Prepregs with long service life. 2. Rheokinetic selection of industrial types of epoxy resins and curing agents

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INTRODUCTION

The potential for primary kinetic selection of binder components for prepregs with a long service life using an isothermic calorimeter has already been demonstrated [1]. This method enabled the reactivity of binder components at prepreg storage temperatures $T_{store}$ to be evaluated from the initial rates of the curing process. It does not, however, allow the maximum kinetic service life ($\tau_{20}^\text{gel}$), linked to the gelation time for the binder at $T_{store}$ [2], to be forecast, because the latter also depends on the functional properties of the components. As a result, the secondary stage of binder component selection, using rheokinetic methods [3,4] enabling the physical kinetics of the curing process to be studied, i.e. the variation in time of the physical characteristics of the initial binder, governed by the degree of its chemical structuring, becomes important. These methods are also essential for correct regulation of the process parameters in the manufacture of products made from composite materials. In the curing process, the binder may pass successively through three physical states: viscous-fluid, highly-elastic and vitreous. Most important from the process aspect is the time spent in a viscous-fluid state and the time of its transition to a highly-elastic state, i.e. the gelation time ($\tau_\text{gel}$). The value of $\tau_\text{gel}$ at room temperature $-$ $\tau_{20}^\text{gel}$ $-$ is roughly equal to the binder service life, and governs its yield point, and consequently also the capacity of a prepreg to be further processed into a product after storage [2]. This stage of the physical transformation of a binder is most effectively studied using high-sensitivity rotary viscosimeters [5,6]. The torsion pendulum method [7-15] is the most convenient and commonly used method of studying the physical kinetics of the curing process for a composite mixture in the highly-elastic and vitreous states. The torsion pendulum is used to investigate the variation in rigidity of microplastic, i.e. a complex glass fibre impregnated with binder solution. Its use enables the binder setting time to be determined at a set curing temperature and at $T_{store}$ for the prepreg, which is linked to the technological service life [2]. Use of a torsion pendulum also enables an approximate assessment to be made of the degree of cross-linking of the binder depending on the structure of the initial components and the curing conditions. Since the degree of cross-linking of an interlaced polymer to a considerable degree governs the level of its functional properties [16,17], this makes it possible to run the third stage of binder component selection in a guided way [1,2] for a prepreg with a high service life based on the functional properties of the STP.

The aim of this work was therefore to make a rheokinetic analysis of curing processes for a number of the cheapest industrial grades of epoxy resins and curing agents produced in large volumes and selection of them for implementation in various types of prepreg technology.

EXPERIMENTAL SECTION

The epoxy component of the binder that we took was epoxidane resins of grades ED-20 and ED-16 and N,N,N',N'-tetraglycidyl 3,3'dichloro-4,4'-diaminophenyl methane (grade EKhD), while the curing component was the resins aniline-formaldehyde grade PA $-$ “T”, phenolformaldehyde resins grade SF-021, SF-
0113 and phenol-aniline-formaldehyde resins grade SF-
340 A and SF-342 A. The viscosity of the binder during
the course of curing was studied using a Rheotest-2 rotary
viscosimeter with a "plate-cone" type system with automatic
recording over time. The gelation time at various values
of $T_{\text{cur}}$ was determined by extrapolation of the linear
section of the steep rise in viscosity on the X-axis.

The physical state of the binder during the course of the
curing process was studied using a torsion pendulum of
IKhFCh design: torsion bar weight 9 g, working element
- VM-1 glass fibre 60 mm in length, containing 25% by
wt. binder.

RESULTS AND DISCUSSION

I. Study of curing process using rotary
viscosimeter method

The time spent by the cured composition in a viscous-fluid
state $\tau_{\text{gel}}$ depends on the reactivity of the functional groups
of components [1] and on the functional properties of the
initial reagents (epoxy resin $- f_{\text{ep}}$ and curing agent $f_{\text{cur}}$).
Critical conversion of the functional groups in the epoxy
resin $\alpha_{\text{ep}}$ and curing agent $\alpha_{\text{cur}}$ (at the start of gelation),
according to [17, p. 42], is linked to the functional
properties of the initial reagents by the ratio

$$\alpha_{\text{ep}} \times \alpha_{\text{cur}} = 1/(f_{\text{ep}} - 1) - (f_{\text{cur}} - 1)$$

Because of the strongly polydisperse nature of the industrial resin grades studied, it is not easy to determine
the mean functional properties of the components properly. Since it would be difficult to identify the role
played by each of the above-mentioned factors, the
need arises for an experimental determination of the
values of $\tau_{\text{gel}}$ for each binder.

Figure 1 a, b and c show the time/viscosity curves for
compositions based on ED-16 resin and the curing agents
PA-"T" (a), SF-0121 (b) and SF-340 A (c); while Figure 2
a shows curves of gelation time against temperature in
Arrhenius form ($\ln \tau_{\text{gel}} \sim 1/T$) for these, and also for resins
of SF-0113 and SF-342 A. The linear nature of the graphs
of $\ln \tau_{\text{gel}} \sim 1/T$ in the temperature range studied enables the
effective activation energy values (temperature coefficient)
to be calculated for the curing process, and by extrapolation
to $T_{\text{store}}$ to determine the maximum kinetic service life for
these compositions $\tau_{\text{gel}}$ [2]. It may be seen from the data
given in Table 1 that the greatest service life at $T_{\text{store}}$ is
provided by phenolformaldehyde resin grade SF-0121,
and the least by aniline-formaldehyde resin grade PA-"T".
On the other hand, at the CM moulding temperature ($T_{\text{cm}} =
160^\circ$C), the smallest value of $\tau_{\text{gel}}$ is achieved by the resin
PA-"T", and the largest by the resin SF-0121.

These data enable us to conclude that use of phenol-
formaldehyde resins as a curing agent is most effective in
the case of preregs produced using the normal process

![Graph of dynamic viscosity against curing time](image-url)

**Figure 1** Graph of dynamic viscosity against curing time for compositions based on ED-16 epoxy resin and curing agent: a) PA-"T", $T_{\text{cur}}$: 1 – 50, 2 – 60, 3 – 70, 4 – 80°C; b) SF-0121, $T_{\text{cur}}$: 1 – 80, 2 – 100, 3 – 120, 4 – 130°C; c) SF-340 A, $T_{\text{cur}}$: 1 – 80, 2 – 100, 3 – 120, 4 – 140°C
(impregnation by a mixture of components), and aniline-formaldehyde resins for binary prepregs produced using the RNK method [18].

The potential exhibited by rheokinetic and viscosimetric selection of the epoxy resin component of the binder is illustrated by Figure 2b, which compares the graphs of ln $\tau_{gel} \sim 1/T$ for the compositions ED-20 + PA “T” (line 1) and EKhD + PA “T” (line 2). It may be seen from the figure that in the case of the tetrafunctional resin EKhD, as one would expect, comparison with the bifunctional resin ED-20 shows a lower value of $\tau_{gel}$ at $T_{pr} \sim 1.5$ min, with at the same time a sharp rise in service life at $T_{store} \sim 13$ days. This unexpected result is a consequence of the rise in the temperature coefficient of the reaction in the presence of EKhD (from 7.5 to 17 kcal/mol). According to work [2], this should ensure that EKhD grade epoxy resin has a high technical efficiency level.

II. Study of curing kinetics using torsion pendulum method

The dynamic elasticity modulus for the impregnated binder thread or microplastic (or the rigidity modulus of the thread) is normally calculated from the formula [7]:

$$ G = \frac{128 \pi l}{d^4} \times \frac{1}{T^2} = K \times \frac{1}{T^2} $$  \hspace{1cm} (1)

where $l$ is the length of the thread; $d$ is the thread diameter; $I$ is the moment of inertia; $T$ is the oscillation period.

In formula (1), the moment of inertia ($I$) is a parameter that is difficult to determine. But since the disc weight and the length and diameter of the torsion thread do not vary from one experiment to the next, the variation in the inverse of the square of the oscillation period $1/T^2$ remains proportional to the rigidity modulus, where the proportionality coefficient $K = \frac{128 \pi l}{d^4}$. The value of $1/T^2$ may therefore be taken as the conditional value of the elasticity (rigidity) modulus ($G_{cond}$) for the microplastic. When the curing process is performed at $T > T_{vitr}$, i.e. in a hyperelastic state, the value of $1/T^2$ may as an approximation be taken as proportional to the number of cross-links, since according to work [19], the equilibrium modulus of elasticity in hyperelasticity is proportional to the number of cross-links:

$$ E_r = 3 \nu RT $$ \hspace{1cm} (2)

where $\nu$ is the degree of cross-linkage, $T$ is the absolute temperature, $R$ is the universal gas constant. By studying

![Figure 2](image-url)
the graph of the value of $1/T^2 \sim G_{\text{cond}}$ against curing time, therefore, we may determine the time of completion of the process of shaping of the mechanical properties of the microplastic as the time taken to attain the value of $G_{\text{cond}}$, and make an approximate evaluation of the relative level of cross-link density provided by variations in the composition make-up and the temperature.

This is particularly important in developing prepregs for heat-resistant composite materials (CMs) operating at high temperatures, where chemical cross-links play a certain role in shaping the properties of the material [20]. In the event of CMs operating in the temperature range at which the binder is in a vitreous state, the role of chemical cross-links diminishes. A search is needed for the optimum ratio of chemical and physical cross-links, i.e. hydrogen and other physical bonds [21]. The torsion pendulum method thus enables a solution to be found to the problem of achieving the highest cross-link density in the development of heat-resistant CMs and the optimum number of chemical cross-links for CMs operating at low temperature.

Figure 3 shows rheokinetic curves for the variation in the value of $G_{\text{cond}}$ for the microplastic at different values of $T_{\text{cur}}$ for a composition based on ED-16 epoxy resin and PA “TT” curing resin.

It may be seen from Figure 3 that for this composition in the range of $T_{\text{cur}} = 80-160\,^\circ C$, the values of $G_{\text{cond}}$ rapidly exceed limits and subsequently remain virtually the same. The limit is reached by the rheokinetic curves with incomplete conversion of functional groups, which indicates a physical nature of the phenomenon observed, i.e. setting of the composition at $T_{\text{cur}}$. Consequently the time when the curves reach a limit may be taken as the time of setting of binder at a specific temperature ($\tau_{\text{set}}$). The graph of $\ln \tau_{\text{set}} \sim 1/T$ is linear in nature, which makes it possible to calculate the temperature coefficient of the physical process of setting, which is 2 kcal/mol, and, by extrapolation to room temperature, to obtain the value of $\tau_{\text{set}}$, which is around 7 h. So the forecasting significance of the technological service life ($\tau_{\text{tech}}$), which, according to work [2], is the same as $\tau_{\text{set}}$, exceeds the forecasting significance of the maximum kinetic service life for the given composition, but is lower in comparison with the service life determined at $T_{\text{store}}$ (around 2 days) [6]. The higher value of the experimental service life of the binder is apparently caused by the chemical structuring at low temperatures being effected chiefly by the reaction of the primary amino-groups. The secondary amino-groups reaction under these conditions is sterically hindered. This should lead to the preferential formation of mobile linear chains with a longer retention of fluidity of the binder.

We should point out that at $T_{\text{cur}}$ over 160°C for the given composition, secondary steps in the growth of rigidity of the thread appear, and these are linked to the occurrence of side reactions [22]. As is shown in work [22], these reactions lead to a rise in $T_{\text{cur}}$, and consequently to a rise in heat resistance.

For a binder based on ED-16 and SF-0121 phenol-formaldehyde resin, the rheokinetic curves for the variation in thread rigidity (Figure 4) at under 160°C (curves 1-3) also clearly exceed the limit. The temperature coefficient of the setting process for this composition, determined from the gradient of the curves of $\ln \tau_{\text{set}} \sim 1/T$, is $6.7 \pm 1$ kcal/mol, and the value of $\tau_{\text{set}}$ obtained by extrapolation for $T_{\text{store}}$ is around 7 days. For the composition in question, therefore, the limit is set by the technological service life, the values of which significantly exceed the equivalent values for the previous binder.

When $T_{\text{cur}}$ is over 160°C (curve 4), two sections are observed on the rheokinetic curves – a section of rapid rise and a prolonged section of a slow rise in rigidity that is linear in time with a gradual exceeding of limits for the values of $G_{\text{cond}}$. This is apparently caused by the reaction of both phenol (incompletely reacted for steric reasons) and secondary alcohol groups formed through the opening up of epoxy cycles (side reaction) [23]. There is no doubt that both reactions should lead to an increase in heat resistance and at the same time to a fall in the strength of the binder [23].

![Figure 3 Rheokinetic curves of the variation in $G_{\text{cond}}$ for the binder ED-16 + PA “TT” at $T_{\text{cur}}$: 1 – 80; 2 – 100; 3 – 120; 4 – 140; 5 – 160°C](image)

![Figure 4 Rheokinetic curves for the variation in $G_{\text{cond}}$ for binder ED-16 + SF-0121 at $T_{\text{cur}}$: 1 – 120; 2 – 140; 3 – 160; 4 – 200°C](image)
The rheokinetics are more complex (especially with the elevated $T_{\text{cur}}$ values required to attain a high level of heat resistance) for the phenol-aniline-formaldehyde resin SF-340A, which contains in its structure phenol and also primary and secondary amino-groups (Figure 5). At $T_{\text{cur}}$ in the 170-140°C range, the kinetic curves (1-3) for variation in $G_{\text{cond}}$ clearly exceed limits at times significantly in excess of the values of $\tau_{\text{set}}$ set for PA "T".

The temperature coefficient for the setting process for this composition, determined from the gradient of the graph of $\ln \tau_{\text{set}} \sim 1/T$, is $6.5 \pm 1$ kcal/mol, and the value of $\tau_{\text{set}}^{20}$ obtained by extrapolation for $T_{\text{store}}$ is around 26 days. Thus the maximum kinetic service life is the limiting factor for this composition.

At $T_{\text{cur}} = 200°C$, the appearance of the rheokinetic curve becomes considerably more complicated (curve 4). Three sections of rising $G_{\text{cond}}$ may be observed on it: the initial section reaching a plateau after an hour, a second section in the 5-19 h interval and a third in the 28-39 h interval. The process of chemical structurisation of the binder, which takes place in the first section, is apparently governed by the dominant contribution made by the reaction of the epoxy resin with primary amino-groups in the first section, with secondary amino-groups in the second section, and with phenol groups in the third section. The latter reaction may be catalysed by tertiary amino-groups formed during the curing process. We would point out that the complex rheokinetics at high $T_{\text{cur}}$ values in the presence of SF-340A resin may be caused not only by the lowering of steric obstacles to the reaction of the epoxy groups with the above curing agent groups. The capacity of the resol resin SF-340A for self-condensation with the involvement of methylol groups [24] should be borne in mind. This situation was observed in the case of binder ED-16 + PA "T" at $T_{\text{cur}}$ over 145°C [22].

The totality of rheokinetic parameters and the types of service life corresponding to them for these curing agents are gathered in Table 2.

As may be seen from the table, when epoxy resin ED-16 is used, the limiting factor for curing agents PA "T" and SF-340 A is the kinetic service life, and for SF-0121 the technological service life.

Thus rheokinetic studies using the torsion pendulum method may be used to determine the prognostic values of the technological service life of the binder, which is linked to its setting time at $T_{\text{store}}$. In this case they should be carried out over a range of temperatures not exceeding the value of the maximum vitrification temperature ($T_{\text{vit}}$) for the given binder (achieved in the absence of side reactions, taking into account the topological limit [25]).

When performing rheokinetic studies of curing processes for compositions with multifunctional components at temperatures above $T_{\text{vit}}$, observations may be made for additional processes of chemical and physical structurisation, leading to a rise in the degree of cross-linking, and consequently to a further rise in $T_{\text{vit}}$ and, correspondingly, in heat resistance.

Rheokinetic studies enable the influence of various accelerators on the rate and maximum depth of curing to be clearly identified. Let us illustrate this by taking the composition ED-16 + SF-340A with the accelerators resorcin (phenol) and triethanolamine (TEA) – a tertiary amine – as an example. It may be seen from Figure 5 (curve 5) that the introduction of 1% by wt. TEA leads to the disappearance of both steps on the kinetic curves, while the introduction of 5% by wt. resorcin leads to the disappearance of both steps [sic] (curve 6). We should

<table>
<thead>
<tr>
<th>Method</th>
<th>Viscometry Parameters</th>
<th>Viscosimetry</th>
<th>Torsion pendulum</th>
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<tr>
<td>Parameters</td>
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<td>$\tau_{\text{set}}^{20}$</td>
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<td>ED-16 + PAT</td>
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<td>7.5</td>
<td>7</td>
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<tr>
<td>EKhD + PAT</td>
<td>13 days</td>
<td>17.0</td>
<td>12</td>
</tr>
<tr>
<td>ED-16 + SF-340A</td>
<td>~3.5 days</td>
<td>11</td>
<td>26 days</td>
</tr>
<tr>
<td>EKhD + SF-340A</td>
<td>-</td>
<td>-</td>
<td>18 days</td>
</tr>
<tr>
<td>ED-16 + SF-0121</td>
<td>~8 days</td>
<td>8.5</td>
<td>~7 days</td>
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**Figure 5** Rheokinetic curves for the variation in $G_{\text{cond}}$ for the binder ED-16 + SF-340A without accelerator at $T_{\text{cur}}$: 1 – 160; 2 – 170; 3 – 180; 4 – 200°C and with accelerator at 200°C: 5 – 1% by wt. TEA; 6 – 5% by wt. resorcin

*Table 2. Comparison of rheokinetic parameters for various binders*
observe that with actual moulding times usually not exceeding 16 hours, the introduction of resorcin enables the cross-linking density to be practically doubled in comparison with a non-catalysed system, or, to look at it another way, enables the curing time needed to achieve the same level of cross-linking to be halved. Use of catalysed compositions is clearly more effective in producing binary prepregs by the RNK method, since the introduction of phenol-type accelerators leads to a perceptible fall in the life of the compositions at storage temperature.

Of particular interest are rheokinetic studies of the variation in \( G_{\text{cond}} \) for the above curing agents in the presence of tetrafunctional grade EKhD resin (Figures 7-9). In the presence of EKhD resin and PA"T" curing agent, the nature of the rheokinetic curves for the variation in conditional rigidity of the microplastic changes substantially (Figure 6a). The curve goes beyond the limit more rapidly. The values of \( G_{\text{cond}}^- \) rise by more than an order of magnitude and cease to depend on \( T_{\text{cur}} \). The temperature coefficient of the setting process, determined from the gradient of the graph of \( \ln \tau_{\text{set}} \sim 1/T \), is \( 5 \pm 1 \) kcal/mol, and the value of \( \tau_{\text{set}}^{20} \) found by extrapolation to \( T_{\text{store}} \) is around 12 hours. It may be seen from Table 2 and Figure 6b that when EKhD is used, despite the high values of the kinetic service life, the actual prepreg storage times should be governed by the technological service life of the binder. The reason for this is that the process of physical structurisation (setting) of a given binder after attaining \( T_{\text{cur}} = 94^\circ C \) (which corresponds to the point of intersection of dependences 1 and 2 in Figure 7b) becomes the limiting factor. We should point out that at this temperature \( (T_{\text{vit}}) \), according to [26,27], the gelation process corresponds in time with the setting process. Since at \( T_{\text{store}} \) the binder sets before the start of the gelation process, and embrittlement of the binder in the prepreg may be avoided by raising the processing temperature or by introducing a plasticiser [2,6], the actual service life may considerably exceed forecast values.

The influence of the type of epoxy resin in the case of SF-340A curing agent is illustrated in Figure 7a. When EKhD is used, the nature of the kinetic curves undergoes a substantial change. Both the steps on the kinetic curves disappear, and the curves pass beyond limits during setting of the binder at much shorter times and greater values of \( G_{\text{cond}}^- \) than for ED-16. These changes are clearly linked to the structure of EKhD epoxy resin, which contains tertiary amino-groups capable of catalysing the process of conversion of both phenol [22] and primary amino-groups [28]. It seems that the appearance during the curing process of a large number of secondary alcohol groups further enhances the catalytic effect of the tertiary amino-groups [28]. The temperature coefficient of the setting process for this composition, determined from the gradient of the dependence \( \ln \tau_{\text{set}} \sim 1/T \) (Figure 7b), is also \( 6.5 \pm 1 \) kcal/mol, and the value of \( \tau_{\text{set}}^{20} \) found by extrapolation to \( T_{\text{store}} \) is around 18 days. So for SF-340A,
in contrast to PA "T", when ED-16 is replaced by EKhD, no rise in technological service life is observed. The substantial rise in the values of $G_{\infty}$ may, however, be taken as an indication of an increase in the heat resistance of the binder.

The change in the nature of the epoxy resin was manifested to an even greater extent in the case of SF-0121 curing resin. As may be seen from Figure 8, the rate of variation in $G_{\infty}$ in the initial period, as was to be expected, rises as $T_{\text{cur}}$ increases. At later stages in the process, however, there is an inversion, and the cross-linking density is higher at a temperature of 160°C. We may assume that this result comes about because of the capacity of EKhD resin to self-polymerise [29,30] at high temperatures under the influence of the tertiary amino-groups that enter into its structure. The phenol groups in the curing resin may accelerate a side reaction, lowering the effective level of cross-linking for the given composition, and consequently also its heat resistance.

Figure 9 illustrates the influence of the tetrafunctional resin EKhD on the level of $G_{\infty}$ or the effective cross-linking, attained by a mixture composition containing the widely-used diane resin ED-16 and PA "T" curing agent. As may be seen from the figure, variation in the ratio of the epoxy resins EKhD and ED-16 enables a regulation of this parameter to be achieved over a wide range.

Thus use of EkhD resin, either on its own or in conjunction with cheaper diane resins, enables a considerable intensification of the process of moulding of STPs based on prepregs produced both by the traditional mixture process and by the RNK method.

Analysis of the results of the rheokinetic studies performed enables the following conclusions to be drawn:

**REFERENCES**