Structural and kinetic features of strength properties of epoxyamine binders and adhesive compounds at low temperatures

Yu. N. Smirnov, T. E. Shatskaya, and V. I. Natrusov
Institute of Chemical Physics Problems of the Russian Academy of Sciences, Chernogolovka, and the “Stekloplastik” Research and Production Association Open Joint Stock Company, Kryukovo

In a number of recent studies [1–13], in the development of high-strength epoxy binders [1–6], adhesive compounds [7–9], and composites [10–13] based on them, the structural and kinetic approach has been used. This approach essentially consists in the purposeful determination of the relationships between the successive stages of investigations: the structure of the initial reactants $\rightarrow$ the curing conditions $\rightarrow$ the structure of the polymer matrix $\rightarrow$ the relaxation properties $\rightarrow$ the strength properties $\rightarrow$ the thermophysical properties of the final three-dimensional material.

This approach makes it possible to optimise the process of curing from the viewpoint of energy and labour costs and achieving the maximum level of service properties of the final products.

It must be noted that the curing of epoxy composites is normally carried out at final curing temperatures $T_{\text{cur}}$ higher than the limiting glass transition temperature $T_g^\infty$ of the specific binder [1–6]. Here, in the course of synthesis, the binder is normally in the viscous flow or high-elastic (rubbery) state, which, for a three-dimensionally crosslinked epoxy composite, ensures fairly high molecular mobility of the segmental type and, accordingly, makes it possible to achieve a high conversion of the functional groups, right up to the topological limit [14].

However, of particular interest for structural and kinetic analysis are processes of formation of the properties of adhesive compounds and composites in which curing proceeds (often forced) at $T_{\text{cur}}$, considerably lower than $T_g^\infty$. It is such processes that will nominally be categorised below as low-temperature curing (LTC), irrespective of the specific $T_{\text{cur}}$.

Note that, in practice, epoxy composites are most widely used as coatings, lacquers, adhesives, spackling compounds, etc., formed under conditions where low-temperature or cold curing is understood to mean processes occurring at room or lower temperatures [15, 16].

The aim of the present work was a structural kinetic analysis of the effect of LTC processes on the adhesive strength of glass fibre reinforced plastic sheets, and also glass sheets, as an approximate model of adhesion interaction in glass fibre reinforced plastics.

**EXPERIMENTAL**

As the resin part of the adhesive composite, use was made of epoxy–bisphenol A resin of grade ED-20, epoxy–aliphatic resin of grade DEG-1, their mixtures, and also products of the interaction with toluylene diisocyanate of pure ED-20 and DEG-1 (Epur I and Epur III) and their mixture (Epur II). As the curing part, use was made of the “Stekloplastik” commercial-grade product Aramin.

The curing process was controlled calorimetrically using an EK-5 calorimeter designed by the Institute of Chemical Physics Problems of the Russian Academy of Sciences. The controlled parameters were the maximum reduced curing rate $W_{\text{max}}$ (cal/(mol s)), the time of...
achievement of a zero curing rate $\tau_{\text{c}}$ (h), and the limiting heat of curing $Q_{\text{c}}$ (kcal/mol).

The thermomechanical parameters – the softening point $T_s$ and the average glass transition temperature $T_g$ (°C) of the epoxy specimens – were determined on a UIP-70 thermal analyser at a heating rate of 2.5 K/min under a load of 0.4 MPa [17].

The direct-pull adhesive strength of glass sheets $\sigma_{\text{adh}}$ (MPa) was determined by the procedure described in [7], and the shear adhesive strength of glass fibre reinforced plastic sheets was determined according to the GOST state standard.

RESULTS AND DISCUSSION

A characteristic feature of the LTC of epoxy composites is the simultaneous occurrence and mutual influence of processes of chemical and physical crosslinking of the binder (polymer matrix) of the composite material [18–20]. The first process leads to the formation of a network of chemical crosslinks. A critical state of this process is the start of gelation, which is normally recorded as the start of sudden increase in dynamic viscosity [21]. The degree of conversion of the functional groups of the binder that corresponds to this stage is regarded as the critical quantity $\alpha_{\text{cr}}$ regularly associated with the degree of functionality of the initial components [22].

The second process leads to the formation of a network of physical crosslinks. The critical stage of this process is the start of curing or glass transition of the binder at $T_{\text{cur}}$. The start of this process is recorded effectively by the torsion pendulum method [7, 18].

The structure and properties of the final crosslinked polymer depend considerably on the ratio of the rates of processes of chemical and physical crosslinking of the binder and the time sequence of the corresponding critical stages [18–20, 23, 24]. It is obvious that, for effective control of the properties of the binder, adhesive compounds, and composites during LTC, it is necessary purposefully to act both upon the process of chemical crosslinking and upon the process of physical crosslinking, and here this action should occur upon both processes of chemical crosslinking, and upon the process of molecular mobility of the three-dimensional structure of the binder or adhesive, chemical construction of the final three-dimensional structure that ensures lower values of $T_{\text{cur}}$ is required.

In the purposeful chemical construction of the final three-dimensional structure, account must be taken of the fact that the glass transition temperature of the crosslinked polymer depends on two factors determining the degree of segmental molecular mobility of the three-dimensional structure or the degree of cooperation of segmental movement [29, p. 206]. These factors are: the intermolecular interaction of fragments of the three-dimensional structure, determining the contribution of interchain cooperation; and the intrachain rigidity, determining the contribution of intrachain cooperation of segmental movements in the crosslinked polymers. Accordingly, a reduction in intermolecular interaction
can be achieved by introducing the above-mentioned plasticisers into the binder, and intrachain rigidity can be lowered by introducing flexibilisers or active diluents, i.e. binder components incorporated in the three-dimensional structure, changing its topology by reducing the number and functionality of crosslinks and increasing the intercrosslink distance. In particular, different aliphatic epoxy resins can act as flexibilisers [30].

Thus, by varying the action on both molecular mobility factors of the structure and the quantity of plasticisers and flexibilisers, it is possible simultaneously to act selectively upon the physicomechanical properties of adhesive compounds and composites.

On this basis we will examine the effect of additions of water on adhesive strength for adhesives of different composition. Above all, note that, for the initial adhesive composite ED-20 + Aramin, at 35°C all the kinetic parameters (the maximum reduced curing rate \( W_{\text{max}} \), the time of achievement of a zero curing rate \( \tau_{\infty} \), and the limiting released heat of the curing process \( Q_{\infty} \)), depending on the concentration of the water addition, pass through a maximum (Figure 1, curves 1–3). The adhesive strength \( \sigma_{\text{adh}} \) measured after the calorimetric curve has come out at a zero value, i.e. at practically complete cessation of the curing reaction at 35°C, similarly to the kinetic parameters, passes through a maximum (Figure 1, curve 4) in the same region of its concentrations (2.5–3.5 wt.%). This maximum may be connected with the precipitation of water into an individual phase. This is indicated by a visual change in the degree of transparency of the cured specimens, and also data of thermomechanical analysis. In ampoules containing up to 2 wt.% water, complete transparency of the specimens is observed. In an ampoule with 5 wt.% water, appreciable clouding of cured specimens is observed, even more pronounced at 10 wt.%. Data of thermomechanical analysis show (see Table 1) that, with variation in the water content, the initial and average temperatures of the glass transition process of the cured composites hardly change. In the main, there is a change in the values of the softening point, i.e. the range of the glass transition process is broadened towards lower temperatures. The precipitation of water into a separate phase is indicated by the appearance of new low-temperature transitions connected with unfreezing of the mobility of the water itself (from -8 to -4°C), and by the appearance of plasticised structural microregions.

The similarity of change in the kinetic and strength parameters indicates that the observed strengthening of adhesion in the presence of small quantities of water should be caused by an increase in the degree of curing of the adhesive composite. In our view, this effect is not connected significantly with the chemical effect of water as an accelerator of the reaction. The scale of change in the maximum rate of the curing process does not correspond to the scale of change in the adhesive strength. Furthermore, from Table 1 it can be seen that increase in the maximum curing rates is accompanied not with a reduction, as might be expected, but, on the contrary, with an increase in the time of final curing. This gives grounds for assuming that water primarily has a physical effect on LTC processes as a plasticiser. In fact, as indicated above, in the case of LTC, at the instant of achievement of the glass transition temperature, equal to the curing temperature, by the composite being cured, there is a sharp reduction in the rate of interaction of the functional groups of the binder. Water, acting as
a plasticiser increasing the molecular mobility of the composite, causes a reduction in the actual glass transition temperature of the composite. In this connection, physical inhibition of the curing process begins at higher degrees of conversion of the functional groups (with a greater degree of crosslinking), which leads, timewise, to a more drawn out curing process. Here, the former value of the glass transition temperature of the composite, as in the absence of water, is achieved. A new portion of water again lowers \( T_g \), which again stimulates the additional conversion of functional groups, increase in the time of completion of the process, and, accordingly, increase in the degree of crosslinking, compensating for the reduction in \( T_g \) to its previous level. Thus, the unchanged nature of the average glass transition temperature with variation in the water content also confirms the above viewpoint concerning the physical nature of the observed effect of strengthening of adhesion.

A similar extremal dependence of adhesive strength on the water concentration is also observed for an adhesive composite based on the product of interaction of 2,4-toluylene diisocyanate with ED-20 (Epur I). It is known [31] that the modification of epoxy resins with polyisocyanates with the formation of epoxyurethane compounds (Epurs) leads to a considerably increase in cohesive and adhesive strength. This is due to the fact that isocyanate groups interact with the secondary alcohol groups present in the epoxy resins to form urethane groups \( \sim \text{NH–CO–O} \sim \) possessing a high cohesive energy. In fact, as can be seen from Table 1 (Nos. 1 and 6), the use of modified epoxy resin leads to a considerable (sixfold) increase in adhesive strength. Nonetheless, the addition of an optimum quantity of water (~2.5 wt.%) leads, in this case also, to an additional substantial increase in adhesive strength. This effect is also accompanied with an increase in the maximum curing rate, in the degree of conversion (limiting heat release), and in the time of completion of the reaction. It is noteworthy that, when Epur I is used, there is a reduction in the values of \( T_s \) and \( T_g \). This result could be attributed to the flexibilising effect of the urethane groups introduced. However, it is more likely that this effect is due to the following circumstances. Diisocyanates, interacting with the hydroxyl groups of the neighbouring molecules of the epoxy oligomer, may crosslink them among themselves. This should lead to an increase in the functionality of the initial epoxy resin and, accordingly, in the density of three-dimensional crosslinking [31], i.e. to the opposite effect to flexibilisation. Owing to this, transition to a glassy state occurs at a lower degree of conversion of the functional groups than in the case of ED-20 and, accordingly, at lower values of \( T_s \) and \( T_g \).

It is important to stress that, in the case observed, a positive effect of water on adhesive strength is achieved at \( T_g^\infty \) values of the adhesive composites that differ markedly from \( T_{g\infty} \) i.e. under conditions of LTC. In the case of an adhesive composite based on the product of interaction of diisocyanate with DEG-1 (Epur II), the

<table>
<thead>
<tr>
<th>No.</th>
<th>Water, wt.%</th>
<th>( W_{max}, \text{cal/mol s} )</th>
<th>( Q_{\infty}, \text{kcal/mol} )</th>
<th>( \tau_{\infty}, \text{h} )</th>
<th>( \sigma_{adh}, \text{MPa} )</th>
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<th>( T_g^{\infty}/T_g, ^\circC )</th>
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The introduction of the optimum amount of water into this composite has no effect on the completeness of its curing and, moreover, lowers the adhesive strength considerably. Below it will be shown that a similar effect is observed for other flexibilised composites with a low $T_g$ value.

Thus, these results indicate the considerable structural and kinetic (physical) effect of water as a plasticiser in LTC processes.

It is evident that, if the interpretation of results is correct, the same strengthening mechanism of the LTC adhesive composite should be observed when the optimum quantity of typical plasticisers is introduced. These assumptions were confirmed for the case of an adhesive composite of ED-20 + m-PDA by introducing 2.5, 5.0, 10, and 15 wt.% of typical plasticiser dibutyl phthalate (DBP). Investigations of the strength of an LTC bond for the above composites were carried out after holding of adhesive joints at $T_{cur} = 80^\circ$C for 1, 2, 3, 4, 5, and 6 h. Note that $T_g$ for the given composite amounts to $\sim 145^\circ$C. From Figure 2 it can be seen that the time dependences of $\sigma_{adh}$ pass through two maxima. With increase in the DBP concentration, extremal values of the adhesive strength increase, and here a particularly substantial increase in $\sigma_{adh}$ is observed in the case of the primary maximum. Without going into detail concerning the complex time dependence of adhesive strength during LTC, examined earlier [7–9], we will point out that these results can serve as confirmation of the physical effect of water on adhesive strength as a plasticiser. However, note that DBP, in contrast to water, does not accelerate, but, on the contrary, slows down the process of epoxyamine curing, but in this case it promotes the achievement of a higher final conversion of the functional groups.

The introduction as a flexibiliser of epoxy aliphatic resin DEG-1 into the initial composite of ED-20 + Aramin also leads to a considerable increase in adhesive strength. As can be seen from Table 1 (Nos. 1 and 12), when a considerable quantity of DEG-1 is introduced (80 wt.% in relation to 20 wt.% ED-20), there is a tenfold increase in the values of $\sigma_{adh}$. Here, there is a considerable increase in limiting heat release $Q_\infty$ and, accordingly, an increase in the curing time $\tau_\infty$, although the maximum rate of the process increases. There is also a marked reduction in the softening point $T_s$ (from 62 to 28°C) and in the average glass transition temperature $T_g$ (from 76 to 49°C) of binder specimens cured at 35°C. These results make it possible to assume that, at a given composition of an adhesive composite constructed using a flexibiliser, its curing did not occur in an LTC regime but under structural and kinetic conditions similar to the optimum, i.e. at $T_{cur} = T_g$. From this stem the following: practically full completion of chemical conversions in a topologically more homogeneous system, a copolycondensation three-dimensional structure of the binder, and accordingly high adhesive strengths. It is significant that the addition of the optimum quantity of water (2.5 wt.%) into this adhesive composite, as in the case of the initial composite, accelerates the curing process slightly. This indicates the retention of a purely chemical effect of water in this system. However, the amount of heat released (the degree of conversion) remains constant, while the adhesive strength in this case decreases appreciably. This should mean that the above structural and kinetic (physical) effect of water as a plasticiser on the extent of the LTC process disappears. Its effect as a plasticiser on the properties of the final product remains, i.e. reduction in the elastic modulus [27] of the adhesive composite and, accordingly, in the adhesive strength. The effect of small additions of plasticiser [28] on an adhesive composite close to the high-elastic (rubbery) in physical state seems to be small.

A considerable effect of flexibiliser DEG-1 also appeared in an investigation of the interlayer shear strength of adhesive joints based on glass fibre reinforced plastic sheets. As can be seen from Table 2, with increase in the DEG-1 content in the mixture with ED-20, the interlayer shear strength $\sigma_b$ of the bond, practically the same as the cohesive tensile strength $\sigma_c$ of the adhesive composite itself, passes through two maxima. One of them appears in the region of a mass ratio ED-20/DEG-1 of 5:1, and the second in the region of a mass ratio of 5:4. At the same time, the tensile strain of the adhesive composite $\varepsilon_b$ increases continuously with increasing DEG-1 content, and values of the elastic modulus $E_t$ initially remain constant and then decrease. It seems that small additions of DEG-1 primarily increase the relaxation characteristics of the adhesive composite.
thereby lowering the magnitude of the residual internal stresses and increasing the packing density of the crosslinked polymer in the glassy state [30]. A secondary maximum of significant increase in adhesive strength, by analogy with the above result of increase in direct-pull adhesive strength, may be connected with transition of the LTC process to the condition $T_{cur} \approx T_g^{\infty}$, during which practically complete conversion of the functional groups of the adhesive composite cured in the given case at room temperature is achieved.

CONCLUSIONS

Thus, the conducted analysis and experimental results make it possible to draw the following conclusions:

1. During the forming of high-strength adhesive joints under conditions of low-temperature curing it is important to take into account and control by means of plasticisers and flexibilisers the ratio of the rates of the processes of chemical and physical crosslinking.

2. It has been shown that water, during bonding under conditions of low-temperature curing, plays the important structural and kinetic role of a plasticiser promoting an increase in the degree of conversion of the functional groups of the adhesive composite and, accordingly, the degree of three-dimensional crosslinking.

3. It has been shown that, for adhesive composites with high values of the limiting glass transition temperature, the effect of water is extremal in nature both for the mechanical (adhesive strength) and the kinetic parameters of the curing process. For adhesive composites with low values of the limiting glass transition temperature, the effect of water on the completeness of curing is absent, while the adhesive strength in its presence decreases.

4. The important structural and kinetic role of flexibilisers in the forming of high-strength adhesive joints under conditions of low-temperature curing has been shown experimentally.

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REFERENCES


Table 2. Effect of additions of DEG-1 as flexibiliser on shear adhesive strength of glass fibre reinforced plastic sheets

<table>
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<th>No.</th>
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<th>$\sigma_t$, MPa</th>
<th>$\varepsilon_b$, %</th>
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31. Yu. N. Smirnov et al., Plastmassy, No. 12, 1985, pp. 41–43. (No date given)