile strength of the specimens \( \sigma_1 \) in accordance with GOST 11262-80 on an R-05 tensile testing machine with a maximum loading limit of 5 kN, a scale factor of 0.01 kN, and a force gauge error of ±0.1%.

In the tests, the load and the elongation of the specimen were measured continually or at the moment of failure of the specimen. The testpieces, in the form of plates of 150 mm length and 10 ± 0.5 mm width, were manufactured by casting the binder into moulds, with subsequent curing at a temperature of 150°C for 2 h. The testpiece, with a length and width of the working zone of 60 ± 0.5 mm and 10 ± 0.5 mm respectively, was fastened in the clamps of the tensile testing machine and subjected to an increasing load at a clamp speed of 20 mm/min until its failure. From the scale, the magnitude of the load at which failure occurred was noted, and at the same time the magnitude of the tensile strain (elongation) of the material was recorded.

The tensile strength was calculated by means of the formula:

\[
\sigma_1 = \frac{F}{A_0}
\]

where \( F \) is the load at the moment of failure, N, and \( A_0 \) is the initial cross-section, m².

The relative strain, %, was defined as:

\[
\varepsilon = \frac{\Delta l}{l_w} \times 100\%
\]

were \( \Delta l \) is the elongation at break, and \( l_w \) is the length of the working part, m.

The microplastic was prepared on a laboratory stand consisting of a stand with two strand tensioners, a heated dipping bath with a thermometer, a wringer, a strand separator, and a receiving frame. Roving from the packer, passing through the strand tensioners and the bath with the binder, entered the wringer, which made it possible to control the amount of binder in the microplastic, and then through the strand separator to the receiving frame, comprising two arms of 180 mm length, manufactured from aluminium rods of 15–20 mm diameter, rigidly connected to each other by the same tubes of 300 mm length. The roving spacing on the frame was 3 mm. After curing by the prescribed regime, the microplastic was removed from the frame and cut into segments of 130 ± 5 mm length. The microplastic was glued into a paper frame.

Mechanical tests were conducted on an R-0.05 tensile testing machine with a constant speed of the lower clamp, which, during elongation of the specimen should ensure load measurement with an error of no more than 1%. The distance between the clamps was set equal to 70 mm, which corresponded to the working length of the microplastic specimen. The speed of the moving clamp was determined on the basis of 3–4 preliminary tests such that the average duration of elongation of the specimen before failure was equal to 10 ± 2 s.

The breaking load of the microplastic was taken to be the arithmetic mean value of all test results.

The specific breaking load \( P_0 \) was calculated by means of the formula:

\[
P_0 = \frac{P}{T}
\]

where \( P \) is the breaking load, N, and \( T \) is the linear density of the roving, tex.

The initial (base) composition for the investigations was the epoxy anhydride binder EDI most frequently used in the production of glass-fibre- and basalt-fibre-reinforced plastics, with a ratio of the components epoxy resin (ED-20)/isomethyltetrahydrophthalic anhydride (IMTHPA)/2,4,6-tris(dimethylaminomethyl)phenol (UP 606-2) = 100/85/1 [parts], which ensured a viscosity at a temperature of 50°C of ~0.5 Pa s and a life of 3 h.

In the capacity of modifying oligomer, epoxy resin EA was examined – a product of the reaction of aniline with epichlorohydrin. Its use was predetermined by its low viscosity (0.27 Pa s at 25°C), high content of epoxy groups (33.8%), good compatibility with thermosetting bisphenol A resins, and capacity to be polymerised using the same curing agents.

Experiments showed that the introduction of EA changes little the initial value of viscosity, but has a considerable influence on the kinetics of increase in viscosity (Figure 1). The replacement of 10% ED-20 resin with EA makes it possible to lengthen the time for which the viscosity of the composite does not exceed 1 Pa s to 5 h instead of 3 h for the base composition.

From literature sources it is known that epoxy oligomers with anhydride curing agents form three-dimensional polymers in which the network density and the structure of the crosslinked points and the chains between them are determined by the composition of the oligomer and the type of curing agent [4, 5]. Low-viscosity resin EA (mainly containing monomer), being cured by IMTHPA, forms a polymer with an increased network density, which gives it higher strength and heat resistance, but greater brittleness (Table 1).

Increased brittleness can be avoided by creating a heterogeneous composite with elastic inclusions dispersed in the densely crosslinked glassy matrix. In it, the mass of cured polymer ensures rigidity and strength.
of the composite, while the elastic component, changing the nature of failure, promotes a reduction in brittleness and an increase in cracking resistance. In the case of an epoxy oligomer binder, a heterogeneous structure can be formed by introducing special modifying additives – elastifiers, which generally are flexible-chain oligomers and polymers capable during curing of forming a three-dimensional block copolymer with the epoxy oligomer, and are present in the cured binder in the form of an independent finely dispersed elastic or plastic phase.

In the capacity of the elastifier of the selected blend of resins, use was made of low-molecular-weight nitrile butadiene rubber of grade SKN-18-1A containing functional groups capable of interacting with epoxy and hydroxyl groups of the oligomers.

The introduction of the rubber into the binder EDI in fact ensured an increase in its elasticity in the cured state, but in this case there was an increase in the viscosity of the composite and a reduction in its life (Table 1).

The combined use of modifying additives made it possible to retain the viscosity of the composite at its original level and to increase the time of its processing (Figure 2). Here, the optimum, ensuring a satisfactory combination of processing and strength characteristics of the binder, is the component ratio $EA/SKN-18-1A = 10:5$.

The positive effect on strength that was achieved by modifying the binder was confirmed in plastic manufactured using different basalt rovings: the specific breaking load of the microplastic on modified binder increases by comparison with the base composition by 17–30% depending on the characteristics of the roving (Table 2).

### Table 1. The characteristics of the epoxy binders

<table>
<thead>
<tr>
<th>Content of additive, %</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta$, Pa s</td>
</tr>
<tr>
<td>EA</td>
<td>SKN-18-1A</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>—</td>
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<tr>
<td>10</td>
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<td>15</td>
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<td>—</td>
<td>2.5</td>
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<tr>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>7.0</td>
</tr>
</tbody>
</table>

### Table 2. The strength characteristics of basalt rovings and microplastics based on them

<table>
<thead>
<tr>
<th>Fibre grade</th>
<th>Roving</th>
<th>Characteristics</th>
<th>Microplastic</th>
<th>Modified composition of binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, tex</td>
<td>$P_0$, mN/tex</td>
<td>$K_r$</td>
<td>$P_0$, mN/tex</td>
<td>$K_r$</td>
</tr>
<tr>
<td>NRB 13-1209-KV-02</td>
<td>1200</td>
<td>404</td>
<td>570</td>
<td>1.4</td>
</tr>
<tr>
<td>RB 9-500</td>
<td>450</td>
<td>302</td>
<td>578</td>
<td>1.9</td>
</tr>
</tbody>
</table>
| a The coefficient of reinforcement $K_r$ is determined by the ratio of the specific breaking loads of the microplastic and roving.

![Figure 1](image1.png)  
**Figure 1.** The time dependence of the viscosity of the binders at a temperature of 50°C and with different contents of resin EA: 1 – 0%; 2 – 5%; 3 – 10%; 4 – 15%.

![Figure 2](image2.png)  
**Figure 2.** The time dependence of the viscosity of the binders at a temperature of 50°C and with different modifiers: 1 – 2.5% SKN-18-1A; 2 – initial; 3 – 10% EA + 5% SKN-18-1A; 4 – 10% EA + 2.5% SKN-18-1A.
CONCLUSIONS

Thus, the experiments conducted showed that modification of binder EDI by the combined use of epoxy oligomer EA and nitrile butadiene rubber SKN-18-1A ensures an increase in its physicomechanical characteristics with retention of the necessary level of viscosity for processing by the method of ‘wet’ winding for 4 h. Here, the conditions are created for increasing the strength of the basalt fibre in the plastic by a factor of 1.7–2.5.

REFERENCES