Empirical model of the viscosity of an epoxy binder at the initial stage of the polymerization process

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Abstract. This article presents the results of an experimental study and numerical simulation of the kinetics of curing of an epoxy binder at the initial stage of the polymerization process. Object of research: two-component composition of epoxy resin L and hardener EPH 161, certified as a binder for composite materials for aerospace purposes. The ordinary differential equation is used as the basic model for describing the polymerization process. The values of the material parameters required to perform the calculation operations were obtained by the rheological method using the analysis of changes in the viscosity of the binder depending on the time and temperature of polymerization. Isothermal and non-isothermal polymerization cases are considered. The modes in which the increase in the temperature of the process leads to a decrease in the viscosity of the epoxide composition, despite the polymerization process, were highlighted. The estimates of the model parameters obtained by processing the data of full-scale experiments are also given.

1 Introduction

Epoxy adhesive compositions are widely used due to their high strength properties, good adhesion to various materials, resistance to external factors and low shrinkage. In practical use of such compositions and composite materials on their basis, the main parameters are temperature dependences of viscosity and degree of conversion determining "viability" of binder and duration of product formation.

In the general formulation, the kinetics of curing of reactive oligomers is one of the central problems, the solution of which allows, firstly, to consider the chemistry of the process; secondly, to introduce quantitative parameters for comparison between the composition of different materials, and, thirdly, to give reasonable forecasts of the productivity and efficiency of real technological processes [1].

Two significantly different approaches are possible to evaluate the kinetics of curing: microkinetic and macrokinetic. In the first case, direct experimental methods are used to determine the change in the concentration of certain reactive groups. So traditionally, the degree of curing is estimated by the content of the gel fraction, which is determined by the extraction of cured binders with organic solvents [2]. However, this indicator is not sensitive to the presence of reaction centers in polymer chains. Chromatographic methods of analysis based on the different solubility of substances in the mobile and stationary phases are close to this approach. IR analysis [3], NMR methods [4], and Raman spectroscopy [5] are used to determine the amount of reactive groups in a polymer matrix.

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More effective from the practical point of view is macrokinetic approach based on the observation of changes in time of one or another integral parameter reflecting the totality of chemical transformations occurring during oligomerization. For this purpose, various physic-ochemical methods are used, including rheological analysis.

The curing of epoxy oligomers by the rheological method has been studied in a number of works [6–11]. Thus, [6, 7] defines the activation energy and discusses the applicability of different models to describe viscosity versus curing time. Kinetic characteristics of the curing process of ED-20 oligomeric resin were established in [8]. As a result, an equation was obtained that establishes the change in viscosity as a function of the average molar mass, density, and mass fraction of the cured product. Mathematical models of the kinetics of curing of thermosetting resins and the increase in viscosity during curing are considered in [9–11]. In [9], the main conclusions are based on the analysis of units of measurement. In [10, 11], the considered model takes into account the change in the concentration of fragments of the molecules of the reaction mixture during curing. However, these models make predictions mainly on the transition of the binder to the gel fraction. In a real technological process, the most interesting is the first (initial) stage of changing the viscosity of the binder, when the curable material can be molded into the required shapes. A significant factor in the course of the actual curing process is a change (usually an increase) in temperature. Even if some constant curing temperature is selected, the actual chemical process turns out to be non-isothermal.

The purpose of this work is to consider a method for estimating changes in viscosity at the initial (technological) stage of polymerization, both in the isothermal case and under conditions of programmable temperature change.

2 Object of study. details of the experiment

In the experiments was used "cold-curing" epoxy composition, which consists of epoxy resin L and hardener EPH 161, certified for use in structural composite materials for aviation purposes. The weight ratio of epoxy resin to hardener was 4:1, which is the manufacturer's recommended ratio. After preparation, the mixture was thoroughly mixed for 1–2 minutes with an electromechanical mixer and for an additional 5–10 minutes in a Digital Ultrasonic Cleaner CD 4820 ultrasonic bath at 40 kHz at room temperature. The last of these operations also contributes to the degassing of the mixture. Measurements of the mass of solutions and their components necessary to calculate the concentration of the mixture were performed using analytical scales LV-210A of the 2nd accuracy class, the absolute error of measurement of which was ±0.4 mg.

Rheological measurements were performed on a Physica MCR 501 rotary rheometer. The "cone-plate" system with cone diameter $d = 25$ mm and cone angle $\alpha = 1°$ was used in all measurements. Such geometry ensures uniformity of the shear velocity gradient in the measurement gap. A special temperature device H-PTD 200 based on the Peltier effect was used to maintain and change the temperature mode. During the experiment, approximately 0.07 ml of the solution was placed on the working surface of the rheometer plate. The thickness of the solution layer along its outer radius was 0.047 mm, which ensured the rapid establishment of the operating temperature in the sample even under heat release conditions due to the polymerization reaction.

The measurements were performed under the conditions of shear deformation according to a harmonic law with a frequency of 1 Hz in the mode of control of the value of deformation, which allows us to estimate not only the viscous but also the viscoelastic characteristics of the samples.

The change in binder viscosity at the initial stage of the polymerization process is shown in figure 1(a).
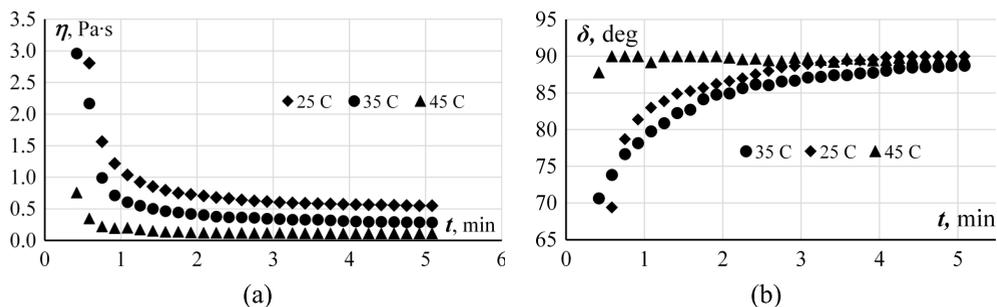
Figure 1. The initial stage of the polymerization process. (a) Viscosity change at the beginning of the polymerization process. From top to bottom: 25, 35, 45°. (b) Change of the phase angle at the initial stage of the polymerization process. From top to bottom: 25, 35, 45°C
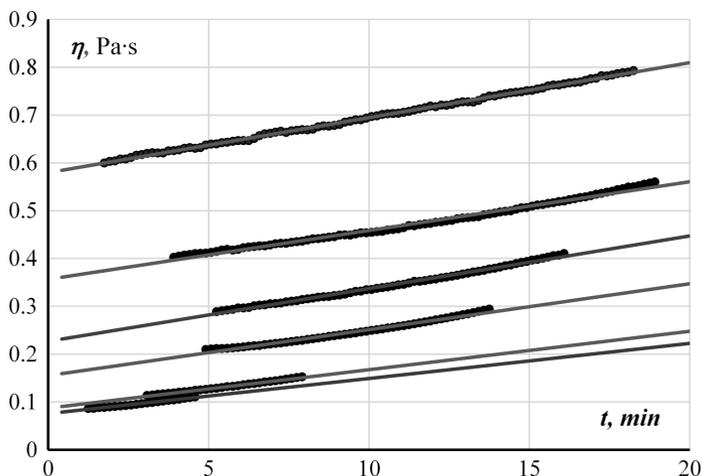
Figure 2. Change in viscosity at the initial stage of the polymerization process. Top–down: $T = 25$, 30, 35, 40, 45, 50°C

As you can see from figure 1(a), immediately after the start of measurements for all samples, the effective viscosity decreases with increasing shear rate, but eventually reaches a constant value practically independent of the shear rate, which can be conditionally interpreted as the second Newtonian viscosity.

The oscillation mode allows us to evaluate not only the viscous but also the viscoelastic characteristics of the samples. In this mode, the deformation γ is given by the harmonic law $\gamma = \gamma_0 \sin(\omega t)$, where γ_0 is its amplitude value, ω is the cyclic frequency. In the region of small deformations, the stress τ also varies according to the harmonic law $\tau = \tau_0 \sin(\omega t + \delta)$, where δ is the phase shift angle between the shear stress and deformation. If the phase shift angle differs by $\pi/2$, such body is called viscous. If the phase shift angle is in the range $\pi/2 > \delta > 0$, such a body is called viscoelastic.

Figure 1(b) shows the change in the phase shift angle δ between the shear stress and the deformation γ depending on the measurement time. Immediately after the start of measurements, the binder exhibits viscoelastic properties: $\delta < 90°$, but as the shear rate increases, the phase shift angle tends to 90°, which corresponds to a purely viscous behavior. This corresponds to the viscosity curves in terms of reaching the second Newtonian viscosity.

The second Newtonian viscosity is commonly used to correctly compare the behavior of non-Newtonian fluids. When analyzing the viscosity curves measured at different temperatures, it was found that reaching the second Newtonian viscosity provides pre-mixing for no more than 5 minutes. Accordingly, the following test mode was chosen: first, the flow curve was measured in the range of shear rates from 0.3 to 30, with which the output to a constant viscosity value was additionally controlled. The measurements were then continued at a shear rate of 30 s up to the required moment of time.

The results of viscosity measurements at the initial stage of the isothermal regime are shown in figure 2.

It can be seen that at the initial stage of polymerization in the considered temperature range, in all cases, there is a section where the viscosity behaves almost linearly. Note that the duration of this quasi-linear section decreases with increasing temperature.

3 Isothermal polymerization analysis

Earlier work by the authors [12] measured the temperature dependences of the viscosity for the resin (ep index) and hardener (am index) separately:

$$\eta_{ep}(T) = 4.512 \cdot 10^{-5} \exp\left(\frac{937.6}{72.42 + T}\right), \quad \eta_{am}(T) = 1.277 \cdot 10^{-5} \exp\left(\frac{1120.3}{87.42 + T}\right). \tag{1}$$

Here and in the future, T is expressed in Celsius degrees. We construct the dependence of the viscosity of the epoxy composition at the zero moment of time, taking into account the ratio of stoichiometric equilibrium 4:1 in multiplicative form [12]:

$$\eta(0, T) = \eta_0(T) = \eta_{ep}^{0.8}(T) \cdot \eta_{am}^{0.2}(T). \tag{2}$$

We approximate the quasi-linear sections of viscosity changes (figure 2) by a linear dependence of the form

$$\eta(t, T) \approx \eta_0(T)(1 + \alpha_1(T)t). \tag{3}$$

The calculated values of $\eta_0(T)$ (marked by dots) in comparison with the empirical functional dependence (2) are shown in figure 3(a). It can be seen that there is good agreement between them.

The authors [13] proposed and experimentally tested the simplest kinetic model, which describes the process of polymerization of similar binder. This model is a Cauchy problem for ordinary differential equations, which has an analytical solution, which in the case of stoichiometric equilibrium looks like:

$$\frac{d\psi(t, T)}{dt} = K(T)(1 - \psi(t, T))^2, \quad \psi(0, T) = 0, \quad \psi(t, T) = \frac{K(T)t}{1 + K(T)t}, \tag{4}$$

where $\psi(t, T)$ is the fraction of the reacted resin molecules (or hardener). In the same place, based on the processing of the experimental data, the function $K(T)$ was approximated by the Arrhenius function:

$$K(T) = 51590 \cdot \exp\left(-\frac{5020}{T + 273.15}\right). \tag{5}$$

Let's write down the model of change of viscosity of epoxy composition from temperature and fraction of reacted molecules, characterizing the degree of curing in the form:

$$\eta(t, T) = \eta(\psi(t, T), T) = \eta_0(T) \eta_1(\psi(t, T), T), \quad \eta_1(\psi(0, T), T) = 1. \tag{6}$$
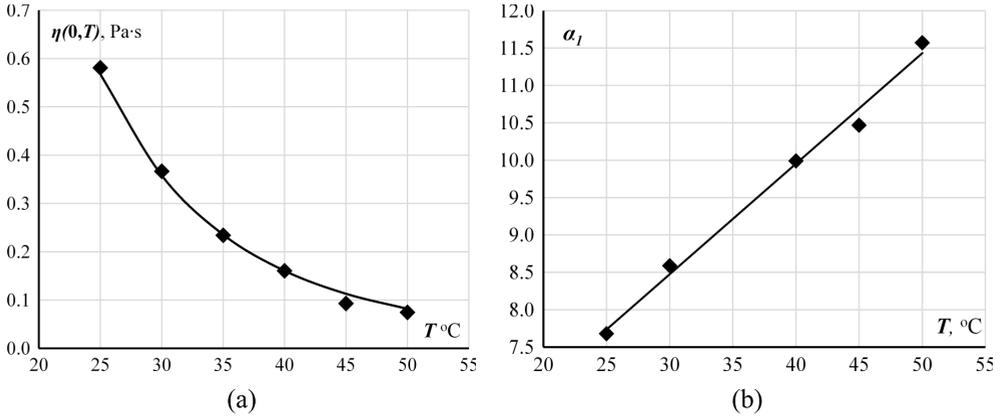
Figure 3. Change in viscosity and parameter α_1 as a function of temperature. (a) Initial viscosity values depending on temperature. (b) Change of parameter α_1 from temperature: squares are calculated values obtained on the basis of experimental data according to formula (3), a solid curve is an approximation of the calculated data
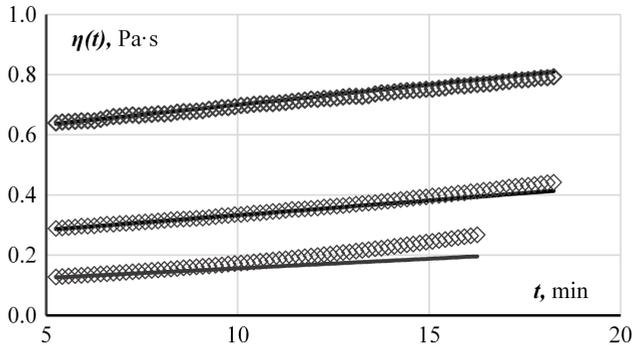
Figure 4. Comparison of experimental data with model (7). From top to bottom: $T = 25, 35, 45°C$. Rhombuses—experiment, solid lines—calculation

Decomposing function (6) into Taylor series in the vicinity of point $t = 0$, we obtain

$$\eta(t, T) = \eta(0, T) + \frac{d\eta(0, T)}{dt}t + \ldots = \eta_0(T)\left(1 + \frac{\partial\eta_1(\psi(0, T))}{\partial\psi}\frac{d\psi(0, T)}{dt}t\right) + \ldots$$

According to model (4): $\dfrac{d\psi(0, T)}{dt} = K(T)$. Comparing this result with the empirical dependence (3) we have: $\dfrac{\partial\eta_1(\psi(0, T))}{\partial\psi} = \dfrac{\alpha_1(T)}{K(T)}$. The results of this comparison are shown in figure 3(b).

The result of approximation of the experimental data: $\dfrac{\partial\eta_1(0, T)}{\partial\psi} = 4.04 + 0.15T$. Analytical solution of the problem (4) in linear approximation is $\psi(t, T) \approx K(T)t$. Thus, dependence (6) at the initial stage of curing can be written in the form:

$$\eta(t, T) \approx \eta_0(T)\left(1 + \frac{\partial\eta_1(0, T)}{\partial\psi}\psi(t, T)\right). \tag{7}$$

Figure 4 shows the results of comparing the experimental data with approximations according to model (7). Note that, the area of the linear section decreases with increasing temperature, according to the model.

4 Analysis of nonisothermal polymerization

The temperature change was modeled by the following law to analyze the behavior of the binder viscosity at the initial stage of nonisothermal polymerization:

$$T(t) = \begin{cases} T_0, & t \in [0, t_0), \\ \alpha(t - t_0), & t \in [t_0, t_1), \\ T_1 = \alpha(t_1 - t_0), & t \geq t_1. \end{cases} \tag{8}$$

In all cases $t_0 = 5.5$ min, $T_0 = 25, 30, 35°C$, $T_1 = 50°C$ were used and the rate of temperature change was varied: $\alpha = 0.1, 0.2, 0.3, 0.4, 0.5$ deg/min. The non-isothermal polymerization revealed the influence of two mechanisms on viscosity change: a) viscosity increase as a result of chemical reaction, b) viscosity decrease as a consequence of temperature increase.

Figure 5(b) shows the change in viscosity during the first 45 minutes of the polymerization process at $T_0 = 25°C$, $\alpha = 0.1$ and $\alpha = 0.5$ deg/min.
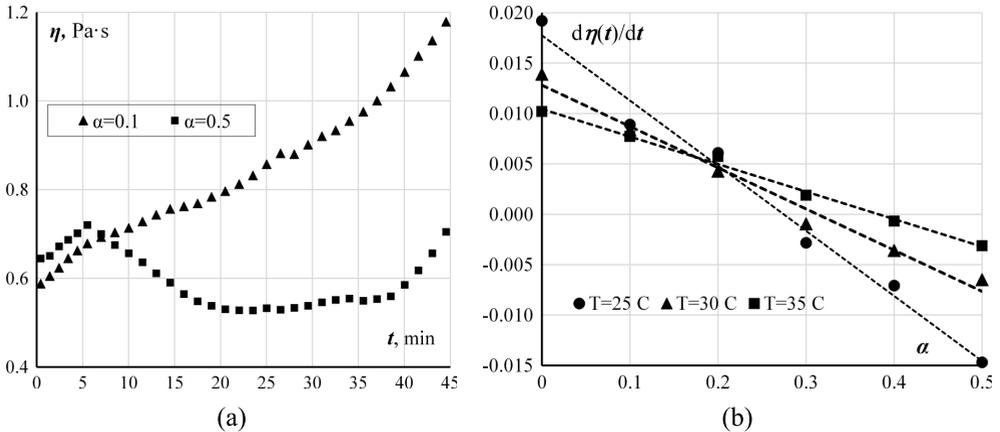
Figure 5. Viscosity change during the first 45 minutes of the polymerization process. (a) Change in viscosity depending on the heating rate. $T = 25°C$. (b) Dependence of the rate of change of viscosity on the parameter α and temperature T_0

At $\alpha = 0.1$, there is a monotonic increase in viscosity over the entire time interval (the first mechanism dominates). At $\alpha = 0.5$ in the isothermal region ($t < 5.5$, $T(t) = T_0$) the viscosity increases and then decreases till about $t = 20$ min (the second mechanism dominates).

Processing of experimental data shows that, here, as well as in the isothermal case, during the first 10–15 minutes, the viscosity of the non-isothermal area from the time can be approximated by decomposition of the form:

$$\eta(t, T(t); \alpha) = \eta(t_0, T_0) + (t - t_0)\frac{d\eta(t_0, T_0; \alpha)}{dt} + \ldots$$

The change in the value $\dfrac{d\eta(t_0, T_0; \alpha)}{dt}$ depending on the rate of temperature increase (parameter α) for $T_0 = 25$, 30, and 35°C is shown in figure 5(b). Such curves can be approximated by the expression $\dfrac{d\eta(t_0, T_0; \alpha)}{dt} = b_0 + b_1\alpha$.

Note that at this stage of the polymerization process, at $\alpha < 0.25$ the viscosity increases and at $\alpha > 0.4$ it decreases. We will evaluate the parameters b_0 and b_1 using a modified model (6): $\eta(t, T(t)) = \eta(\psi(t, T(t))) = \eta_0(T(t))\eta_1(\psi(t, T(t)))$.

In this case:

$$\frac{d\eta(t, T(t))}{dt} = \frac{d\eta_0(T(t))}{dT}\frac{dT(t)}{dt}\eta_1(\psi(t, T(t))) +$$
$$+ \eta_0(T(t))\frac{d\eta_1(\psi(t, T(t)))}{d\psi}\left(\frac{\partial\psi(t, T(t))}{\partial t} + \frac{\partial\psi(t, T(t))}{\partial T}\frac{dT(t)}{dt}\right).$$

Taking into account that $\dfrac{dT(t_0)}{dt} = \dfrac{dT(t_0 + 0)}{dt} = \alpha$ the model expression for the parameters b_0 and b_1 takes the form:

$$\tilde{b}_0 = \eta_0(T_0)\frac{d\eta_1(\psi(t_0, T_0))}{d\psi}\frac{\partial\psi(t_0, T_0)}{\partial t}, \tag{9}$$

$$\tilde{b}_1 = \frac{d\eta_0(T_0)}{dT}\eta_1(\psi(t_0, T_0)) + \eta_0(T_0)\frac{d\eta_1(\psi(t_0, T_0))}{d\psi}\frac{\partial\psi(t_0, T_0)}{\partial T}. \tag{10}$$

Note that in the non-isothermal case the analytical solution of problem (4) has the form:

$$\psi(t, T(t)) = \frac{\hat{K}(T)t}{1 + \hat{K}(T)t}, \quad \hat{K}(T(t)) = \frac{1}{t}\int_0^t K(\tau)\, d\tau. \tag{11}$$

To determine the parameters $\tilde{b}_0$ and $\tilde{b}_1$ it is enough to differentiate equations (2), (5) by T and for the functions $\eta_0(T)$, $\psi(t, T)$ and $\hat{K}(T(t))$.

The results of processing experimental data (see figure 5(b)) and calculations by formulas (9)–(10) are presented in table 1, while it was assumed that $\dfrac{\partial\eta_1(t_0, T_0)}{\partial\psi} \approx \dfrac{\partial\eta_1(0, T_0)}{\partial\psi}$.

Table 1. Comparison of experimental and calculated data

T_0, °C	$b_0 -$ exp	$\tilde{b}_0$	$b_1 -$ exp	$\tilde{b}_1$
25	0.0178	0.0170	−0.0647	−0.0640
30	0.0128	0.0139	−0.0409	−0.0382
35	0.0105	0.0118	−0.0273	−0.0241

Comparison of the calculated and experimental data shows their sufficient agreement (maximum deviation is not more than 10%).

Thus, the viscosity behavior at the initial stage of polymerization (the first 15–20 min of the process) for the epoxy composition under consideration is largely determined by the viscosity of the resin and hardener separately and by the degree of hardening using model (4).

5 Conclusions

This artical has detailed the experimental study and numerical simulation of changes in the viscosity of an epoxy binder at the initial stage of the polymerization process. It is shown that a linear approximation is possible at the initial period of time, which allows quantifying the mutual influence of two mechanisms of viscosity change:

a) viscosity increase as a result of chemical reaction;

b) viscosity decrease as a result of temperature increase.

The ranges of the rate of temperature change, in which one or another mechanism of viscosity behavior is the main one, were also determined. It is shown that the proposed mathematical model that takes into account the degree of curing of the binder allows us to describe the real process in good approximation.

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