Optimization of the technological curing modes of glass fiber reinforced composites

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Abstract. The aim of this study was to optimize the curing mode of glass fiber reinforced epoxy composites. In this article, the change of the thermos-physical characteristics of epoxy binders depending on the state of aggregation of the binders during their curing is investigated. The kinetic parameters of the epoxy binders used are determined. The obtained thermos-physical and kinetic parameters were used to simulate the process of curing fiberglass. Different modes of curing for fiberglass based on epoxy binders were simulated at different heating rates. The method of optimization of the curing mode was carried out. As the result of the calculations, it was found that the optimal mode: the heating rate in the first section 2 °C/min and in the third section 3 °C/min.

1. Introduction

Modern carbon and glass fiber reinforced plastics are used as structural materials in the manufacture of products in mechanical engineering, aeronautics, rocket and space manufacturing, and many other industries [1]. The design, technology and properties of materials are interrelated in the process of designing products made of composite materials. The quality of parts made of polymer composites is finally formed at the technological operation - curing [1, 2].

In the manufacture of parts made of composites, the curing process is one of the most expensive technological operations, especially if large-sized parts are made, for example, for aircraft manufacturing. Cost reduction (without loss of quality) is one of the priorities for the development of aviation material science and many others.

Thermo-physical properties, for example, heat capacity, thermal conductivity of resins, and kinetic properties of resins, such as the activation energy are important in the study of the kinetics of the curing process of polymer composites [3-6]. These properties affect the heat transfer during the curing process of epoxy composites, which affects the temperature state and curing degree of composite parts.

In this paper, we optimized the two-step curing mode for glass fiber reinforced epoxy composites, depending on the kinetics of the curing process. Typical two-stage curing mode is shown in Fig.1. In sections I and III, there is an increase in temperature, in sections II IV - remained constant temperature and in section V - cooling. It has been assumed that the second section begins when the degree of cure is reached up to 20%, and ends when the degree of cure reaches up to 55%. In this work, the optimized parameters of the technological mode include: the heating rate in the first and third sections, the holding temperature in the second section. Traditionally, in the first and third sections it is carried out with a single speed.
The purpose of this study is to optimize the curing modes of epoxy composites, depending on the kinetics of the curing process.

2. Determination of thermos-physical characteristics of resins

The work consists of two parts: experimental and theoretical. In the experimental part of this work, the coefficients of heat capacity and thermal conductivity of resins, which affect heat transfer during the curing process of composites, are determined.

The values of heat capacity and thermal conductivity were evaluated directly depending on aggregation state of the binders during the curing process (liquid, gel and solid state). The specific heat coefficients of the binder, depending on the conversion degree of the binders, are determined by the differential scanning calorimeter method. Tests to determine the heat capacity of the binder was carried out before the curing reaction start. The thermal effect was determined by the method of differential scanning calorimetry and the degree of conversion was experimentally evaluated [7].

Thermal conductivity coefficients depending on the conversion degree of binders in the curing process are determined by laser flash. The peculiarity of conducting thermal conductivity studies is the use of a special crucible [7], since the liquid binder is transparent to laser radiation. In the process of research, the coefficient of heat capacity, the density of binders were first determined and then the value of the effective thermal diffusivity was determined, and then the value of the thermal conductivity was determined.

The obtained values of the experimental data are shown in table 1.

Table 1. The results of the experimental evaluation of the thermo-physical characteristics of the epoxy resins.

| Conversion degree, % | \( C_p \), J/(kg/K) | \( \lambda \), W/(m/K) |
|----------------------|---------------------|-----------------------|
| 0                    | 1973                | 0.08                  |
| 16                   | 1921                | 0.14                  |
| 30                   | 1820                | 0.19                  |
| 50                   | 1626                | 0.20                  |
| 75                   | 1406                | 0.22                  |
| 100                  | 1338                | 0.25                  |
It was established that with an increase in the degree of conversion of the binder, its heat capacity decreases by 29%, and the thermal conductivity increases about three times.

Table 2 shows the thermos-physical properties of glass fabric.

| Density, kg/m³ | Specific heat, J/(kg·K) | Thermal conductivity, W/(m·K) | Permeability coefficient, m² |
|---------------|------------------------|-------------------------------|-----------------------------|
| 2565          | 1205                   | 0.1                           | 1·10⁻⁹                      |

The above-defined thermos-physical properties will be used to simulate the process of curing epoxy composite.

3. Determination of kinetic parameters of resins

In the process of studying the temperature state of fiberglass in the curing process, it is necessary to investigate the exothermic effect of binders, which are determined from the kinetic characteristics of the binders.

There is the kinetic equation to describe the relationship between temperature and degree of cure:

\[
\frac{d\alpha}{dT} = k(T)f(\alpha)
\]

(1)

where \( \alpha \) – curing degree of resins, %; \( k(T) \) – curing rate constants; \( f(\alpha) \) – the functionality of curing degree.

According to the Arrhenius equation [8] and the Kamal model [9], the kinetic equation for describing the process of non-isothermal curing of the binders can be written as:

\[
\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) \cdot \alpha^m \cdot (1 - \alpha)^n
\]

(2)

where \( A \) - frequency factor, s⁻¹; \( E \) - activation energy, J/mol; \( T \) – absolute temperature, K; \( R \) – universal gas constant, J/(mol·K); \( m, n \) – reaction order for the epoxy resin used.

To determine the kinetic parameters \((A, E, m, n)\) during the curing of the binder, DSC curves of binder were used at heating rates of 0.5, 1, 3, 5 K / min. The temperature values at the peak of the DSC curve for different speeds are shown in table 3.

| Heating Rate, K/min | Temperature at the peak, Tp, °C | Reaction heat, J/g |
|---------------------|---------------------------------|-------------------|
| 0.5                 | 131.47                          | 213.1             |
| 1                   | 147.13                          | 278.2             |
| 3                   | 170.02                          | 302.5             |
| 5                   | 183.43                          | 320.7             |

The activation energy for epoxy resin is defined by equation Kissinger-Akahira-Sunose (KAS)[8,9]:

\[
\frac{d\ln\left(\frac{T_p^m}{\beta}\right)}{dT_p} = -\frac{E}{R}
\]

(3)

where \( T_p \) – temperature at the peak of the DSC curve, K.

The frequency factor for epoxy resin is defined by equation:

\[
A = \frac{\beta \cdot E \cdot \exp\left(\frac{E}{RT_p}\right)}{RT_p^2}
\]

(4)

The value of \( m \) and \( n \) is determined by equation 5.
The obtained kinetic parameters $E$, $A$, $m$, $n$ are shown in the table 4.

| Table 4. Curing kinetic parameters |
|-----------------------------------|
| Activation energy $E$, J/mol | Frequency factor $A$, s$^{-1}$ | $m$ | $n$ |
| 61844 | 3.6·10$^4$ | 0.12 | 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 mode of fiberglass

ESI PAM-RTM was used to simulate the curing process. The thickness of the model is 25 mm.

The Fourier equation of thermal conductivity was used to model the process of curing fiberglass [10,11]:

$$\rho C_p \frac{\partial R}{\partial t} = \lambda_z \frac{\partial^2 R}{\partial t^2} + \rho H_r \frac{\partial \alpha}{\partial t}$$

(5)

where $\rho$ – density of GFRC, kg/m$^3$; $C_p$ – specific heat, J/(kg·K); $T$ – absolute temperature, K; $k_z$ – thermal conductivity in the direction vertically on the surface of fiberglass, W/(m·K); $H_r$ – total reaction heat during curing, J; $\alpha$ – curing degree.

The heating rate in the first and third sections was chosen from 0.5 to 5 K / min, 25 variants. All modeling options are shown in table 5.

| Table 5. Variants of curing cycle modeling |
|--------------------------------------------|
| № of Variant | Heating rate in the third section (°C/min) |
|              | 0.5 | 1 | 2 | 3 | 4 | 5 |
| 0.5          | 1   | 2 | 3 | 4 | 5 |
| 1            | 6   | 7 | 8 | 9 | 10 |
| 2            | 11  | 12| 13| 14| 15 |
| 3            | 16  | 17| 18| 19| 20 |
| 5            | 21  | 22| 23| 24| 25 |

As the result of simulation, the temperature state and the degree of curing of fiberglass for different curing modes are obtained.

All listed in Table. 5 variants of technological regimes were investigated using the ideal point method [13]. The most acceptable is considered an alternative, in which the distance from the "ideal point" is minimal:

$$R_{AI} = \sqrt[N]{\sum_{i=1}^{N} (x_{id,j} - x_{i,j})^2}$$

(6)
where $R_{Ai}$ – the distance of the point of the $i$-th alternative from the ideal point; $N$ – number of criteria for evaluating alternatives; $x_{idj}$ - ideal value according to the $j$-th criterion for the ideal variant; $x_{ij}$ – value by the $j$-th criterion for the $i$-th alternative.

The following criteria were used to optimize the curing mode: the average and maximum value of the temperature difference inside and on the surface of the fiberglass during the curing process: $T_a$, $T_{max}$; the average and the maximum value of the difference of curing degree inside and on the surface of the fiberglass: $\alpha_a$, $\alpha_{max}$; the duration of curing process: $t$. As initial data for optimization, the corresponding simulation results are used. Options and the value of the criteria are shown in table 6. The number of optimization options corresponds to the number of simulation in table 5.

### Table 6. Optimisation criteria

| № optimization options | $T_a$, K | $T_{max}$, K | $\alpha_a$, % | $\alpha_{max}$, % | $t$, min |
|-------------------------|---------|-------------|--------------|-----------------|---------|
| 1                       | 4.2     | 7.1         | 1.1          | 6.2             | 396.7   |
| 2                       | 4.8     | 9.8         | 1.3          | 5.6             | 332.8   |
| 3                       | 5.5     | 10.7        | 1.7          | 5.7             | 286.0   |
| 4                       | 5.9     | 18.2        | 1.8          | 11.0            | 287.5   |
| 5                       | 6.4     | 37.1        | 1.9          | 17.6            | 288.3   |
| 6                       | 7.0     | 14.1        | 2.2          | 12.5            | 273.0   |
| 7                       | 8.2     | 14.2        | 2.7          | 11.7            | 222.2   |
| 8                       | 8.1     | 14.5        | 2.6          | 11.5            | 188.0   |
| 9                       | 8.6     | 15.5        | 2.5          | 11.4            | 181.0   |
| 10                      | 9.1     | 17.2        | 2.5          | 11.2            | 185.7   |
| 11                      | 10.7    | 27.6        | 4.0          | 25.0            | 194.2   |
| 12                      | 13.0    | 27.5        | 4.7          | 23.8            | 156.8   |
| 13                      | 14.0    | 27.5        | 5.1          | 23.6            | 128.2   |
| 14                      | 14.0    | 27.4        | 5.0          | 23.4            | 124.8   |
| 15                      | 13.7    | 27.4        | 4.4          | 23.1            | 130.8   |
| 16                      | 13.2    | 40.4        | 5.5          | 35.7            | 156.8   |
| 17                      | 16.2    | 40.2        | 6.2          | 34.4            | 124.5   |
| 18                      | 17.1    | 40.2        | 6.6          | 34.1            | 109.2   |
| 19                      | 16.7    | 40.2        | 6.1          | 33.9            | 113.8   |
| 20                      | 16.9    | 40.2        | 5.8          | 33.6            | 115.2   |
| 21                      | 16.2    | 58.0        | 8.4          | 40.9            | 116.2   |
| 22                      | 18.7    | 57.9        | 8.3          | 40.2            | 102.0   |
| 23                      | 19.3    | 57.9        | 8.0          | 42.5            | 105.1   |
| 24                      | 20.3    | 57.8        | 7.9          | 46.5            | 105.0   |
| 25                      | 21.3    | 57.8        | 7.7          | 51.6            | 104.8   |

As the result of the calculations, it was established that the smallest value of $R$ was obtained for mode No. 14, $R = 4.2$, at which the heating rate in the first section is 2 K / min, the heating rate in the third section is 3 K / min. The temperature state and the curing degree of fiberglass for the optimized curing mode are shown in fig 2.
Figure 2 Optimized Curing Model. (a) The curing degree inside the sample (1) and on the surface of the sample (2) depending on the time for the specified temperature program (3). (b) Temperature condition inside the sample (4) depending on the time for the specified temperature program (3).

In this mode, the average value of the temperature difference inside and on the surface of fiberglass is 14 °C; the maximum value of the temperature difference is 27.4 °C; the average value of the degree of cure inside and on the surface of the fiberglass is 5.0%, the maximum value of the temperature difference is 23.4 %, the total duration of the curing process is 124.8 min.

5. Conclusion
The results of the research allowed us to determine the thermos-physical properties and kinetic properties of binders in the process of curing epoxy composites. It was established that the heat capacity of the binders in the curing process decreases by 29%, and the thermal conductivity increases about three times.

As the result of simulation of the curing process of fiberglass, temperature and the degree of curing of fiberglass were obtained. The largest temperature gradient occurs in the first section of the heating process, where value of the heat capacity of the binders is higher, and the thermal conductivity is lower. Due to the exothermic effects of binders in the area of temperature rise in the curing mode, it has a moment where the temperature inside the sample is higher than the temperature on the surface of the sample.

As the initial data for optimization of the curing process, the simulation results are used. It has been established that the optimal mode is when the heating rate in the first section is 2 K / min and the heating rate in the third section is 3 K / min. The developed method of optimizing of the curing mode can be used for any composites based on thermosetting binders.

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