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Effect of Experimental Conditions and Methods for Processing DTA and DSC Results on Reliability of Kinetic Calculations of Parameters of Curing Thermoset Prepregs

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Abstract—The methods of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used to study the kinetics of curing a thermoset epoxy binder, complicated by intensive self-heating, in an adhesive prepreg based on aramid Ruslan fiber. The most adequate reaction scheme has been chosen and the kinetic parameters of the curing reaction have been determined for each elementary stage. A generalized kinetic model of the reaction has been constructed based on experimental data obtained by DTA and DSC. The selected model has been tested by solving an opposite problem—namely, constructing a series of calculated DTA and DSC curves and evaluating their compliance with the experimental data.

Keywords: prepreg, epoxy binder, thermal analysis, curing kinetics

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INTRODUCTION

The polymer composite materials (PCMs) that are applied in the products of new aviation and space technology offer significant advantages due to the combination of high structural properties and low level of weight characteristics. For a number of years, there has been an active introduction and growth of the volume of PCM application. The range of materials of this promising class is expanding [1–4]. At the same time, the quality and operational reliability of PCM products depend on the properties of the initial components and semifinished products (prepregs) used in their manufacture. In the aviation industry in the past, and often now, the main criteria for the quality of final products are traditionally indicators of operational properties, structural ones (strength, stiffness, and hardness) and special ones (thermal, electrical, and radiophysical, etc.) [4–6]. At present, when creating sophisticated modern technology, the materials used should meet the higher requirements. The compositions of the starting components and semifinished products are complicated. In this situation, there is a need for careful and, at the same time, operational control and/or reliable prediction of their properties, not only for final indicators, but at all stages of the technological scheme from the initial components to the semifinished product and the final product [6–9]. This means that professionals who develop materials and technologists who use these materials when manufacturing parts of real products need indicators that characterize the process of turning a semifinished product into a ready-for-use material. The wide distribution and improvement of modern technological equipment, as well as instruments and research complexes intended for experimental studies in materials science, has become a serious incentive for the widespread introduction of instrumental methods of analysis into the development and quality control of initial components, semifinished products, and products made of PCMs. At the same time, the spread of computer equipment has greatly simplified the execution of computational tasks in processing experimental data.

Against the background of the accelerated development of experimental and computer technology, one of the most effective means of studying the properties of materials and processes occurring in them at a change in temperature is represented by the methods of thermal analysis [8, 9]. Research instrumentation that is currently produced by leading global companies and constantly improved by them performs the functions of thermoanalytical minilaboratories and is widely used both in the development of new materials and to control their quality in the conditions of various areas of industrial production.

This paper presents the results of experimental and computational studies carried out in the framework of the implementation of "Strategic Directions for the Development of Materials and Technologies for Their Processing for the Period until 2030," integrated research area no. 2 "Fundamentally Oriented

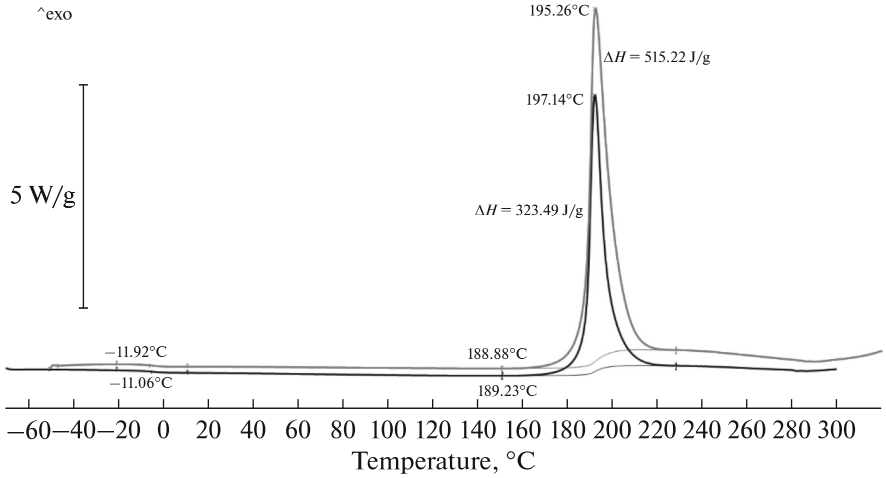

Fig. 1. The results of the DSC curing reaction of unfilled binder and prepreg based on it.

Research, Materials Qualification, Nondestructive Testing" [10].

MATERIALS AND METHODS

In the course of research, samples of prepreg based on glue epoxy binder and reinforcing filler in the form of a satin fabric from aramid Ruslan fiber were selected. It has been proposed to use this structural organoplastic in the creation and modernization of structural elements of promising aviation equipment that are subjected to cyclic alternating loads during operation—namely, impact and abrasive effects (flaps, platings, sewings, etc.)—as well as in the development of hybrid structures in combination with carbon-fiber-reinforced polymers, fiberglass, and organoplastics [11–14].

The surface of this filler, due to its chemical nature, is able to exhibit enhanced sorption and chemisorption activity with respect to the binder or its individual components.

The main active component contained in the composition of the prepreg and that determines both the technological properties of the semifinished product under study and the level of performance characteristics of the polymer matrix of the cured material in the composition of the product is a thermoset epoxy binder, the curing process of which deserves special attention.

The main method used in the work to obtain experimental data for kinetic calculations was the method of differential scanning calorimetry (DSC). Along with the results of calorimetric measurements, experimental data obtained in the differential thermal analysis (DTA) mode were used in measuring the temperature characteristics under conditions of intensive self-heating of the binder during its curing. The DTA method is based on measuring the temperature difference between the test sample and the reference sample as a function of temperature.

Experimental data for the calculations and construction of the kinetic model of the curing reaction were obtained in a single series of experiments on a Mettler Toledo DSC-1 instrument (Switzerland), which uses a single-channel DTA, which is a variation of the classical DTA. Kinetic processing of the results was carried out using data obtained in the DSC format itself and in the single-channel DTA format. Experimental samples were tested by heating at rates of 1.5, 2.5, 5, and 10 K/min in static air in the temperature range from 25 to 300°C.

The control of the conditions for experimental work, measurements, and the initial processing of the results were performed using the STAR^e computer program of the equipment developer. For in-depth kinetic analysis of research results, The Peak Separation and Thermokinetics software from NETZCH (Germany) was used [7–9].

RESULTS AND DISCUSSION

According to the experimental results obtained by DSC and DTA, the curing reaction takes place in a narrow temperature range with high values of heat release intensity and heat effect (Fig. 1). This is typical for compositions containing latent-type hardeners. The magnitude of the exothermic thermal effect of the curing reaction of the unfilled binder ranges from 505 to 525 J/g. As a result, when the hardener is activated in the molten epoxy oligomer medium, the curing of the epoxy resin already at the initial moment proceeds at a high rate and the probability of intensive self-heating of the semifinished product increases. This is especially noticeable when considering the experimental results of DSC and DTA obtained under heating at different rates. A significant influence on the results is due to the self-heating deviation of the mode of tem-

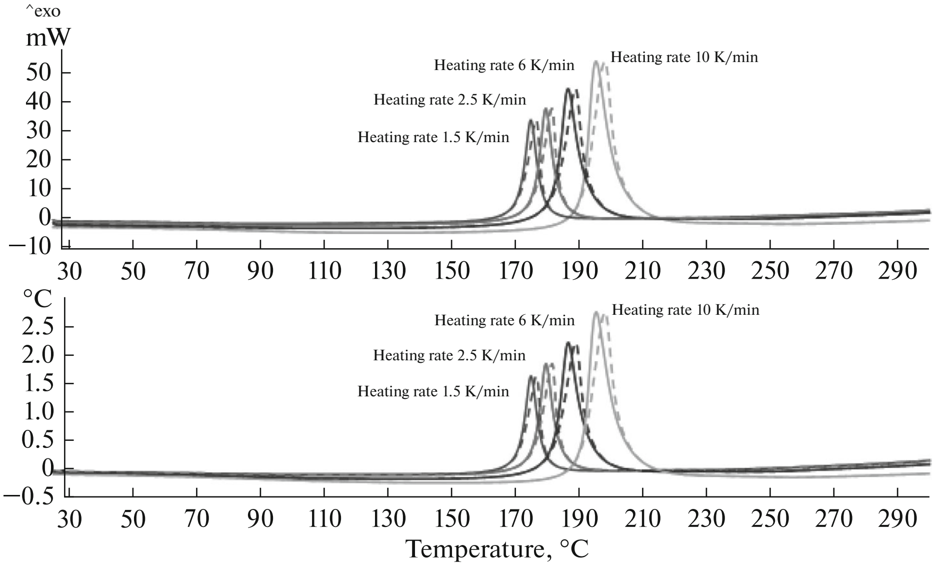

Fig. 2. Starting DSC and DTA curves measured by heating with rates of 1.5, 2.5, 5, and 10 K/min and constructed depending on temperature of the sample T_S (dashed line) and temperature of the reference sample T_{SR} (solid line).

perature variation of the sample (T_S) in the active reaction zone from the given and experimentally implemented in the reference sample T_{SR}. As a reference sample, an empty aluminum cup was used, similar to the one in which the sample was placed. The difference between temperatures T_S and T_{SR} depending on the heating rate is from 1 to 2.5°C with the weight of the active part of the sample under study being from 5 to 30 mg (Fig. 2). This is the minimum difference between temperatures T_S and T_{SR}, despite the fact that the sample weigh is chosen in inverse proportion to the heating rate. At the same time, a further decrease in the sample will lead to an increase in the drift in the experimental curve, which significantly affects the accuracy of the kinetic calculations.

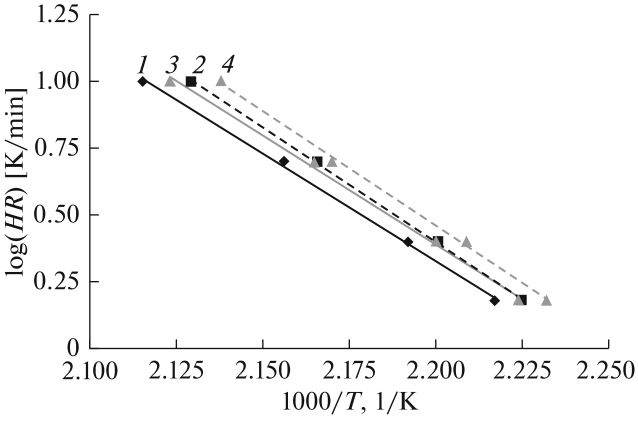

Fig. 3. Results of preliminary calculation of kinetic parameters using the model-free kinetics method (ASTM E698). Correlation coefficients R^2 with linearization of the Arrhenius dependence are (*1*) 0.9982, (*2*) 0.9993, (*3*) 0.9967, and (*4*) 0.9982.

Preliminary calculations were carried out according to a simplified scheme using the model-free kinetics method. The initial DSC and DTA data for the calculation, which are temperature dependences of the heat flow rate (thermal power W, mW) and the temperature difference between the experimental sample and the reference sample (ΔT, °C), were used in differential form (see Fig. 2).

Figure 3 shows the graphical dependences of the logarithm of the conditional rate constant on the reciprocal of the absolute temperature of the curing reaction peak in the coordinates of the Arrhenius equation according to the DSC and DTA results. The values of thermodynamic and kinetic parameters are summarized in Table 1.

The values of the calorimetric indicators of the curing process obtained at the preliminary stage of research in the DSC and DTA modes are close. At the same time, an attempt to present this process as a simple one-step reaction is incorrect, as previously obtained data showed that in the temperature range from 150 to 200°C, at least three reactions occur simultaneously, involving the interaction of two forms of dicyandiamide (DCDA) to form melamine [15, 16].

This is also confirmed by comparing the experimental DSC curve and the calculated one obtained under the condition that it is considered as a simple one-step process (Fig. 4): the calculated DSC curves shown in Fig. 4 differ significantly from the experimental ones. The greatest difference between the experimental and calculated curves is observed when

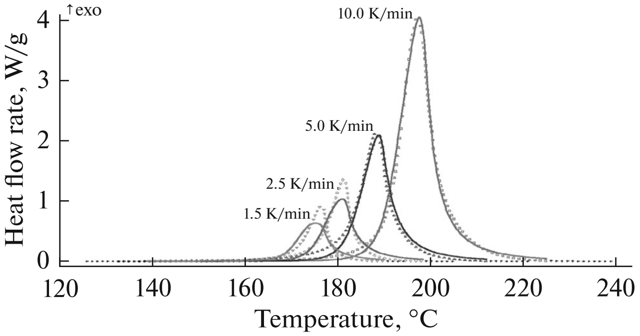

Fig. 4. Comparison of the experimental DSC curve (points) with the calculated (solid line) constructed for the kinetic model of the process considered as a one-step simple reaction with kinetic parameters calculated by the model-free kinetics method (ASTM E 698).

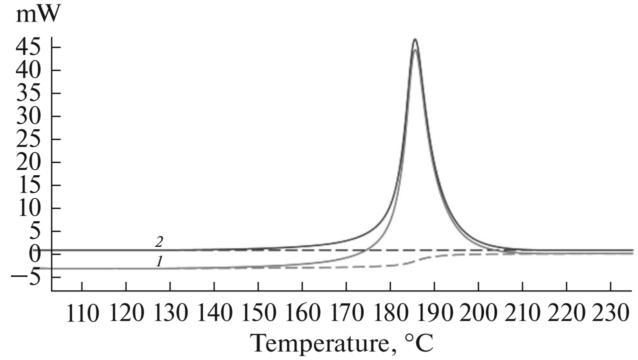

Fig. 5. DSC thermogram of the binder curing reaction in the prepreg: (*1*) baseline; (*2*) the curve after selecting the type and graphic baseline subtraction.

comparing the results obtained in the conditions of heating with the minimum rates.

When performing a detailed calculation, the number of possible elementary stages of the curing reaction was determined first by the Peak Separation graphical separation program using experimental DSC and DTA curves. For correct operation of the graphic separation of the peaks, it is very important to choose the type of baseline correctly. The Peak Separation program provides only one option, which is a straight baseline, but for the process under study it is unacceptable because of the abrupt change in heat capacity during the curing of the binder and the associated distortion of the original DSC (or DTA) data used for kinetic calculations. For this reason, the original DSC curves were previously converted in the STAR^e program. In the temperature range of the exothermic heat of the curing reaction, the most appropriate type of baseline was chosen—namely, the "integral tangent"—and the operation of graphical subtraction of baselines from the original DSC and DTA curves was performed (Fig. 5). The complete set of experimental DSC and DTA data, obtained at four different heating rates, prepared in this way was used for further kinetic calculations.

During the first stage of the graphical separation, it was established that there are three elementary stages and the shape and location of the divided peaks relative to each other on all curves are the same. Deviation from this order is observed only at the maximum heating rate used, 10 K/min. Thus, despite the apparent simplicity of the experimental DSC and DTA curves,

Table 1. Results of experimental analysis of prepreg samples by DSC and DTA methods and preliminary calculation of the kinetic parameters of the curing reaction

Indicator	Method			
	DSC		DTA	
	experimental data format			
	$f(T_S)$*	$f(T_{RS})$**	$f(T_S)$*	$f(T_{RS})$**
Temperature of the beginning of the active reaction T_0, °C	191	191	190	191
Peak T_m, °C	198	195	198	195
Heat effect of the curing reaction ΔH, J/g	228	229	228	229
Preexponential factor log(A, 1/s)***	14.34	15.33	14.67	15.98
Activation energy E, kJ/mol***	146.59	155.91	148.97	160.98
Correlation coefficient R^2 (number in Fig. 3).	0.998 (1)	0.999 (2)	0.997 (3)	0.998 (4)

* Depending on the temperature of the sample.
** Depending on the temperature of the reference sample (empty encapsulated aluminum cup).
*** Calculation using the model-free kinetics method.

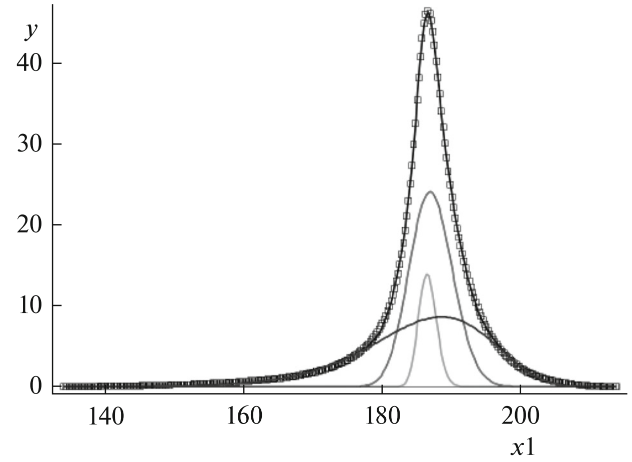

Fig. 6. Graphical separation of the peak on the DSC thermogram of the binder in the prepreg. Heating rate, 5 K/min.

the curing process can be considered from the kinetics point of view as a complex three-step reaction. An example illustrating the procedure of dividing the main peak into components characterizing the individual stages of the process is shown in Fig. 6.

From the set offered by the Kinetics 3.1 program [7–9, 11], in the automatic mode, the type of reaction of the *n*-th order with autocatalysis was chosen. This type of reaction corresponds to the *n*-th order extended Prout–Tompkins equation with autocatalysis:

$$\mathrm{d}c/\mathrm{d}t = -A\exp\left(-E/RT\right)c^n p^a,$$

where c is the concentration of reagents; A is the preexponential factor; E is the activation energy; R is the universal gas constant; T is the absolute temperature, K; n is the reaction order for the reagents; a is the reaction order for the final product; and p is the concentration of the final product (degree of conversion).

The criterion for choosing the optimal type of reaction was the minimum sum of deviations of the calculated values from the experimental ones calculated using the least squares method. The results of the calculation of kinetic parameters are given in Table 2 and Fig. 7.

Our analysis of the results of kinetic calculations given in Table 2 suggests that kinetic parameters obtained using experimental data in the form of graphical dependences on temperature of the reference sample T_{RS} are most convincing. The values of the kinetic parameters obtained by the DSC and DTA

Table 2. Kinetic parameters of the curing reaction of the epoxy binder in an adhesive prepreg based on aramid Ruslan fiber fabric

Indicator	Method			
	DSC		DTA	
	data format			
	$f(T_{\mathrm{S}})$	$f(T_{\mathrm{RS}})$	$f(T_{\mathrm{S}})$	$f(T_{\mathrm{RS}})$
Preexponential factor A_1, s^{-1}	17.3253	17.4901	9.2294	17.4007
logA_1	2.1149×10^{17}	3.0910×10^{17}	1.6959×10^{9}	2.5159×10^{17}
Activation energy E_1, kJ/mol	168.1882	176.6543	102.8656	174.1969
Reaction order n_1	0.9814	2.1424	0.9291	2.2697
Autocatalysis constant a_1	0.6698	4.7234×10^{-2}	0.4296	0.2166
Preexponential factor A_2, s^{-1}	0.1736	25.7101	9.9885	26.7872
logA_2	1.4914	5.1298×10^{25}	9.7387×10^{9}	6.1263×10^{26}
Activation energy E_2, kJ/mol	0.4285	229.7370	97.7770	238.6239
Reaction order n_2	1.9916	1.0111	1.8652	0.9573
Autocatalysis constant a_2	7.8967	1.8137	1.5105	1.7603
Preexponential factor A_3, s^{-1}	–2.3186	5.8343	26.6129	5.3547
logA_3	4.8018×10^{-3}	6.8281×10^{5}	4.1011×10^{26}	2.2631×10^{5}
Activation energy E_3, kJ/mol	0.3240	66.1301	246.0836	61.6341
Reaction order n_3	2.4041×10^{-4}	1.1587	0.5738	1.1905
Autocatalysis constant a_3	23.7902	1.2243×10^{-2}	0.6862	4.0777×10^{-2}

The model is the three-step Prout–Tompkins reaction of the *n*-th order with autocatalysis.

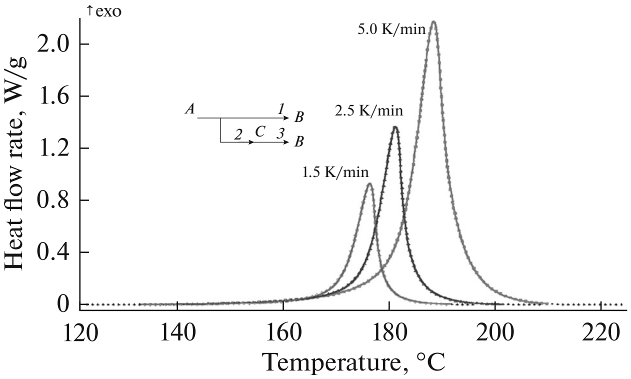

Fig. 7. Comparative analysis of the calculated (solid line) and experimental (points) DSC curves obtained at three heating rates.

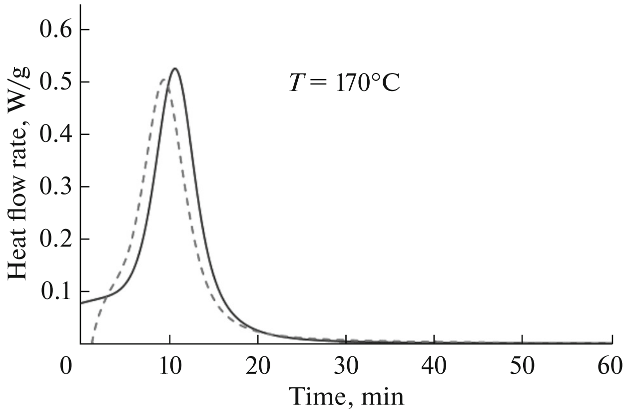

Fig. 8. Comparative analysis of the calculated (solid line) and experimental (points) DSC curves obtained at three heating rates.

methods practically coincide. This fact is confirmed by the solution of the inverse problem. The experimental and calculated values of the DSC curves completely coincide (Fig. 7). A similar result is obtained by comparing the DTA curves.

An additional evidence of the correctness of the kinetic model constructed are the results of comparing the experimental DSC curve obtained under isothermal conditions and the calculated DSC isotherm obtained using non-isothermal kinetics data (Fig. 8). The results of the comparison can be considered quite satisfactory. A certain displacement of the curve along the time axis can be explained by the impossibility of experimentally reproducing the pure isotherm using the existing equipment.

Thus, the results of the performed thermoanalytical studies have shown that the curing reaction of the adhesive binder in the presence of aramid filler consists of at least three elementary stages. For each of them, kinetic parameters were determined. A generalized kinetic model of the reaction was constructed, and its consistency was confirmed by solving the inverse problem.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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