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Investigation of epoxy matrix viscosity in the initial stage of its formation

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Abstract. The present study includes experimental investigations of rheological properties of the epoxy composite matrix based on epoxy resin L and hardener EPH 161. It is shown that the temperature dependences of the oligomer viscosity and the hardener can be satisfactorily described by the Arrhenius equation. Dependence of epoxy resin viscosity on temperature and volume concentration of the hardener at the initial stage of the polymerization process is investigated. It is shown that the experimental results can be generalized with one universal dependence of concentration and temperature.

1. Introduction

Due to their unique properties, epoxy-based polymer materials are widely used in industrial processes and in creating various polymer constructions and structures. They have high dielectric and strength properties, radiation resistance, so these materials can be used both on Earth and in space [1, 2]. A number of studies suggest that epoxy compositions are to be used for bulky space structures, which are supposed to get cured directly in space in high vacuum, cosmic radiation and extreme temperatures [3-5]. The curing process, as well as end-use properties of the curable composites, largely depend on the evaporation process of epoxy active components. Experiments in space flights are complicated and expensive. Therefore, the terrestrial experiments in vacuum and plasma, as well as theoretical modeling of the processes of epoxy compositions are more realistic.

In the literature there are many studies devoted to the curing processes of epoxy resins (see for example [6-8]). Physical and chemical properties of structural materials are also quite well investigated.

At the same time, the studies of the processes occurring in the initial stage of polymerization (i.e. immediately after the components are mixed) are not numerous. Among the studies covering these problems is [9]. By the methods of NMR and dielectrometry it investigates the kinetics of macromolecule formation and their mobility in the mixture of epoxy resin and polyethylene polyamine immediately after mixing at temperatures of 20 °C and 100 °C, and makes an assumption that the final properties of the product are formed at the initial stage of formation of the macromolecules occurring in the reaction of the oligomer and the hardener. Calorimetric, chemical and spectroscopic methods are widely used as experimental methods for studying epoxy oligomer structuring processes, as they allow us to obtain analytical expressions describing the kinetics of hardening of epoxy resins. Strictly speaking, the immediate registration of varying concentrations of reactive groups is possible only with IR spectroscopy and NMR. However, in some cases the use of these methods leads to ambiguity in the interpretation of the obtained results due to the complexity of spectra of real multicomponent
compositions. At the same time, for observation of macroscopic properties of curable compositions we can apply rheological investigations which allow us not only to determine the location of the gel point at which the evaporation of the binder active components decreases, but also to connect macrokinetic description of the reaction with physical and mechanical properties of the reacting system such as binder viscosity and prepreg elasticity modulus directly affecting the ability of the uncured composite to unfold from a shipping container in the space orbit. Of course, viscosimetric flows may affect the process of composite polymerization, but any technological process at its initial stage is connected to shear deformations.

In the present study we measured the effective viscosity of solutions of the oligomer and its hardener depending on the temperature and hardener concentration at the initial stage of the polymerization process.

2. The object of study and preparation of samples

In the experiments we used the epoxy composition - epoxy resin L and EPH 161 hardener certified for use in constructional composites applied in aircraft industry. The mixture was prepared in the required proportions in a weight ratio of epoxy resin and curing agent (hardener). After preparations, the mixture was thoroughly mixed for 1-2 minutes with the electromechanical mixer and further for 1-2 minutes in the ultrasonic bath Digital Ultrasonic Cleaner CD 4820 (at 40 kHz). The last operation degases the mixture. It took 3-4 minutes to prepare the samples – quite a short period – as the rate of polymerization processes is rather high under normal conditions, and the composition properties change rapidly after its components get mixed.

Measurements of the mass of solutions and their components necessary to calculate the concentration of the mixture were performed using the analytical balance LV-210A (accuracy class 2, absolute measurement error ± 0.4 mg).

To measure the density of samples necessary for calculation of the volume concentration of solutions we used the digital vibration densimeter DMA 5000 M with an absolute measurement error not more than 0.000005 g/cm³. The densimeter has a built-in Pelletier thermostat to study temperature dependences of the density.

Rheological measurements were performed using a rotary rheometer Physica MCR 501. This device gives rheological data in a wide range of fixed and dynamic tests in a controlled shear stress (CS) and controlled shear rate (CR) modes from measurements of flow curves to dynamic analysis of complex fluids.

The "cone-plate" system was used in all the measurements (the cone diameter \(d = 25\) mm and the angle \(\alpha = 1^\circ\)). The used geometry provides shear rate gradient uniformity in the measurement gap. To verify the data, several measurements were performed using a cone with \(d = 50\) mm (cone angle 1°). The temperature of the sample was controlled by a Peltier temperature controller with accuracy less then 0.1 °C. The header and measuring system were kept inside a protective cover for uniformity of the sample temperature. During the experiment, about 0.07 ml of the solution was located on the rheometer work surface. The thickness of the solution layer on its outer radius was 0.047 mm, which ensured the sample to achieve the working temperature quickly even in conditions of heat release due to the polymerization reaction.

Preliminary experiments showed that at temperatures below 15 °C the flow curves of the oligomer and hardener are similar to pseudoplastic materials: the viscosity decreases slightly as the shear rate increases, and then becomes constant – its value becomes correspondent to the second Newtonian viscosity. Non-Newtonian behavior is observed for the resin and hardener solutions.

When measuring the viscosity of Newtonian liquids the CR and CS modes have equal opportunities and give identical results. This statement is no longer valid for rheological tests of non-Newtonian fluids. Given that the CS-rheometers provide higher sensitivity at low shear rates, the controlled shear stress mode was selected as the main research method, as it is more consistent with the actual application conditions.
Comparison at constant shear stress has another advantage: although different classes of fluids may have different viscosity curves, the analysis of curves obtained at constant shear stress, enables us to compare them with each other, and the character of their flow is similar to the flow in capillaries. In all experiments, we used the value of shear stresses of 2 Pa, which provides an egress of the flow curves to the second Newtonian viscosity throughout the range of all the investigated temperatures and solution concentrations. The realizable shear rate range was from 0.015 to 150 s⁻¹, depending on the solution concentration and medium temperature.

3. The measurement results and their analysis

Temperature dependences of resin density and hardener in the temperature range of 10 to 80 °C is very well approximated by expressions of the form: \( \rho_0 = -0.0007135 T + 0.9783 \) and \( \rho_0 = -0.0007777 T + 1.1656 \) for the hardener and resin respectively. If the temperature is presented in °C, then the density dimension is shown in g/cm³. The approximation error does not exceed 3%.

The results of measurements of the temperature dependences between the resin effective viscosity and the hardener are shown in Fig. 1. The inset shows large-scaled sections of these dependences (ordinate direction).

![Figure 1. Dependence of effective viscosity on temperature: ■ – epoxy resin; ○ – hardener; Solid lines – approximations of dependencies](image)

Solid lines in Fig. 1 present experimental data approximations by the Arrhenius equation:

- For the hardener: \( \eta_o = 1.277 \times 10^{-5} \exp \left( \frac{1120.3}{87.42 + T} \right) \)
- For the resin: \( \eta_o = 4.512 \times 10^{-5} \exp \left( \frac{937.6}{72.42 + T} \right) \)

If the temperature \( T \) is presented in °C in these formula, the viscosity \( \eta \) is shown in Pa·s. The approximation error does not exceed 3%.

The measured values of the epoxide compound viscosity (hardener concentration is 20%) are greater than the corresponding values of resin viscosity. This means that the polymerization starts in the process of mixing.

It is well known that viscosity variations occurring in the course of epoxy hardening have quite a complicated character, but at the initial stages of the reaction the linear growth of macromolecules prevails. In this case, the viscosity of the reaction system with time \( t \) usually conforms to the power law \( \eta = k t^a \), where \( a \) takes values ranging from 1 to 3.5 [10].

Actually, the measurements showed that the dependences of the effective viscosity of resin and hardener solutions on time at the initial stage of polymerization are linear (\( a = 1 \)) with the coefficient \( k \) which depends on the concentration of the hardener (Fig. 2). This allows us to extrapolate them to the
value $t \to 0$ in order to bring all the viscosity values measured at different concentrations to the same time, since in experiment it is not possible to get the same time in sample preparation. These values of viscosity are used in all experimental results hereinafter.

In Fig. 3 shows the results of measurements of the solution viscosity depending on the volume concentration of the hardener $C$ for 17 °C.

![Figure 2](image1.png)

**Figure 2.** Dependences of solution effective viscosity on time at the initial stage of the polymerization process. From top to bottom hardener solutions $C$: 0.025; 0.02; 0 (resin); 0.3; 0.4; 0.6; 0.8; 1 (hardener)

![Figure 3](image2.png)

**Figure 3.** Dependence of epoxy composition effective viscosity on hardener concentration. Solid lines - calculation by formulas (1) - (2) and (4). Details are given in the text

The viscosity curve has a characteristic maximum which value is bigger than the oligomer viscosity, but after reaching its maximum the solution viscosity decreases so that within the limit $C \to 0$ it corresponds to the resin viscosity. It should be noted that the measurement results are well reproduced both at different time points, and at other – bigger value of tangential stresses.

To assess the effect of the polymerization process at the initial stage of epoxide compound formation we use a simplified version of the model of kinetics of the process proposed in [11]. Curing of the epoxy composition occurs inhomogeneously so at any time there are reacted macromolecules with chemical bonds and also there are initial macromolecules, which did not yet react. Assume that at
the initial stage of the process all molecules are initial. In this case, the Cauchy model of the corresponding dynamic system takes the form:

\[
\begin{align*}
\frac{dn_0^{ep}(t)}{dt} &= -(K_{0.0}n_0^{am}(t) + K_{1.0}n_1^{am}(t))n_0^{ep}(t), \\
\frac{dn_1^{ep}(t)}{dt} &= (K_{0.0}n_0^{am}(t) + K_{1.0}n_1^{am}(t))n_1^{ep}(t), \\
\frac{dn_0^{am}(t)}{dt} &= -(K_{0.0}n_0^{ep}(t) + K_{0.1}n_1^{ep}(t))n_0^{am}(t), \\
\frac{dn_1^{am}(t)}{dt} &= (K_{0.0}n_0^{ep}(t) + K_{1.0}n_1^{ep}(t))n_1^{am}(t).
\end{align*}
\] (1)

Here the index "ep" denotes the resin concentration, and "am" – the hardener concentration. The assumption made above leads to the following balance equation:

\[
n_0^{ep}(t) + n_1^{ep}(t) = n_0^{ep,0}, \quad n_0^{am}(t) + n_1^{am}(t) = n_0^{am,0}, \quad n_0^{ep,0} + n_0^{am,0} = 1.
\] (3)

To account the viscosity variations the Chong formula was used in the form [11];

\[
\eta_{solution}(t) = \eta_{solution}(0) \left(1 + \frac{1.25 \varphi(t)}{1 - \varphi(t) / \varphi_{max}}\right)^2,
\]

where \( \varphi(t) = \frac{V_{ep}n_1^{ep}(t) + V_{am}n_1^{am}(t)}{V_{ep}n_0^{ep,0} + V_{am}n_0^{am,0}}. \)

The parameters of equations (2) were \( K_{0.0} = 4 \cdot k_a, \quad K_{0.1} = K_{1.0} = 2 \cdot k_a, \) and the constants \( k_a \) and \( \frac{V_{ep}}{V_{am}} \) were determined by the least squares method with the use of experimental data (see Fig. 3.). The result of numerical solution of the problem at \( t = 3 \) min is also presented in Fig. 3. Here we also can see the curve calculated by the known relation for determining the viscosity of the mixture:

\[
\eta_{S} = \eta_{0}^{am,0} \cdot \eta_{c}^{n_0^{ep,0}}
\] (4)

Thus, we can conclude that the observed effect (see. Fig. 3) is actually the result of the polymerization initial stage.

On the other hand, dimensions of macromolecule aggregates formed at the initial stage of polymerization depend on the concentration of components in the solutions. To compute the intrinsic viscosity of such an aggregate we can use the hypothesis that the ratio of characteristic viscosities is proportional to the ratio of aggregated molecules volume to the total volume of individual unreacted molecules. In other words, from the macroscopic point of view the solutions can be regarded as heterogeneous systems with two different medium fractions. This approach is widely used to analyze the viscosity of disperse systems taking into account the interaction of particles [12] and is successfully applied in [11] to approximate the dependence of the epoxy composition viscosity on the polymerization time. This gives grounds for using the obtained experimental data (Fig. 3) to determine the empirical viscosity dependence on the hardener concentration. At that, one of the main requirements is the need for the selection of a simple expression, enabling an adequate description of the experimental data and the ability to generalize the results to other parameters of the medium.
The regression analysis yields

$$\eta_S = \frac{1.329}{C} \eta_O \exp\left(-\frac{0.179}{0.0398 + C}\right),$$  \hspace{1cm} (5)

where $\eta_S$ and $\eta_O$ are the viscosities of the solution and hardener, respectively; $C$ is the hardener volume concentration. Substituting the dependence of hardener viscosity on temperature to this expression, we obtain

$$\eta_S = \frac{1.697 \cdot 10^{-5}}{C} \exp\left(-\frac{0.179}{0.0398 + C} + \frac{1120.3}{87.42 + T}\right)$$  \hspace{1cm} (6)

which is the empirical relationship allowing estimation of the solution viscosity in relation to the medium temperature and hardener concentration at $C > 0.015$, as at lower concentrations approximation dependence has a special feature: at $C < 0.015$ the estimated value of the viscosity increases and tends to infinity. In order to verify the obtained expression, effective viscosity measurements were carried out at different temperatures. The results of the comparative analysis of the experimental and calculated data are shown in Fig. 4.

**Figure 4.** Dependence of effective viscosity on hardener concentration and medium temperature. *From top to bottom: $T = 17; 20; 25, 30; 40^\circ$C. Markers show the experimental results, solid lines present the formula (6) evaluation.

The relative error of approximation in the range $C > 0.015$ is 5% on the average. As can be seen from the figure, the empirical relationship adequately describes the experimental data in relation to the volume concentration of solutions and medium temperature.

4. **Conclusion**

The physical properties of epoxide compound (epoxy resin L, hardener EPH 161) are investigated. Empirical dependences of resin density and viscosity and hardener on temperature within the range of 10 to 80 °C are obtained. Dependences of composite solution viscosity in relation to hardener volume concentration and medium temperature are measured. Finally, the investigation presents the empirical relationship adequately describing the experimental results, enabling estimation of the corresponding variation in a wide temperature range according to measurements of the viscosity concentration dependence measured at a certain temperature.
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