Study of the laws governing the structure formation of epoxy oligomer cured with diaminodiphenylsulphone

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SUMMARY
A study was made of the effect of thermoplastic modifiers on the kinetics of curing of the epoxy binder. The kinetic and diffusion constants of the curing process were determined.

INTRODUCTION
The study of curing processes is very important in the production of materials with specified properties. Features of the structure formation process determine the production technology of the binders, the degree of curing (i.e. the constancy of the properties during service), and the final service characteristics. Therefore, investigation of the curing of composites based on reactive oligomers and their mathematical description are important tasks.

In this work, the process of curing an epoxy oligomer-diaminodiphenylsulphone system was investigated by different methods: differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and viscometry at different temperatures. Another important task was to compare experimental data obtained by the different methods, and to determine whether they adequately describe the curing process at different stages. In the literature there is a fair amount of information on the combined application of different methods of investigation [1-5], and here the agreement or lack of agreement of experimental data often depends on features of curing of the investigated composites.

MATERIALS AND METHODS
The investigations were conducted on a composite based on epoxy oligomer ED-20 (70 wt%) cured with diaminodiphenylsulphone (DADPS) (30 wt%); the modifiers used were polysulphone (PSP) of grade PSK-1 with $M = 6 \times 10^4$ and polyarylene ether ketone (PAEK). The modifiers (5, 10, 15, and 20 wt%) were dissolved in the epoxy oligomer (with periodic stirring) at 120°C without the addition of solvents. The time of combination (until complete dissolution) varied from 2 h with the addition of 5% modifier to 24 h with the addition of 20% modifier. The mixtures obtained do not separate out during storage. Curing agent was added as needed, and specimens were prepared for all types of measurement.

The curing process was studied by DMA on an MK-3 torsion pendulum in a regime of freely attenuating oscillations with determination of the mechanical loss tangent $\tan \delta$ and the dynamic modulus $G'$, and also by DSC on a Mettler Toledo 822e differential calorimeter with determination of the heat effect of the chemical reaction. In the present work, this method was used for studying the change in the degree of transformation in the process of curing at 160, 170, and 180°C. The degree of transformation $\beta$ was calculated by means of the equation:

$$\beta = \frac{Q}{Q_{\text{max}}}$$

where $Q$ is the heat of the process under an isothermal
curing regime, and $Q_{\text{max}}$ is the maximum heat of the process in a scanning curing regime with a heating rate of 1°C/min.

The glass transition temperature $T_g$ was determined by DMA from the maximum $\tan \delta$ and on a Höppler consistometer. In the latter case, the specimen had the shape of a pellet of 10 mm height and 10 mm diameter, and the heating rate of the specimen was 1°C/min.

RESULTS AND DISCUSSION

The most widely used method for investigating the processes of curing of reactive oligomers is DSC [6, 7], as it makes it possible to obtain the fullest information about the interaction of all reactive groups by recording the heat released during the chemical reaction (Figure 1).

The dependence of the conversion $\beta$ on the curing time at different temperatures is given in Figure 2.

The DSC method established that change in the degree of transformation during curing is described by a first-order kinetic equation taking into account the effect of autoacceleration (the differential form of the equation):

$$\frac{d\beta}{dt} = k \cdot (1 - \beta) \cdot (1 + C \cdot \beta)$$

(1)

where $k$ is the rate constant of the reaction, and $C$ is a constant reflecting the effect of autoacceleration.

By plotting the dependence of the degree of transformation on the curing time in coordinates of the given equation:

$$\ln \left( \frac{\beta}{1 - \beta} \right) = -t$$

we obtain a direct dependence (Figure 3), which indicates the goodness of fit of the given model. The curing of epoxy resins with amines is generally described by this very equation, and here use is made of the integral form of Equation (1):

$$\ln C + \ln \beta (1 - \beta) = (1 + C) \cdot k t$$

(2)

From the data in Figure 3 it is possible to determine the constants $k$ and $C$ at different curing temperatures. From the temperature dependence of $k$, which is described satisfactorily by the Arrhenius equation, the activation energy of the curing process was calculated, which amounted to 65 kJ/mol. It is significant that temperature influences only the value of constant $k$, and not $C$.

The introduction of modifiers does not alter the general nature of the kinetics of the curing process, but it leads to a small reduction in the rate of the reaction (Figure 4). Reduction in the curing rate is probably due to the fact

Figure 1. Isotherms of curing (the dependence of the heat release rate on the curing time), obtained by the DSC method, for ED-20 + DADPS + 10% PSP. Curing temperature: 1 – 180°C; 2 – 170°C; 3 – 160°C

Figure 2. The time dependences of the degree of transformation determined by the DSC method for ED-20 + DADPS + 10% PSP. Curing temperature: 1 – 160°C; 2 – 170°C; 3 – 180°C

Figure 3. Dependence of the degree of transformation on the curing time of ED-20-DADPS in the coordinates of Equation (1)
that the addition of a thermoplastic component leads to an increase in the viscosity of the reaction mixture. Furthermore, there is a reduction in the concentration of reactive groups on account of dilution of the composite being cured by the thermoplastic. From Figure 4 it can also be seen that the DSC method practically ceases to record changes in the system after 40 min at 180°C.

The process of curing an epoxy-amine composite was also studied by DMA. Values of the dependence of the dynamic modulus $G'$ and the mechanical loss tangent as a function of the curing time at different temperatures were obtained. The nature of the $G' - t_{\text{cur}}$ curves (Figure 5) also indicates that the introduction of polysulphone leads to a slowing down of the curing process. This slowing down is much more evident than in the study of the curing process by the DSC method.

It is well known that, in the model of an ideal network in the high-elastic (rubbery) state, the elastic modulus is directly proportional to the crosslink density in the crosslinked polymer. Then, in the investigation of the rheokinetics of the process of formation of the crosslinked polymer, its magnitude characterises the degree of curing. Accordingly, the higher the elastic modulus, the greater is the degree of completion of the curing process. However, this relationship is observed only in the rubbery state, provided the distance from the glass transition point is adequate. At low curing temperatures, the investigated systems do not meet this requirement, as they undergo glass transition directly during curing, which leads to the appearance of diffusional constraints. At the same time, the change in the elastic modulus remains a sensitive method for following the change in structure (properties) during curing.

In the study of the kinetics of the curing process by the DMA method it was established that the material undergoes glass transition during curing. Here, the final elastic modulus $G'$ is much greater than the high-elastic modulus, and the time dependence of $\tan \delta$ passes through a maximum, which indicates relaxation transition (glass transition) in the system. The glass transition time of the system during curing is given in Table 1.

As can be seen from the data in Table 1, the glass transition time decreases considerably with increase in the curing temperature. Here, for composites containing PAEK, it is slightly lower than for the corresponding composites with PSP. Reduction in the curing time when PAEK is added to the system may be due to the more considerable reduction in mobility when PAEK is added than when PSP is added.

In studies by Wisanrakkit and Gillham [8] it was shown that there exists a clear relationship between the conversion and the glass transition temperature of the system. At the same time, the glass transition temperature is a parameter that changes considerably with change in $\beta$ at the final stages of the curing process, when other

![Figure 4](image-url)  
**Figure 4.** The dependence of the degree of transformation on the curing time for different composites: 1 – ED-20 + DADPS; 2, 3 – with the addition of 10 wt% PSP and PAEK; 4, 5 – with the addition of 20 wt% PSP and PAEK. Curing temperature 160°C

![Figure 5](image-url)  
**Figure 5.** The dependence of the dynamic modulus on the curing time for different composites: 1 – ED-20-DADPS; 2 – ED-20-DADPS-10% PSP. Curing temperature 180°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time of glass transition for a composite with 10% PSP (min)</th>
<th>Time of glass transition for a composite with 10% PAEK (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>50</td>
<td>40</td>
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<tr>
<td>170</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>180</td>
<td>22</td>
<td>17</td>
</tr>
</tbody>
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**Table 1.** The glass transition temperature of modified composites at different curing temperatures

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methods become insensitive to change in the degree of transformation. Here, it is pointed out that the relationship between $T_g$ and $\beta$ exists only for an entirely relaxed polymer, and during low-temperature curing the rate of the relaxation processes is low, and the observed $T_g$ is considerably lower than the $T_g$ that should correspond to the given conversion.

In the general case, for the relationship of the glass transition temperature with the degree of transformation, it is convenient to use the Di Benedetto equation:

$$\frac{T_g-T_{g0}}{T_{g0}} = \frac{[C_1-C_2]}{1-(1-C_2)} \beta$$

(3)

where $T_{g0}$ is the glass transition temperature of the non-crosslinked oligomer, and $C_1$ and $C_2$ are constants.

The dependence of the change in the glass transition temperature of the composites during curing was obtained by the DMA method. It was shown that the relationship between the glass transition temperature and the degree of transformation can be described adequately by the Di Benedetto equation (Figure 6), and therefore, at times that do not make it possible to determine the degree of transformation by DSC, it is possible to calculate the conversion from the change in the glass transition temperature.

Figure 7 presents the time dependence of the degree of transformation, calculated by means of the first-order equation with autoacceleration and determined from the change in the glass transition temperature. As can be seen from the graph, the DSC method gives overestimated values of the degree of transformation when calculated data are used. It is well known that, after gelation, and especially at the start of glass transition of the system, the rate of the reaction may decrease by comparison with the calculated rate on account of system mobility constraint. As can be seen from the graph (Figure 7), the real degree of transformation decreases by comparison with the calculated degree of transformation after curing for 25 min. Therefore, the use of the glass transition temperature as the criterion of the degree of transformation is more expedient [9].

It is well known that, after the gel point has been reached, the curing process slows down, which is normally due to diffusional constraints. To assess the effect of diffusion on the rate of the reaction, the value of the diffusion component of the rate constant, $k_d$, is estimated by different methods. Dusek calculated the value of $k_d$ using the Adam-Gibbs theory [10]:

$$k_d = k_{d0} D(T, \beta)$$

(4)

where $D$ is the coefficient of self-diffusion, and $k_{d0}$ is a constant determining the local conditions of chemical bond formation.

Gillham proposed that, for calculation of $k_d$, an equation similar to the Williams-Landel-Ferry (WLF) equation be used:

$$\ln k_d = \ln k_{d0} + \frac{\beta(T-T_g)}{C_1 + (T-T_g)}$$

(5)

where $k_{d0}$ and $C_1$ are empirical quantities, although Gillham assumes that $C_1 = 51.6$ [9].

It is well known that the total rate constant $k_0$ is connected with the diffusion constant $k_d$ and Arrhenius constant $k_a$ by the following equation:

$$\frac{1}{k_0} = \frac{1}{k_d} + \frac{1}{k_a}$$

(6)
At the initial stage of the curing process, the constant is very high and hardly affects the rate of the process. This can be seen from the graph of the time dependence of the degree of transformation: discrepancies between the experimental and calculated degrees of transformation begin after a certain time interval. Therefore, we can assume that the constant calculated by means of a second-order equation for the initial stage of the curing process is equal to the Arrhenius rate constant. At the final stages of the curing process, we can calculate the degree of transformation from the glass transition temperature. The rate constant of the process at each given moment in time can be calculated by means of the equation:

\[
k_0 = \frac{d\beta}{dt} \frac{1}{[1-\beta]^*/[1+C\beta]}
\]  

Knowing the rate constant \(k_0\) and its Arrhenius component, we can calculate the values of its diffusion component at each moment in time by means of the equation

\[
k_d = k_0 \cdot k_a / (k_a - k_0)
\]

The results are presented in Figure 8. This method of calculation is preferable, as in the present work it was not possible to obtain a satisfactory temperature dependence of the diffusion constant in coordinates of the WLF equation. As can be seen from the graph, at the initial stage of the curing process, the diffusion constant is very high, and therefore the limiting stage is chemical interaction.

Thus, in the course of studying the curing process it has been shown that the introduction of a modifier into the system, has no effect on the chemistry and kinetics of the curing process. The kinetic equation for describing the process of curing modified and unmodified systems remains constant. The kinetic and diffusion constants of the curing process have been determined.

REFERENCES
