Optimization of curing mode of epoxy resin based composites

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Abstract. In this article the techniques for determining the thermos-physical properties of epoxy binders depending on their different state of aggregation are presented. The epoxy composition based on epoxy resin and modified aliphatic polyamine was used as an object of research. Experimental studies were carried out to determine heat capacity and thermal conductivity of epoxy binders, depending on their degree of conversion. Mathematical modeling of the curing process of epoxy binder at different heating rates by the finite element method was carried out. When using the results of mathematical modeling, the kinetics of the curing process was optimized depending on different heating rates by the ideal point method. Moreover, a study was conducted on the effect of limit condition on optimization results.

1. Introduction
Epoxy oligomers are widely used in aircraft manufacturing, shipbuilding, and in the production of space technology, since they have a series of distinctive features: their good adhesive properties with respect to a large number of fillers and substrates, good water resistance and unique technological properties [1-3].

In the process of curing epoxy oligomer (and thermosetting binders of any chemical nature) there is a change in its aggregative state and the material from the liquid initially goes into a gel state and then into a solid [4,5].

A typical two-stage technological process of curing the binder consists of five sections: on the first and third, there is an increase in temperature, on the second and fourth - remained constant temperature, and on the fifth section - cooling [6]. The time and temperature of exposure in the second section are determined, as a rule, experimentally for each particular product. The time and temperature of exposure in the fourth section completely depends on the chemical structure of the binder used and is set by its developers. Thus, during the development of the curing process, the technologist must independently determine the modes in the first, second and third sections [7].

In this work, it is assumed that the second section begins after the start of the gelation process and continues until its completion. At the end of the third section is the final formation of the structure of polymer matrices.

The purpose of this study is to optimize curing modes of epoxy binders, taking into account changes in the state of aggregation during their heating.

2. Methodology
As an object of research used epoxy binder hot curing, consisting of an epoxy resin and a hardener based on aromatic amine.

2.1. Method of dynamic mechanical analysis

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The holding temperature at second section corresponds to the gelation temperature. Experiments to estimate the gelation temperature depending on the heating rate were performed using dynamic mechanical analysis at heating rates: 1, 3, 5, 7 °C / min [7]. According to the Flory-Stockmayer Theory, the degree of conversion at the gelation point does not depend on the heating rate and is constant for a particular resin [8, 9]. Therefore, in this work, we can use the Ozawa theory, and the method of approximation is used to determine the relationship between the gelling temperature and heating rates. Thus, the gelling temperature was determined at heating rates of 2, 4, 6 °C / min. The obtained values of the gelling temperature depending on the heating rate are shown in table 1.

| Heating rate (°C/min) | Gelling temperature (°C) |
|-----------------------|--------------------------|
| 1                     | 65                       |
| 2                     | 80                       |
| 3                     | 98                       |
| 4                     | 102                      |
| 5                     | 107                      |
| 6                     | 122                      |
| 7                     | 130                      |

2.2. Differential Scanning Calorimeter (DSC) Method

In this work, the change of the thermophysical properties of the binder at different degrees of conversion during the curing process is investigated. The values of heat capacity and thermal conductivity were evaluated directly in the curing process (for liquid, gel and solid state). The coefficients of heat capacity of the binder, depending on the conversion, are determined by the DSC method. The tests were carried out before the curing reaction start. The thermal effect was determined by the DSC method and the degree of conversion was experimentally evaluated [10].

2.3. Laser flash method

The values of thermal conductivity coefficients are determined by the laser flash method. The peculiarity of these studies is the use of a special crucible (Fig. 1) [9], since the liquid binder did not allow withstanding the required dimensions and is transparent to laser radiation.

![Fig. 1. Special mandrel for determining thermal conductivity. (a) Lid; (b) Crucible; (c) Crucible with lid. 1,5. Graphite grease; 2. Lid; 3. The crucible; 4. Binder.](image)

The mandrel consists of a crucible and a lid made of a platinum-rhodium alloy. Manufacturer determined the thermophysical and geometrical properties of the crucible material and the cover (heat capacity, density, thermal diffusivity). With the help of graphite grease in an aerosol, the external surfaces of the crucible and the lid are blackened to create the same optical properties of the surfaces. In the process of research, the effective thermal diffusivity of the binders was first determined, and then the thermal conductivity was determined. The results of the experiment are shown in Table 2.
Table 2. Dependence of heat capacity and thermal conductivity on the degree of conversion

| Conversion degree, % | \(C_p\), 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             |

3. Modeling and optimization

3.1. Modeling the heating process

The simulation of heating process was carried out by taking into account the change in the aggregative state of the binder in the process of its curing at heating rates on the first and third sections: 1-7 °C/min. The 49 modeling options are shown in Table 3. The temperature gradients on the surface and inside the sample are presented in Fig. 2, 3, and the duration of the heating process for different modeling options are presented in Fig. 4.

Table 3. Modeling Options

| № Modeling Options | Heating rate in the first section (°C/min) |
|--------------------|--------------------------------------------|
|                    |   1   |   2   |   3   |   4   |   5   |   6   |   7   |
| Heating rate in the third section (°C/min) |-------|-------|-------|-------|-------|-------|-------|
| 1                   | 1     | 8     | 15    | 22    | 29    | 36    | 43    |
| 2                   | 2     | 9     | 16    | 23    | 30    | 37    | 44    |
| 3                   | 3     | 10    | 17    | 24    | 31    | 38    | 45    |
| 4                   | 4     | 11    | 18    | 25    | 32    | 39    | 46    |
| 5                   | 5     | 12    | 19    | 26    | 33    | 40    | 47    |
| 6                   | 6     | 13    | 20    | 27    | 34    | 41    | 48    |
| 7                   | 7     | 14    | 21    | 28    | 35    | 42    | 49    |

Fig. 2. The temperature gradients on the surface and inside the sample for modeling options 1-28
3.2. **Method of optimization the curing process**

All of the above options for technological regimes were investigated for optimization. For the optimization criterion in this paper, it is proposed to use:

1. The maximum temperature difference on the surface and inside the sample in the area of the first section $\Delta T_{maxI}$;
2. The maximum temperature difference on the surface and inside the sample in the third section $\Delta T_{maxIII}$;
3. The total duration of the heating process $\tau$.

All listed in table. options for technological regimes were investigated using the ideal point method [11, 12]. The most acceptable is considered an alternative, in which the distance from the "ideal point" is minimal:

$$R_{Ai} = \sqrt{\sum_{i=1}^{N} (x_{id,j} - x_{ij})^2}$$  \hspace{1cm} (1)

where $R_{Ai}$ is the distance of the point of the i-th alternative from the ideal point; $N$ – number of criteria for evaluating alternatives; $x_{id,j}$ – 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.

3.3. **Study of the influence of the restriction condition on the optimization results**

If without condition of limitation:
In this case, the coordinates of the ideal point: \((4.2 \ 2.0 \ 22.2)\), \(N = 3\), \(i = 49\). The minimum distance from the ideal point: \(RA_{28} = 6.95\).

It has been established that mode 28 is optimal, in which the heating rate on the I stretch is 4 °C / min, the heating rate on the III stretch is 7 °C / min, and the holding temperature is 102 °C.

Limit condition 1:
(1) \(\Delta T_{\text{maxI}} < 20 \ ^\circ\text{C}\), (2) \(\Delta T_{\text{maxIII}} < 10 \ ^\circ\text{C}\), (3) \(\tau < 60 \ \text{min}\).

In this case, the coordinates of the ideal point: \((8.8 \ 3.9 \ 34.85)\), \(N = 3\), \(i = 9\). The minimum distance from the ideal point: \(RA_{19} = 6.95\).

It has been established that mode 19 is optimal, in which the heating rate on the I stretch is 3 °C / min, the heating rate on the III stretch is 5 °C / min, and the holding temperature is 98 °C.

Limit condition 2:
(1) \(\Delta T_{\text{maxI}} < 22 \ ^\circ\text{C}\), (2) \(\Delta T_{\text{maxIII}} < 10 \ ^\circ\text{C}\), (3) \(\tau < 60 \ \text{min}\).

In this case, the coordinates of the ideal point: \((8.8 \ 3.9 \ 31.2)\), \(N = 3\), \(i = 13\). The minimum distance from the ideal point: \(RA_{26} = 4.72\).

It has been established that mode 26 is optimal, in which the heating rate on the I stretch is 4 °C / min, the heating rate on the III stretch is 5 °C / min, and the holding temperature is 102 °C.

Limit condition 3:
(1) \(\Delta T_{\text{maxI}} < 20 \ ^\circ\text{C}\), (2) \(\Delta T_{\text{maxIII}} < 15 \ ^\circ\text{C}\), (3) \(\tau < 60 \ \text{min}\).

In this case, the coordinates of the ideal point: \((4.2 \ 7.6 \ 30.25)\), \(N = 3\), \(i = 17\). The minimum distance from the ideal point: \(RA_{21} = 5.21\).

It has been established that mode 21 is optimal, in which the heating rate on the I stretch is 3 °C / min, the heating rate on the III stretch is 7 °C / min, and the holding temperature is 98 °C.

Table 4 shows the optimization results for different constraint conditions.

| Limit condition               | Heating rate in the first section (°C/min) | Heating rate in the third section (°C/min) | Temperature in the second section(°C) |
|-------------------------------|-------------------------------------------|--------------------------------------------|--------------------------------------|
| Without limit condition       | 4                                         | 7                                          | 102                                  |
| Limit condition 1             | 3                                         | 5                                          | 98                                   |
| Limit condition 2             | 4                                         | 5                                          | 102                                  |
| Limit condition 3             | 3                                         | 7                                          | 98                                   |

4. Conclusion

A technique has been developed for determining the heat capacity and thermal conductivity of epoxy binders depending on their different state of aggregation (in a liquid, gel-like, and solid state). It was found that with an increase in the degree of conversion, the heat capacity of epoxy binders decreases, and the thermal conductivity increases.

The mathematical modeling of the curing process was carried out for different heating rates: 1-7 °C /min, the temperature gradient and the duration of the heating process were calculated in the curing mode.

The optimization of the curing mode was carried out depending on different heating rates. It was found that limitation No. 3 is the most severe, and in this case the best option: the heating rate on the first section is 3 °C / min, the heating rate in the third section is 5 °C / min the temperature in the second section is 98 °C.
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