Carbon fiber plastics for vehicles manufactured by resource-saving formation technology

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Abstract The advantages of the technology of molding carbon plastics based on pre-pregs with separate application of components (SAC-technology) of epoxy binders cured by the mechanism of migration polymerization of epoxy cycles are presented. Using the methods of linear dilatometry and dynamic mechanical tests, the molecular mobility of the segmental and local types in polymer matrices of carbon fiber reinforced plastics based on traditional mixed pre-pregs and binary pre-pregs with separate application of components has been investigated. The question of the influence of the activation ability of an acid catalyst during the curing of an epoxy binder on the degree of decrease in internal stresses and the realization of an increased packing density of polymer chains in the polymer matrix of the composite is considered. The importance of choosing an acid catalyst for the curing of a polymer binder is shown, which for CFRP composites provides the necessary combination of elastic and dissipative properties. The use of the considered binders makes it possible to improve a number of important operational characteristics, especially in the case of the production of large-sized products: solidity, crack resistance, impact resistance, fracture toughness. These properties are very significant during the composite materials applying in transport engineering.

1. Introduction
The progress in the development of world mechanical engineering requires the necessity for widespread use of polymer composite materials (PCM), which have a low weight in combination with high specific strength characteristics. At the same time, the specifics of the manufacture of PCM products impose additional requirements on them in terms of manufacturing technology [1, 2]. The large-scale production of PCM products for vehicles requires a transition to a semi-finished technology - production on the basis of pre-impregnated reinforcing materials – pre-pregs. The use of pre-preg semi-finished technology in mechanical engineering makes it possible to increase its productivity, improve working conditions and enhance the production culture [3]. Intensification of the modeling process of products provides a high economic effect both due to the efficient use of autoclave equipment and due to energy-savings with a possible decrease in the molding temperature.

Its main disadvantage is the low viability of pre-pregs and limitations in the use of a number of binders, in particular binders with a high reactivity, providing the planned properties of composite materials [4].
One of the most effective technological methods for increasing the viability of pre-impregnated reinforcing materials – pre-pregs is the method of separate application of components (SAC) [5]. A characteristic feature of the processing of the resulting binary pre-pregs is that the mixing of the components occurs directly during the molding of the semi-finished product. The initial mixing of the components is achieved as a result of their joint filtration through the layers of reinforcing material under the action of the molding force throughout the volume of the semi-finished product. The completeness of the process of obtaining a composite will be determined by the completeness of the passage of the chemical interaction of the reactive groups of the binder components at the final stages of the physical structuring of the polymer matrix.

The main physicochemical feature of the process of forming a product by the method of separate application of components is a kind of frontal propagation of the curing process, in which the components of the binder-resin and hardening parts, fixed on various reinforcing elements, when the latter are joined during molding, they inter-diffuse against the background of a chemical reaction [6]. As a result, the chemical process already at the early stages is determined by the rate of interdiffusion of the components, and the diffusion process, in turn, at the later stages will increasingly depend on the intensity of the crosslink density growth. In the case of using epoxy reaction systems cured by the poly-addition mechanism, preconditions are created for the occurrence of an uneven distribution of components and, consequently, cross-link density gradient and physical parameters of the structure and realizable properties from its middle to the surface of the reinforcing filler. The combination of these factors affects the degree of homogeneity of the network structure of the composite matrix and means that when it is formed on the basis of SAC-pre-pregs, complete alignment of the components over the volume of the binder interlayer cannot be achieved and the process of formation of the structure of the polymer matrix is local in nature. Moreover, the degree of homogeneity of the structure will be the more disturbed, the greater the proportion of emerging regions of nonstoichiometric compositions.

As a result, it is of interest to conduct research on the development of composites based on SAC-pre-pregs using epoxy binders cured by the polymerization mechanism [7]. Since the polymerization of α-oxides in most cases is of a migratory nature, the completeness of mixing of the initial components, in our opinion, should not so effectively affect the degree of completion of the chemical structuring process, which is inherent in epoxy systems cured by the poly-addition mechanism (epoxyanhydride or epoxyamine).

2. Research methodology

The components of the binder were epoxy resin mark ED-20 (oligomer) with epoxy equivalents of ≈207 g/mol and an acid-type catalyst - a complex of boron trifluoride with an amine. The selection of the catalyst for the activation ability to epoxy resin was carried out by using amines of different reactivity. A number of amines are represented by the following compounds: aniline (I), para-toluidine (II), benzylamine (III), isophorone diamine (IV). A polymer composite based on T-2 carbon fabric of plain weave was prepared by impregnation with individual binder components: an alcohol-acetone solution of epoxy resin and an acetone solution of an acid catalyst. The latter was originally used as a 30 % solution in diethylene glycol.

After drying, the monolayers were cut, filled into a bag by alternating with a resin and an acid catalyst component, placed in a vacuum bag and molded in an autoclave according to the following temperature regime: 120 °C - 1 hour + 150 °C - 5 hours with compression parameters:
- rarefaction in the cover - 0.08 MPa;
- overpressure in the autoclave - 0.4 MPa.

Control (cast) samples of cured binders were obtained by pouring into a mold, holding for a day (until the solvents volatilized), followed by a polymerization regime similar to molding in an autoclave. The activation temperature of the curing of the compositions was determined by the method of differential thermal analysis on the Paulik-Paulik-Erdey system thermogravimetric analyzer at a heating rate of 1.3 deg/min. The magnitude of the residual stresses (σ_res) of the block samples was
determined by the tensometric method. The linear elongation of the sample was recorded using a
digital raster system at a temperature rise rate in the test chamber of 2 deg/min.

The degree of curing of the binder was controlled by the yield of the gel, the value of which
corresponded to the amount of the dry residue of the crosslinked polymer after extraction with boiling
acetone in a Soxhlet apparatus for 48 hours.

The tensile strength was determined on a tensile testing machine at a crosshead speed of 1 mm/min.

Dynamic mechanical tests were carried out in the mode of forced resonance oscillations of a
cantilever-mounted sample in the frequency range 20-200 Hz (Figure 1).

![Figure 1. Laboratory cell for dynamic-mechanical testing of polymeric materials.](image)

### 3. Main material and results

Since one of the main conditions for obtaining a high-strength composite is the achievement of
minimum residual stresses in it, the character of the change in $\sigma_{res}$ for the indicated binders is
considered in this work. It was found that a certain relationship is observed between the relaxation
properties of cast (block) samples of binders and the temperature-time conditions of their gelation. For
polypexides with a low activation temperature for curing, increased values of contact pressure were
observed. With an increase in the activation temperature, which is typical for the compositions
obtained in the presence of complexes of $BF_3$ with benzylamine and isophorone diamine, the level of
$\sigma_{res}$ decreases. However, after relaxation at room temperature for 60 days, the values of residual
stresses for the above compositions are practically equalized (table 1).

![Table 1. Influence of the substituent type in the complex on the $\sigma_{res}$ of epoxy binders.](image)

| Amine substituent of the $BF_3$ complex | Sol-fraction substance, % | Curing activation temperature, K | Gelation time at activation temperature, min | $\sigma_{res}$ | Relaxation degree of $\sigma_{res}$ |
|----------------------------------------|--------------------------|---------------------------------|----------------------------------------------|--------------|-------------------------------|
| (I)                                   | 9.4                      | 309-312                         | 2.5                                         | 10.8 / 6.5$^a$ | 0.398                         |
| (II)                                  | 7.6                      | 340-343                         | 7                                           | 9.7 / 6.9$^a$  | 0.289                         |
| (III)                                 | 7.1                      | 383-387                         | 9                                           | 9.2 / 7.4$^a$  | 0.196                         |
| (IV)                                  | 6.9                      | 392-396                         | 12                                          | 8.9 / 7.7$^a$  | 0.135                         |

$^a$ Numerator - after 1 day, denominator - after 60 days.
Analysis of the obtained data shows that the values of the stresses and the degree of their relaxation are uniquely determined by the type of catalyst. Thus, in the case of using catalysts with a low activation temperature, the content of the sol-fraction in the cured polymers is much higher than in the systems obtained at elevated temperatures. This unequivocally indicates that the conditions for additional packaging of structural elements of the polymerization web for polyepoxides with an increased gelation temperature deteriorate and, accordingly, the polymer material is characterized by a low relaxation ability.

The ongoing relaxation processes are reflected in a certain way on the nature of changes in the thermomechanical characteristics of composites (Figures 2, 3). Analysis of dilatometric data shows that, depending on the type of binder components used, there is a decrease in the linear expansion curve, the value of which decreases with an increase in the activation temperature of the reaction system and an increase in the glass transition temperature of the finished composite [8]. This operation of the composite is typical both for those obtained by the technology of separate application of (SAC) on the layer-preg, and for pre-pregs of the mixed type. Attention is drawn to the fact that the higher the degree of relaxation of internal stresses in block specimens (table 1), the higher is the magnitude of the decrease in the dilatometric curves of carbon fibers. It is known that epoxy polymers of the same type obtained under different temperature conditions can have different structures due to the fact that the proportion of the polymer with a non-equilibrium web formed at the stage of isothermal glass transition is not the same. Therefore, from our point of view, binders sewn at a relatively low temperature, the degree of non-equilibrium of the web should be higher. This parameter can be estimated by the indicators of relaxation spectrometry (table 2).

![Figure 2](image)

**Figure 2.** Dilatometric curves of carbon fiber, obtained by the mixed technology of binder applying, cured with a boron trifluoride complex with additive: 1 – aniline, 2 – para-toluidine, 3 – benzylamine, 4 – isophorone diamine.
**Figure 3.** Dilatometric curves of carbon fiber, obtained by the SAC-technology of binder applying, cured with a boron trifluoride complex with additive: 1 – aniline, 2 – para-toluidine, 3 – benzylamine, 4 – isophorone diamine.

**Table 2.** Relaxation properties of carbon plastics based on epoxy binders.

| Catalyst | Intensity index of the angle tangent of mechanical losses at characteristic temperatures | $G_{T_{C+50}} - G_T$, GPa |
|----------|--------------------------------------------------------------------------------------|-------------------------|
|          | at 293 K, β-transition, α-transition                                               |                         |
| (I)      | 0.008 / 0.006$^a$, 0.021 / 0.018$^a$, 0.071 / 0.066$^a$                          | 0.12 / 0.07$^a$         |
| (II)     | 0.008 / 0.005$^a$, 0.024 / 0.021$^a$, 0.077 / 0.073$^a$                          | 0.13 / 0.06$^a$         |
| (III)    | 0.011 / 0.009$^a$, 0.029 / 0.024$^a$, 0.085 / 0.081$^a$                          | 0.07 / 0.02$^a$         |
| (IV)     | 0.014 / 0.009$^a$, 0.036 / 0.024$^a$, 0.088 / 0.079$^a$                          | 0.05 / 0.02$^a$         |

$^a$ Numerator - CFRP obtained by the SAC-technology, denominator - CFRP obtained by the mixed technology.

So, taking into account the calculated value of the difference between the dynamic shear modulus in the highly elastic state of the composite ($G_{T_{C+50}} - G_T$) it is possible to indirectly characterize the material’s ability to achieve the limiting structural parameters after molding. Judging by this indicator, the conformational mobility of macromolecules increases to the highest extent when the curing of epoxy compositions is initiated at low temperatures. Since the conditions for cooling (in an autoclave) and heating of CFRP specimens during dilatometric research were constant, the presence of anomalies (in the form of “pits”) on these curves indicates a reduced degree of packing of polymer chains of the binder in the composite [9].

At the same time, it should be noted that the degree of mobility of kinetic units (fragments) of polymer chains of binders increases with an increase in the activation temperature of curing in molded composites [10]. Moreover, the effect of energy dissipation is more specific for composites obtained by the technology of separate application of components in the entire investigated temperature range. The combination of the presented indicators makes it possible to assume that the material has sufficiently high viscoelastic properties, which are responsible for its resistance to the action of loads,
both in the static mode and in the mode of shock loads. Thus, to obtain carbon plastics with a complex of stable indicators from the presented series, we can recommend those, in which the binder tends to polymerize in the autoclave molding mode at elevated temperatures - in the presence of complexes of boron trifluoride with benzylamine and isophorone diamine.

As can be seen from the data (Figure 4), the strength of carbon plastics obtained by the technology of separate application of the binder components is not inferior to those obtained by the mixed technology.

![Figure 4](attachment:image.png)

**Figure 4.** Dependence graphs of carbon plastics tensile strength on the amount of acid catalyst III (curves 1, 1') and acid catalyst IV (curves 2, 2') with SAC-technology (curves 1, 2) and mixed technology of binder applying (curves 1', 2').

Moreover, with an increase in the activation temperature of the curing process, which is typical for the polymerization of epoxycycles in the presence of a complex based on isophorone diamine, increased strength indicators are realized for CFRP.

Also, it should be noted that the amount of added catalyst does not significantly affect the strength of CFRP, which is provided by the weak dependence of the quantitative ratio of the components on the rate of migration polymerization of epoxycycles during the formation of the composite. This is the special appeal of this binder type and in fact guarantees reducing the likelihood of quasi-adiabatic overheating due to the use of small doses of the catalyst in the formation of large-sized objects from carbon fiber reinforced plastic.

Experimental data (table 3) shows the results of physical and mechanical tests of CFRPs based on selected epoxy binders obtained from pre-pregs using the technology of separate application of components and mixed type.

| Catalyst base          | Density, kg/m³ | Tensile strength, MPa | Specific tensile strength, 10³, m²/s² | Shear modulus, GPa | Specific shear modulus, 10⁶, m²/s² | Impact strength, kJ/m² |
|------------------------|----------------|------------------------|----------------------------------------|--------------------|-----------------------------------|------------------------|
| Benzylamine            | 1476 / 1489ᵃ   | 620 / 604ᵃ             | 42.0 / 40.5ᵃ                           | 39 / 39ᵃ           | 2.6 / 2.6ᵃ                        | 41.7 / 38.4ᵃ           |
| Isophorone diamine     | 1481 / 1497ᵃ   | 718 / 697ᵃ             | 48.5 / 46.6ᵃ                           | 41 / 41ᵃ           | 2.8 / 2.7ᵃ                        | 48.3 / 37.9ᵃ           |

ᵃ Numerator - from pre-pregs using a SAC-technology, denominator - from pre-pregs of mixed type.

As can be seen from the presented data (table 3), the strength of the polymer composite based on carbon fiber is largely determined by the technological properties of the binder, its wetting ability, which, in our opinion, is realized upon relatively long heating to the effective activation temperature of the binder during formation. To a greater extent, the improvement in strength and elastic properties is clearly manifested in the example of their specific indicators. Of particular interest is the fact that
composites obtained by the method of separate molding have increased impact strength. Moreover, with the transition from the curing catalyst from aromatic amine to cycloaromatic - isophorone diamine, the impact strength increases sharply, which is in full agreement with the intensity indices of the angle tangent of mechanical losses in the low temperature relaxation zone and normal conditions.

4. Conclusions
The proposed type of epoxy binder makes it possible to expand the range of available binder components within the framework of the considered technology and to carry out an almost waste-free production cycle for the manufacture of thick-walled composite sheet products for vehicles. It should be noted that the use of pre-pregs by the SAC-technology makes it possible to achieve not only significant technological advantages in comparison with mixed pre-pregs, which was the initial aim of developing a new technology. It is important to emphasize that their application can improve a number of important performance characteristics, especially in the case of the production of large-sized products: solidity, crack resistance, impact resistance, fracture toughness. These properties are very significant when using composite materials in transport engineering. The observed combination of elastic and dissipative characteristics of the obtained composites makes it possible to consider them in the future as functional elements for structural systems of various vehicles, taking into account the minimization of creep and relaxation processes in it.

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