Research of the viscosity of unfilled polymers using quality functionals

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Abstract. Kinetic processes of unfilled polymers structure formation are explored and mathematical method of polymer composites modelling using kinetic (transient) processes quality functionals is proposed. Advisability of kinetic (transient) processes consideration as necessary and sufficient sign of thermosetting binder structure formation is justified. The processes occurring during the formation of the modified polymer and appearance of qualitatively new properties while maintaining chemical individuality of each component are considered. Application of mathematical method is carried out in the construction of mathematical model and study of unfilled epoxy resin ED-16 viscosity.

1. Introduction

The epoxy resin brand ED-16 is a highly viscous transparent liquid from light yellow to brown color, soluble in toluene, xylene, ketones; resistant to water, solutions of salts, acids, alkalis and radiation. According to its rheological properties, ED-16 epoxy resin refers to low-viscosity Newtonian fluids with viscosity at 40 °C 20000-60000 cP [1].

Due to its high molecular weight, ED-16 epoxy resin is more suitable than others for the preparation of composite materials. But the manufacture of various composite materials based on ED-16 resin is a very time-consuming process, since at ordinary (room) temperature this resin can’t be used due to its high viscosity.

2. Research methods and principles

The viscosity and modifier effects were studied on a VZ-4 viscometer using a standard method.

In the course of research, an experimental dependence of the viscosity $B(t)$ on the temperature of the resin $t$ was obtained, which has the form:

\[ B(t) = A \cdot \exp (-b \cdot t), \]

\[ B(t) \] – the viscosity of resin, sec; \( t \) – the temperature of resin, °C; \( A \) and \( b \) – constant coefficients equal \( A = 7267.2 \) and \( b = -0.0723 \).

Equation (1) is a modified Arrhenius fluidity equation:

\[ B(t) = B(t_i) \cdot \exp \left( \frac{-E}{R \cdot T} \right), \]

\( B(t) \) – the viscosity of resin; \( B(t_i) \) – the viscosity of resin at \( i \)-temperature; \( E \) – activation energy; \( R \) – gas constant; \( T \) – temperature.
It is obvious that equation (2) is easily transformed into equation (1). However, the use of equation of the form (1) can significantly facilitate the assessment of the effectiveness of the action of modifiers on the viscosity of the resin. Visual assessment of the effectiveness of modifiers is difficult due to errors in determining viscosity, inaccuracy of graphical constructions, randomness in the choice of scale, the set of compared curves, etc.

Differentiating a viscosity equation of the form (1) and equating the first derivative to zero, it is easy to find the tangent of the angle (or the angle itself) of the slope of the tangent to the abscissa at any point on the curve. Let it be a point of 40 °C, corresponding to the limiting temperature of the combination of resin and hardener (figure 1). Figure 1 shows that $\angle \alpha > \angle \beta$. This means that the viscosity of the system described by function "I" will be higher than the viscosity of the system described by function "II" at the temperature of 40 °C. With a large number of experiments and in the presence of experimental errors, this method can significantly speed up the process of data analysis (through the use of computers), as well as improve its quality.

Using this method, the concentrations of plasticizers and modifiers were found.

![Figure 1. Illustration of a method for determining the effectiveness of modifiers on the unfilled resin ED-16 viscosity.](image)

3. The main results
There are no theoretical aspects of plasticization of these systems for highly viscous materials based on ED-16 resin and, of course, there are no optimal formulation and technological parameters of the compositions. Therefore, the optimal concentrations of plasticizers and modifiers were determined during practical testing of the method. The simplest, but also rather rough, is a stepwise approximation. It can be used either with a fine grid in the space of the argument $x$, or with a special stepwise form of the function itself. During creating a mathematical model of the viscosity of unfilled epoxy resin the problem of approximating the function of several variables can be solved on the basis of the least squares method, representing it as the sum of one variable. For the case of a function of two variables $f(x_1, x_2)$ with a rectangular region of variation of the arguments

$$d_{11} \leq x_1 \leq d_{12}, d_{21} \leq x_2 \leq d_{22}$$

the solution to the problem is obtained in the form:
\[ f_i(x_1, x_2) = \overline{f}^{i_1} + \overline{f}^{i_2} - \overline{f}^{i_1i_2}, \]

here

\[ \overline{f}^{i_1} = \frac{1}{(d_{12} - d_{11})} \int_2 \int_1 f(x_1, x_2) \, dx_1, \]

\[ \overline{f}^{i_2} = \frac{1}{(d_{22} - d_{21})} \int_2 \int_1 f(x_1, x_2) \, dx_2, \]

\[ \overline{f}^{i_1i_2} = \frac{1}{(d_{12} - d_{11})(d_{22} - d_{21})} \int_2 \int_1 \int_2 \int_1 f(x_1, x_2) \, dx_1 \, dx_2. \]

In the case of approximation \( f(x_1, x_2) \) in the form of a factum of two one-dimensional functions, introducing \( \phi(x_1, x_2) = \ln f(x_1, x_2) \) and executing the approximation of this function by the sum \( \phi_1(x_1) + \phi_2(x_2) \), we obtain:

\[ f(x_1, x_2) = f_1(x_1) f_2(x_2). \]

here \( f_i(x_i) = \exp \phi_i(x_i) \), \( f_i(x_i) = \exp \phi_i(x_i) \).

A new mathematical method is proposed for modeling multidimensional tabulated functions by generalized polynomials in obtaining a mathematical model of an unfilled epoxy resin viscosity. It is based on the solutions described above. In two-dimensional approximation the approximating polynomial is defined as:

\[ Q_q = a_1 f_1(x) \phi_1(y) + a_2 f_2(x) \phi_2(y) + \cdots + a_q f_q(x) \phi_q(y), \]

here \( f_p(x) \phi_p(y) \) – selected from experimental data functions.

Then the coefficients \( a_q \) are determined from the minimum condition

\[ \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \sum_{p=1}^{q} a_p f_p(x_i) \phi_p(y_j) - W_{ij} \right]^2, \]

here \( W_{ij} \) – table values \( f_i(x, y) \), which leads to a system of equations:

\[ \begin{align*}
C_{11} a_1 + C_{12} a_2 + \cdots + C_{1q} a_q &= b_1 \\
C_{21} a_1 + C_{22} a_2 + \cdots + C_{2q} a_q &= b_2 \\
& \vdots \\
C_{q1} a_1 + C_{q2} a_2 + \cdots + C_{qq} a_q &= b_q.
\end{align*} \]

Here

\[ C_{\alpha, \beta} = f_{\alpha, \beta} \phi_{\alpha, \beta}, \quad \alpha = 1, 2, \ldots q, \quad \beta = 1, 2, \ldots q; \]

\[ f_{\alpha, \beta} = \sum_{i=1}^{n} f_\alpha(x_i) f_\beta(x_i) \phi_{\alpha, \beta} = \sum_{j=1}^{m} \phi_\alpha(y_j) \phi_{\beta}(y_j) \]

\( \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \sum_{p=1}^{q} a_p f_p(x_i) \phi_p(y_j) - W_{ij} \right]^2, \)

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C_{q1} a_1 + C_{q2} a_2 + \cdots + C_{qq} a_q &= b_q.
\end{align*} \]
The implementation of the proposed method is shown on the example of unfilled and modified epoxy resin ED-16. Table 1 shows the data for determining the dependence of viscosity $B$ of a binder based on epoxy resin ED-16 on temperature $t \, ^\circ C$ and special additives (MO) in various concentrations $x, \%$.

**Table 1.** The relation of the viscosity (s) of the epoxy binder on the temperature and the percentage of plasticizer (MO).

| $t, \ ^\circ C$ | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
|----------------|----|----|----|----|----|----|----|----|----|----|-----|
| $x, \ %$       | 0  | 1  | 5  | 10 | 15 |
| 0              | 172| 119| 84 | 65 | 50 |
| 1              | 210| 145| 105| 80 | 65 |
| 5              | 250| 160| 115| 90 | 75 |
| 10             | 97 | 65 | 45 | 33 | 22 |
| 15             | 132| 91 | 62 | 47 | 36 |

The possibility of approximation $B = B(x, t)$ in the form shown in Figure 2 follows with obviousness.

**Figure 2.** Two-factor relation of the epoxy composites viscosity on temperature and percentage MM.

The mathematical model of the unfilled epoxy resin viscosity, according to the mathematical method for modeling viscosity presented above, can be obtained in the form:

$$B = \left( C_0 + C_1 x + C_2 x^2 + C_3 x^3 \right) e^{k(x-50)}, \quad 50 \leq t \leq 100$$
\[ B = \left( 0.5395x^3 - 12.609x^2 + 65.469x + 165.81 \right) e^{-(0.003x+0.0476)(x-50)} \]  

(17)

4. Discussion
As is known, there are two methods for modifying polymers by introducing plasticizing additives — molecular plasticization and structural plasticization [2, 3]. Molecular plasticization implies a change in the mechanical properties by introducing mainly low molecular weight substances into them, combining with the polymer at the molecular level. The effect of such plasticizers is that due to the interaction of the polymer with the plasticizer molecules, the forces of interaction of the macromolecules with each other are weakened. Because of this, it becomes possible to rearrange the units of macromolecules under the influence of external mechanical fields and, accordingly, the system's flexibility increases. Structural plasticization is associated with the effect of a change in mechanical properties upon the introduction of relatively small amounts of low molecular weight substances that are practically incompatible with the polymer. In this case, the plasticizer is distributed between the structural elements in the form of thin layers and exerts a peculiar “lubrication” effect. In this work, the following substances were used as plasticizing additives: mineral machine oil – MO, vegetable oil – VO, sunflower oil – SO, DBP – dibutyl phthalate. Figure 3 shows how the ED-16 resin viscosity changes from additives of optimal oil concentrations SO, VO and MO.

![Figure 3](image-url)

**Figure 3.** The effect of various plasticizers of optimal concentration on the of unfilled epoxy viscosity: 1 – pure resin; 2 – VO at a concentration of 5 %; 3 – SO at a concentration of 5 %; 4 – MO at a concentration of 10 %; 5 – DBP at a concentration of 15 %.

The chemical composition of mineral and vegetable oils is very complex. They contain paraffinic, naphthenic, aromatic, asphalt-resinous substances, as well as mixtures of highly unsaturated, unsaturated and saturated fatty acids with a number of other hydrocarbons. Some of these substances are reactive plasticizers and carry out molecular plasticization, while the other part is practically incompatible with epoxy resin and acts as structural plasticizers. Therefore, in the case of the use of modifiers such as MO, VO, and SO, complex plasticization takes place. Some of the molecules of the plasticizer MO interacts with the polymer molecules, weakening the forces of interaction of the macromolecules
with each other. At the same time, another part of the molecules of the plasticizer MO with their hydrocarbon radicals spreads the chains of polymer macromolecules, creating slip planes [3, 4].

In order to describe the processes of plasticization of polymeric materials, it seems promising to use dynamic models defined in the class of differential equations. For homogeneous systems, such a model in the class of ordinary differential equations is considered in [5–7]. An increase in the order of the differential equation allows one to describe the kinetic processes in heterogeneous, dispersed, and polydisperse systems for many controlled parameters [8, 9]. Moreover, as a rule, it turns out to be possible to restrict oneself to the class of ordinary differential equations with constant coefficients [10]. For the processes of the form shown in figure 4, with the asymptotic output of the controlled parameter to the operational value, you can use a model of the form:

$$\ddot{x} + 2n \dot{x} + \omega_o^2 (x - x_m) = 0.$$  \hspace{1cm} (18)

Here the abscissa of the inflection point is defined as:

$$t_n = \frac{1}{(\lambda_1 - \lambda_2)} \ln \left( \frac{\lambda_1}{\lambda_2} \right),$$  \hspace{1cm} (19)

here $\lambda_1, \lambda_2 (\lambda_1 > \lambda_2)$ – the modules of the (negative) roots of the characteristic polynomial.

The value of $\lambda_2$ can be determined at the end of the transition process. You can show the validity of the ratio $r^{\frac{1}{\lambda_2}} = e^{-\nu}$, here $r = (\lambda_1 / \lambda_2)$, $\nu = \lambda_2 t_n$. It allows to determine the value of $\lambda_1$, and, therefore, the process $x(t)$.

![Figure 4. Kinetic process view.](image)

It is easy to experimentally determine the dependences $\lambda_1$, $\lambda_2$, $x_m$ (the process $x(t)$) on the model parameters $\omega_o$ and $n$ (you can use the dimensionless damping coefficient $\xi = n / \omega_o \geq 1$ instead of $n$), taking into account the correlation between $\lambda_i$ and $F(S)$.

5. Conclusions

As can be seen from figure 3, the optimal concentration of plasticizer is 10% by weight of the resin, which means that 2-4 resin molecules have 1 plasticizer molecule. Such a quantitative ratio of substances is typical, for example, for the polycondensation reaction between an epoxy resin and aliphatic amines. Therefore, it would be fair to assume the interaction between the macromolecules of the epoxy resin and the reactive components of the plasticizer MO, which proves the effect of molecular plasticization. The viscosity curves obtained using MO are close to the curves obtained using a tradi-
tional non-reactive plasticizer – dibutyl phthalate (figure 3). This proves the presence of the effect of structural plasticization. However, unlike the case of DBP, engine oil in epoxy resin promotes cross-linking, is well distributed in the resin mass, which does not lead to a sharp softening of the structure.

Epoxy polymers are known to possess a static glomerular conformation with strong interlacing at the molecular level [11]. The introduction of small amounts of plasticizer (1-5%) leads to the formation of aggregates from epoxy oligomers and the reactive part of the plasticizer MO, which causes a slight increase in the viscosity of the system. A further increase in the concentration of plasticizer to 10-15% leads to crushing of the formed aggregates, the appearance of smaller globules and packs and a decrease in the friction forces between neoplasms, tangles and individual molecules of the epoxy oligomer, leading to effective molecular and structural plasticization of the system. The effect of complex plasticization can also explain the fact that when introducing MM plasticizer into the system, the decrease in physical and mechanical properties does not exceed 10%, while when using DBP plasticizer, these properties are reduced by 35-40%.

The proposed mathematical methods and models make it possible to effectively solve the problem of plasticizing highly viscous polymers using the quality functionals of kinetic (transient) processes for the purpose of multicriteria synthesis of polymer composite materials.

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