Regulation of Mechanical Properties of Advanced PCM Products with the Aid of Catalysts

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Abstract. The article considers the problem of the effect of uneven curing caused by the temperature gradient across the thickness of the material on the anisotropy of the strength properties of polymer composite materials. The effect of catalysts on the curing of the epoxy binder EDT-69N, used for the manufacture of multilayer polymer composite materials, was studied. According to dielectric spectrometry, the accelerating effect of the selected compounds on the curing process of the EDT-69N epoxy binder during fiberglass molding has been proved. The possibility of controlling the curing process using catalysts to reduce the influence of the temperature gradient on the anisotropy of the strength properties of the matrix in the manufacture of polymer composite materials is shown.

1. Introduction

Recently, one of the most common and economically advisable methods of manufacturing Polymer Composite Materials (PCM) parts is the autoclave molding method. During the molding of polymer composite parts in an autoclave, the convective heating method is realized. The low thermal conductivity of the composite prevents the creation of a uniform temperature field over the cross section of the product and leads to primary curing of the more heated layers of the fitment. As a result of the temperature gradient, anisotropy of the strength properties of the PCM matrix appears through the thickness of the product perpendicular to the heating effect, the strength characteristics decrease, parts are distorted due to the formation of residual temperature stresses [1,2,3]. Recently, during manufacturing products from PCM, there are various ways to reduce the influence of these factors: assembly of parts by gluing together several prefabricated thin-walled parts, using double-sided heating during molding, controlling heating modes and time of the part exposure (step heating). However, these methods have disadvantages: an increase of time and labor-intensiveness of production, the complexity of the equipment and technological fitment.

The uneven curing of the composite can be eliminated by controlling the kinetics of curing the binder in different layers of the composite using inhibitors [4, 5,6] or curing catalysts.

This method does not require special equipment and fitment; also, it does not affect the time and manufacturing laboriousness of the product.

2. Materials and equipment

The aim of this work is to develop a method for regulating the anisotropy of the strength properties of structural glass-reinforced plastics through the thickness of the sample using catalysts curing.
In this study we used following materials: fiberglass plastic based on epoxy binder EDT-69N and structural fiberglass T-10, curing catalysts: dimethylbenzimine (DMBA), 2,4,6-tris(dimethylaminomethyl)phenol (UP-606/2), 2-methylimidazole, various aminotriazoles and benzotriazoles.

As the main hardener according to the recipe of the composition EDT-69N, the latent hardener of catalytic action 4,4'-bis-(N, N-dimethylureido)-diphenylmethane (hardener 9) is already included.

The activation mechanism of this type of compounds can be simplified as the decomposition of a hardener at a certain temperature into isocyanate and a secondary amine, which then participates in the process as a hardener of catalytic action [7,8]. As a result of the interaction reaction of the secondary amine with the epoxy group, a tertiary amine is formed, and after that the reaction proceeds via an anionic polymerization mechanism, which is more regulated than the cationic one. The resulting tertiary amine is the Lewis base. To promote further reaction for Lewis bases, it is necessary that the resulting tertiary amine has a significant electronegative charge and be a compound that does not experience steric impediments [9,10].

The catalysts proposed in this work are tertiary amines and strong Lewis bases that are capable of accelerating the further polymerization reaction of the epoxy composition. It was established experimentally that the activation energy of cure decreases (with increasing concentration) in the presence of DMBA, UP-606/2, 2-methylimidazole, confirming their catalytic ability.

Compounds, selected for the study, have good solubility in the binder, which eliminates its dilution and, consequently, the deterioration of rheological characteristics. Due to its catalytic properties and good solubility, the above compounds can be used as promising catalysts in PCM technology.

The process of curing a sample of a thick-walled product made of a polymer composite material was carried out in a laboratory autoclave having the hardware design shown in Figure 1. Curing took place on a single-stage technological mode: heating to 122 ± 2 °C with a heating rate of 2 deg/min for an hour and holding for 4 hours with a pressing pressure of 4 atm.

![Figure 1. Hardware design of the laboratory autoclave.](image)

To study the kinetics of the curing process, we used the method of dielectric spectrometry (Figure 2).
Using the measuring complex, the dependences of the dielectric loss tangent from time of curing in the presence of catalysts were obtained, which reflect the change in the curing rate in the resulting samples.

The advantage of this method is its applicability to any composite materials, the possibility of obtaining information about the depth of transformation in the technological cycle of the curing process, the accuracy of determining the completion of the curing process.

The criterion by which the curing process of the binder is considered complete is the constancy in time of the dielectric characteristics of the curable material. The obtaining of constant values of the tangent of dielectric loss angle characterizes the deep stages of the macromolecules cross-linking into a three-dimensional structure.

As sensors, flat measuring cells in the form of two metal plates of circular shape were used, between which a sample (dielectric) was placed (Figure 3).

A thick-walled sample was molded from 15 layers of prepreg, the total number of measuring cells was five, and thermocouples were located above and below the sample. The schematic of sample placement into an autoclave is shown in Figure 4. All layers of fiberglass cloth were divided into 5 conditional layers: each conditional layer consisted of 3 layers of fiberglass cloth. Each conditional layer was manually impregnated in a clean binder. The upper conditional layers were impregnated with a solution of a binder with a catalyst.

3. Results of research of curing samples kinetics
The results of our research of curing glass fiber plastic samples kinetics in the presence of catalysts using dielectric spectrometry are shown in Figures 5-7.

For pure samples without the introduction of kinetic modifiers, the temperature of the lower layer on the heat supply side is higher than the temperature of the upper layer of the sample at each specific point of time. In this case the dielectric loss angle ($\tan \delta$) passes through a maximum. At this point, the epoxy binder converts from the liquid state into the glassy. As a result, the temperature difference between the curing rates in the layers is different, which is confirmed by the mixing of $\tan \delta$ maxima on time in different layers [2, 3].

Graphs in Figures 5–7 show that the curing processes in the layers with a pure binder flow slower than in layers with the addition of a catalyst, the introduction of which shifts the point of
gelation in the region of smaller time values. The aim of this work was to select certain concentration of
catalysts for which the difference in the time of gelation onset (maxima in the curve $\tan \delta = f(t)$) of the first and
last cured layer of prepreg will be minimal. Thus, the peaks on the curve $\tan \delta = f(t)$ for the first and last cured
layer of the prepreg should coincide in time.

Figure 5 shows that in the sample with a concentration of 0.25% DMBA in the upper conditional layer, the
peaks corresponding to the gelation temperature of the 1st and 5th layers coincided. For UH-606/2, the
optimal concentration was 0.35% of catalyst (Fig. 6). For 2-methylimidazole, the same curing rate for the 1st
and in the 5th layer was set for a concentration of 0.5% (Fig. 7).

This confirms that the introduction of dimethylbenzylamine, UP-606/2 and 2-methylimidazole allows to
achieve simultaneous curing of the binder in layers of PCM without disrupting the technological process.

The anisotropy of the matrix during the curing process occurs due to the different curing speed of the
binder through the thickness of the sample, which is due to the presence of a temperature gradient.
Therefore, it can be estimated by finding the strength ratio in the two-sided bending test of samples.

During testing the material for bending, part of it is subjected to stretching (reinforcing fiber filler), and
another part is subjected to compression (epoxy matrix). In bending tests, the strength of fiberglass plastic is
determined mainly by the properties of the matrix, i.e. it bears the main load. Therefore, the change in
flexural strength allows us to estimate the effect of the temperature gradient on the mechanical properties of
the matrix [2, 3, 11].

Two-sided testing of samples for static bending according to GOST 4648 was performed with the
application of a load from the inside and outside of the fitment (with temperature T1 and T2, respectively)
(Fig. 8-10).
The anisotropy of strength was estimated as the ratio of the values of the flexural strengths for a versatile load application. The closer the value is to one (Fig. 11), the less the matrix anisotropy will be expressed, the more isotropic the material.

The test results showed that the introduction of 0.25% of dimethylbenzylamine, 0.35% of UP-606/2 and 0.5% of 2-methylimidazole into the upper layer of the composite reduces the anisotropy of the matrix and, moreover, increases the strength of the composite bending in general. In addition, Figure 11 shows, that the optimum concentration of the catalyst at which the anisotropy of strength is minimal is 0.3-0.4%, which is confirmed by experimental data.

4. Summary
Based on a data of previous researches, it has been established that the use of catalysts allows controlling the curing process of the epoxy composition EDT-69N, providing control of the curing rates of the polymer composite material. Uniform curing of the composite material reduces the negative effect of the temperature gradient during the convective heating process in the process of autoclave molding of parts made from PCM.

The use of curing catalysts: dimethylbenzylamine, UP-606/2 and 2-methylimidazole allows to obtain PCM with higher strength, reduces the anisotropy of the strength properties of the matrix caused by thermal stresses during shaping. Reducing the anisotropy of the physical-mechanical properties of the matrix helps to reduce internal stresses in parts made of PCM, also it reduces distortion of parts due to the effect of residual stresses.
Therefore, curing catalysts for regulating the anisotropy of parts made from PCM, can be used in autoclave molding technology for the manufacturing of parts made from PCM.

References
[1] Kerber M L, Vinogradov V M, Golovkin G S et al 2008 Polymeric composite materials: structure, properties, technology: studies manual (St. Petersburg)
[2] Mikhailin Yu A 1996 Requirements for structural PCM matrices (Ufa: USATU)
[3] Vinogradov V M 1995 Production technology of prepregs for PCM (Ufa: USATU)
[4] Chuzhkov M V, Telesh V V, Voitov V N Study of the occurrence of inhomogeneities in glass-reinforced plastics during curing by dielectric spectrometry Bulletin of the GOUVPО "KnAGTU" vol 5 1 pp172-175
[5] Chuzhkov M V, Telesh V V, Voitov V N Study of the effect of the inhibitor on the curing process of epoxy binder EDT-69N Bulletin of the GOUVPО "KnAGTU": vol 5 1 pp 176-179
[6] Mouritz A P 2012 Introduction to Aerospace Materials Woodhead Publishing Limited
[7] Deborah D L 2010 Chung, Composite Materials: Science and Applications Engineering Materials and Processes Springer Science & Business Media
[8] Wang S S, Fitting D W 1993 Composite Materials for Offshore Operations: Proceedings of the First International Workshop, Houston (Texas)
[9] Li H, Neville K M 1973 Epoxy Resins Resource Guide Energy
[10] 1983Hardeners for epoxy resins Survey information (M.: NITEKHIM)
[11] Rana S, Fangeiro R 2016 Advanced Composite Materials for Aerospace Engineering: Processing, Properties and Applications Woodhead Publishing