Simulation of the kinetics of the curing process of polymer composite materials based on epoxy binders

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Abstract. This article investigated the kinetics of the curing process of composite material based on epoxy binders under different conditions of heat transfer. A technique for determining the heat capacity and thermal conductivity depending on the degree of cure of epoxy binders was carried out. The kinetic parameters of the binders used to describe the exothermic effects of binders in the chemical reaction were determined. Taking into account the phase state changes and their exothermic effects of the binders during curing, the simulation of curing process of glass fiber reinforced plastics (GFRP) was carried out. Experimental results of determination of heat capacity, thermal conductivity and kinetic parameters of epoxy binders were used as initial inputs for modeling the curing process of polymer composite materials. The influence of the heat transfer coefficient on the temperature state of GFRP was investigated. It was found that the heat transfer condition strongly affects the temperature state of fiberglass during their curing.

1. Introduction
Modern glass fiber reinforced plastics (GFRP) and carbon fiber reinforced plastics (CFRP) are used as structural materials in the manufacture of products in mechanical engineering, aviation, aerospace and many other industries [1-3]. It is known that technological errors can be inherited, but for parts made of composites based on thermosetting binders, their quality is finally formed during the technological operation — curing [4-6].

The problem of studying the kinetics of curing processes is given much attention, especially in the development of the technology for forming large-sized and complex geometrical shaped products, in which the curing processes proceed unevenly, is solved [7-10]. In the technical literature [11-12], the study of the temperature field of products in the curing process of epoxy (and other thermosetting) materials only in the solid aggregate state is given. The researchers do not take into account the kinetics of changes in thermal properties during heating, which leads to a large error in the study of the temperature state of parts from GFRP during their curing. The curing of polymer composites is carried out, as a rule, in autoclaves or electric furnaces [13-15]. With different heating technologies during curing, the heat transfer coefficients vary from 5 to 200 W/(m²·K). For conditions of free air convection, the heat transfer coefficient is 5-25 W/(m²·K). In forced convection, the heat transfer
The coefficient is 10-200 W/(m²·K). In the process of curing GFRP products, heat transfer conditions between the environment and the sample must be taken into account. The aim of this work is to study the curing process of products taking into account the phase change and exothermic effects of the binders in the curing process under different convection conditions.

2. Determination of the thermophysical properties of resins
As an object of research used epoxy binder hot curing, consisting of an epoxy resin and a hardener based on aromatic amine.

In the process of curing composite materials based on epoxy binders, the thermophysical properties of the binders vary depending on the degree of cure. The heat capacity (Table 1) of the binders, depending on the curing degree, is determined by the differential calorimeter method. The thermal conductivity (Table 1) of the binders, depending on the degree of curing, is determined by the laser flash method. The feature of these tests was the use of a sample in a liquid state, which did not allow to withstand the required dimensions. In addition, the composition used is an optically transparent material for laser radiation. A special crucible was used to measure the thermal conductivity of the material in the liquid state of aggregation.

| Degree of curing, % | \( C_p, J/(kg·K) \) | \( \lambda, W/(m·K) \) |
|---------------------|----------------------|------------------------|
| 0                   | 1973                 | 0.08                   |
| 5                   | 1973                 | 0.08                   |
| 16                  | 1921                 | 0.14                   |
| 28                  | 1820                 | 0.19                   |
| 75                  | 1406                 | 0.22                   |
| 87                  | 1338                 | 0.25                   |
| 100                 | 1300                 | 0.27                   |

It is established that with increasing the degree of curing the heat capacity increases and the thermal conductivity decreases.

3. Determination of cure kinetic parameters of resins
To study the thermal effect of the chemical reaction during the curing of the binders, a differential scanning calorimeter (DSC) was used. Using the DSC method, the curve of the thermal effect of epoxy binders was obtained for different heating rates of 1, 2, 3, 5 K/min (Figure 1). The amount of heat during the chemical reaction is determined by the peak area of the DSC curve.

![Figure 1. DSC curve at the heating rate of 1 K/min (1), 2 K/min (2) 3 K/min (3), 5 K/min (4).](image)
The equation for describing the curing process of these binders is:

$$ C \frac{d\beta}{dT} = A \exp \left(- \frac{E}{RT} \right) \beta^m (1 - \beta)^n $$

(1)

where $C$ – heating rate in the curing mode, K/s; $\beta$ – degree of curing, %; $m$, $n$ – the orders of the chemical reaction; $A$ – frequency factor, s$^{-1}$; $E$ – activation energy, J/mol; $T$ – absolute temperature, K; $R$ – universal gas constant, J/(mol·K).

The activation energy for epoxy resin is defined by equation Kissinger-Akahira-Sunose (KAS)

$$ \frac{d}{dt} \ln \left( \frac{\beta}{T_p^2} \right) = - \frac{E}{R} $$

(2)

where $T_p$ – temperature at the peak of the DSC curve, K.

The kinetic parameters of the binders used were determined from the equations for describing the curing process (1) (2) and the results of DSC (Table 2).

| Parameter                      | Value  |
|--------------------------------|--------|
| Activation energy $E$, J/mol   | 61844  |
| Frequency factor $A$, s$^{-1}$ | 3.6$ \times $10$^4$ |
| $m$                            | 0.12   |
| $n$                            | 0.62   |

The obtained kinetic parameters will be used to determine the exothermic effects of binders during the curing process.

4. Simulation of the curing process

During the curing process of composite materials, the thermophysical and kinetic properties of the binders, the efficiency of convection in the heat transfer process affects the temperature state of the sample. To analyze heat transfer during curing, the equations [19, 20] were used:

$$ \rho C_p(\beta) \frac{dT}{dt} = Q_a + Q_v + Q_x $$

(3)

$$ Q_a = \lambda_{xx} \frac{\partial^2 T}{\partial x^2} + 2\lambda_{xz} \frac{\partial^2 T}{\partial x \partial z} + \lambda_{zz} \frac{\partial^2 T}{\partial z^2} $$

(4)

$$ Q_a = \alpha (T_0 - T) \frac{S_h}{V} $$

(5)

$$ Q_v = \rho H_v \frac{d\beta}{dt} $$

(6)
where \( \rho \) – density of GFRC, kg/m\(^3\); \( C_p \) – specific heat, J/(kg·K); \( T \) – absolute temperature, K; \( t \) – time, s; \( Q_3 \) – heat flux with thermal conductivity, W/m\(^3\); \( \lambda_{xx}, \lambda_{xz}, \lambda_{zz} \) – thermal conductivity of anisotropic material, W/(m·K); \( Q_{\alpha} \) – convective flow to the free surface of the sample, W/m\(^3\); \( \alpha \) – heat transfer coefficient, W/(m\(^2\)·K); \( T_0 \) – the ambient temperature, K; \( \text{Sh} \) – the area of action of convective flow, m\(^2\); \( Q_v \) – heat dissipation, W/m\(^3\); \( H_r \) – the total amount of heat released during the curing process, J/kg.

The ESI PAM-RTM software was used to simulate the curing process. All calculations were carried out on samples with a size of 25x25x25 mm. As the initial data for modeling, the above determined results of the heat capacity of thermal conductivity and kinetic parameters were used. In the curing mode rate of temperature rise is 2 K/min. The curing process (Figure 2, 3) was simulated taking into account the change in the phase state and their exothermic effects of the binders in the ideal case, under conditions of free air convection (heat transfer coefficient: 10 W/(m\(^2\)·K)), with forced convection (heat transfer coefficient 20, 100 W/(m\(^2\)·K)). The temperature state depending on the curing time for different convection coefficients was shown in figure 2. The table 3 shows the temperature gradient under different heat transfer conditions.

![Figure 2](image_url)

**Figure 2.** The temperature field on the surface of the sample in the ideal case (1) (the given curing mode) and when the convection coefficient is 100 (3), 20 (5), 10 (7); the temperature field in the center of the sample in the ideal case (2) and when the convection coefficient is 100 (4), 20 (6), 10 (8).
Figure 3. The curing degree on the surface of the sample in the ideal case (1) and when the convection coefficient is 100 (3), 20 (5), 10 (7); the degree of curing in the center of the sample in the ideal case (2) and when the convection coefficient is 100 (4), 20 (6), 10 (8).

Table 3. The temperature gradient under different heat transfer conditions

| Option Number | Heat transfer coefficient (W/m²·K) | Maximum temperature gradient (°C) |
|---------------|------------------------------------|-----------------------------------|
| 1             | 10                                 | 16.2                              |
| 2             | 20                                 | 21.8                              |
| 3             | 100                                | 26.9                              |
| 4             | ∞                                  | 27.5                              |

It was found that in the first section of the curing process, the temperature on the surface of the sample is higher than the temperature in the center of the sample. Due to the exothermic effects of binders, in the third section of the curing process the gradient of the temperature at the surface and in the center of the sample decreases. At the temperature rise section of the curing mode there is a moment where the temperature inside the sample is higher than the temperature on the surface of the sample. The temperature of the sample reaches its maximum value in the fourth section. In this area, heat release strongly affects the temperature field of the sample. The exothermic effect of the binders can lead to overheat in the fourth section of the curing mode. When the heat transfer coefficient has a larger value (100 and ∞) at the end of the curing process, there is a place where the degree of cure on the surface is higher than the degree of cure in the center of the sample.

5. Conclusion
As the result of simulation, it was found that the increasing the values of the heat transfer coefficients, the difference in temperature state from the set mode is higher. With increasing heat transfer coefficient, the maximum temperature gradient on the surface and in the center of the sample does not increase very much. The value of the heat transfer coefficient strongly affects the temperature state of the sample, and not so much affects the temperature difference on the surface and in the center of the sample.
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