

Curing of Epoxy Systems at Sub-Glass Transition Temperature

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ABSTRACT: Three epoxy-amine thermoset systems were cured at a low ambient temperature. Evolution of the reaction kinetics and molecular structure during cure at the sub-glass transition temperature was followed by DSC and chemorheology experiments. The effect of vitrification and the reaction exotherm on curing and final mechanical properties of the epoxy thermosets was determined. Thermomechanical properties of the low-temperature cured systems depend on the reaction kinetics and volume of the reaction mixture. Curing of the fast-reacting system in a large volume (12-mm thick layer) resulted in the material with T_g exceed-

ing the cure temperature by 70–80°C because of an exothermal temperature rise. However, the reaction in a too large volume (50-mm layer) led to thermal degradation of the network. In contrast, thin layers (1.5 mm) were severely undercured. Well-cured epoxy thermosets could be prepared at sub- T_g temperatures by optimizing reaction conditions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3669–3676, 2006

Key words: epoxy network; chemorheology; gelation; vitrification; glass transition temperature

INTRODUCTION

Epoxy resins are the most frequently used precursors for syntheses of thermoset materials. Many applications of epoxy systems include adhesives, coatings, electronic applications, high-performance materials, etc., According to the application, a great variety of hardeners are used to form epoxy networks under both low- and high-temperature curing regime.

An important class of applications is reinforcement of a rock mass used as a structural and construction element in civil and underground constructions, mining or site restoration. In this application, a low-temperature curing regime at ambient temperature must be applied. Curing at temperatures below the glass transition temperature of the fully cured material, however, brings the problem of vitrification of the system during polymerization and arresting the reaction at a low conversion. In the glassy state the reaction is extremely slow and structure evolution is stopped. The material is severely undercured, which results in poor mechanical properties and material instability. An increase in the reaction temperature is necessary to restart the polymerization. Despite this fact, the low-temperature curing often results in a

material of a high glass transition temperature exceeding significantly the cure temperature. This is the result of heat generation during an exothermic reaction.¹

Curing of polyfunctional systems to form polymer networks involves several reaction stages: (a) growth and branching of a molecular structure, (b) gelation of the system by formation of a three dimensional polymer network at the point of gelation, and (c) postgel curing leading to an increase in crosslinking density of the network. Evolution of the molecular structure during cure is manifested by changes of the rheological behavior of the system. Chemorheology describing such changes due to the chemical reaction is the best technique to follow the formation of the network.^{2–5} The crucial phenomenon during crosslinking is gelation and point of gelation is the basic parameter characterizing processability of the system and network formation. The gelation time depends on the reaction rate, reaction mechanism, composition of the system, and functionality of precursors. Knowledge of gelation is of high importance for processing as well as for properties of the cured material. Therefore, determination of the gel point is the main goal in the study of a crosslinking reaction. The critical point of the network build-up is manifested by appearance of the gel fraction, increase in the viscosity up to infinity, and by a steep rise in the elastic modulus.

Structure evolution during formation of epoxy networks, followed by chemorheology experiments, was studied by many authors.^{1,6–10} They described the network build-up under high-temperature curing re-

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gime where the crosslinking is a reaction limited process. However, there have been very few investigations of the curing and evolution of the structure of epoxy thermosets under low-temperature curing regime, where vitrification occurs and diffusion control becomes operative. In dependence on curing temperature, vitrification may occur even before gelation and, therefore, the formation of a polymer network, gelation, and final structure are significantly affected.

In this paper, we have studied curing of three types of epoxy resins with an aliphatic amine crosslinker, diethylenetriamine (DETA), at temperatures below the glass transition temperature. We have followed the process of cure at a low temperature, including evolution of macromolecular structure, gelation, and vitrification of the reaction mixture as well as thermo-mechanical properties of the cured epoxy network. DSC measurements and chemorheology followed by DMA were used to determine the effect of vitrification during the reaction on the curing kinetics, on network formation, and on final mechanical properties. Also the effect of an epoxy resin type and reaction conditions governing the reaction exotherm, and thus, final network properties are discussed. The competition between the heat evolution due to an exotherm and the heat dissipation from a cured system is crucial and governs the exothermic temperature rise in the reaction system.

EXPERIMENTAL

Materials

The following epoxy resins were obtained from Spolchemie Ústí (Czech Republic): ChS-Epoxy 513, low-molecular weight epoxyacrylate resin; ChS-Epoxy 521, low-molecular weight epoxy resin modified with a reactive solvent based on aliphatic glycidyl ether, and ChS-Epoxy 531, low-molecular weight epoxy resin modified with a reactive solvent based on aliphatic diglycidyl ether. Diethylenetriamine (DETA) was used as a hardener.

Curing of the epoxy systems

The reaction components were mixed in the mass ratio Epoxy 513:DETA = 100:14, Epoxy 521:DETA = 100:11, Epoxy 531:DETA = 100:12. The reaction systems were cured at different cure temperatures $T_C = 8\text{--}150^\circ\text{C}$.

For determination of mechanical properties, the epoxy systems were cured in Teflon molds of various thicknesses $d = 1.5\text{ mm, } 9\text{ mm, } 12\text{ mm, and } 50\text{ mm}$ in the following temperature regimes: (a) 14 days at temperature $T_C = 8^\circ\text{C}$, (b) 3 days at room temperature, $T_C = 20^\circ\text{C}$, or (c) 12 h at $T_C = 150^\circ\text{C}$. The samples for mechanical measurements were cut from the center and from surface of the cured epoxy material.

The temperature in the reaction mixture was followed by the Cu-constantan thermocouple.

Methods

Dynamic mechanical analysis (DMA) was carried out with an ARES apparatus (Rheometric Scientific, Piscataway, NJ). Chemorheology experiments, characterizing evolution of the dynamic viscosity and complex shear modulus during cure, were followed in the parallel-plate geometry using oscillatory shear deformation at a frequency of 6.28 rad/s (1 Hz). The simultaneous multiple frequency testing ranging from 1 to 64 rad/s was used for the gel point evaluation. Rectangular cured network samples of the size $5 \times 1 \times 0.15\text{ cm}^3$ were subjected to torsion measurement of complex shear modulus as a function of temperature from -100°C up to 200°C at a heating rate of $3^\circ\text{C}/\text{min}$ and a shear deformation frequency of 6.28 rad/s.

Dynamic scanning calorimetry (DSC) measurements were performed on a PerkinElmer DSC Pyris 1. The temperature and power scales of the calorimeter were calibrated using indium as standard. The measurement was carried out in helium atmosphere with liquid nitrogen as coolant. Heating rate was 10 K/min for T_g determination and 5 K/min for reaction heat determination. T_g was determined as the midpoint of the glass transition range, using the standard Pyris software.

For determination of the total reaction heat, about 10 mg of the reaction mixture was weighed into an Al pan and quickly cooled to -80°C . The following heating run up to 300°C showed the T_g of the reaction mixture and reaction exotherm. The reaction heat was obtained by integration of this exotherm from -30 to 200°C . A conversion of epoxide groups at time t was calculated from the relation $\alpha_E = (\Delta H_o - \Delta H_t)/\Delta H_o$, where ΔH_o is the total reaction heat and ΔH_t is a residual reaction heat of epoxide sample cured at 30°C for t minutes.

RESULTS AND DISCUSSION

The reaction of the low-molecular weight epoxy resins Epoxy 513, Epoxy 521, and Epoxy 531 with the polyamine hardener DETA results in the formation of the epoxy networks of various crosslinking densities and glass transition temperatures.

Evolution of the molecular structure during cure

The course of the crosslinking reaction and evolution of the structure during cure were followed by chemorheological experiments. Curing of the three epoxy systems at temperature 30°C is illustrated in Figures 1 and 2. Chemorheological curves show evolution of dynamic viscosity η' , shear elastic storage modulus G'

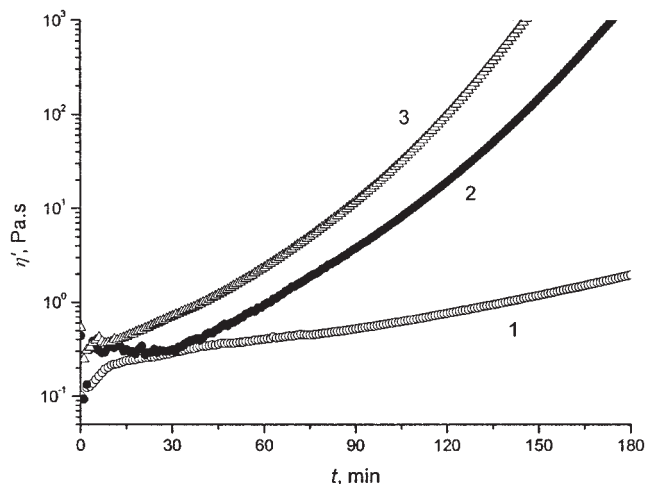


Figure 1 Evolution of dynamic viscosity during cure of the epoxide systems at $T_C = 30^\circ\text{C}$. (1) Epoxy 513-DETA, (2) Epoxy 521-DETA, (3) Epoxy 531-DETA.

and loss factor $\tan \delta$ during the cure. From the initial viscosity growth, one can see that the rate of structure evolution increases in the series Epoxy 513-DETA < Epoxy 521-DETA < Epoxy 531-DETA. The steep growth of the storage modulus should correspond to gelation of the systems. However, the increase of modulus G' , in Figure 2a, is not steep enough to detect gelation reliably. This is probably a result of a slow relaxation of highly branched chains leading to un-equilibrium experimental value of modulus. Consequently, an elastic behavior was observed even before gelation.

The loss factor $\tan \delta (= G''/G')$ in Figure 2b increases at the beginning of the reaction because of an increase in dynamic viscosity $\eta' (= G''/\omega)$. At a later reaction stage, $\tan \delta$ starts to decrease as the elastic part of the complex modulus (G') operates because of the formation of elastically active temporary entanglements before the gel point. Gelation usually occurs in the range^{7,8} $(\tan \delta)_{\text{crit}} = 3-1$. A smooth decreasing passage of $\tan \delta$ through the gel point during cure well below the value 1 is an usual course, at least for a low-frequency measurement,⁷ e.g., at $\omega = 6.28$ rad/s. Figure 2b, however, reveals that the epoxy systems Epoxy 513, Epoxy 521, and Epoxy 531 show, during cure at $T_C = 30^\circ\text{C}$, slowing down of the drop in the loss factor in the neighborhood of the gel point and the value $\tan \delta = 1$ is not even reached in the given time scale.

There are several methods for determination of the gel point. Generally accepted is the precise chemorheological evaluation of the point of gelation based on the application of the power law describing the rheological behavior of the critical system at the gel point,¹¹ $G' \sim G'' \sim \omega^{-n}$, where G' and G'' are dynamic shear storage and loss moduli, ω is the experimental

frequency of the measurement and n is the dynamic critical exponent. In the liquid pregel stage, the loss factor $\tan \delta (= G''/G')$ decreases with increasing frequency, while it grows with frequency in the solid postgel stage. At the gel point the loss factor is independent of frequency. The crossover of the $\tan \delta$ curves for different frequencies during the reaction corresponds to the critical point. The rheological behavior at the gel point is characterized by the dynamic critical exponent n . This parameter is not a universal constant but depends on the system structure and reaction conditions. Its value ranges usually between 0.5 and 0.8. For the epoxy system the critical exponent was found⁷ to be $n = 0.71$, in a very close agreement with the prediction of the percolation theory, $n = 0.72$. n is related to the value of $\tan \delta$ at the critical point by the relation;¹¹ $n = (2/\pi) \cdot \arctan \delta$. The critical exponent determined in the epoxy system corresponds to the value⁷ $(\tan \delta)_C = 2.1$.

We have applied this method for determination of the gel point by using the multiple frequency measurement. Figure 3 illustrates the evolution of the loss factor and its frequency dependence during the cure of the systems Epoxy 521-DETA and Epoxy 531-DETA. After the initial scatter of data the loss factor decreases with the cure time and with increasing frequency of the measurement, which is typical of the liquid state. However, one can see, that the power law is not well applicable in this case. The values of

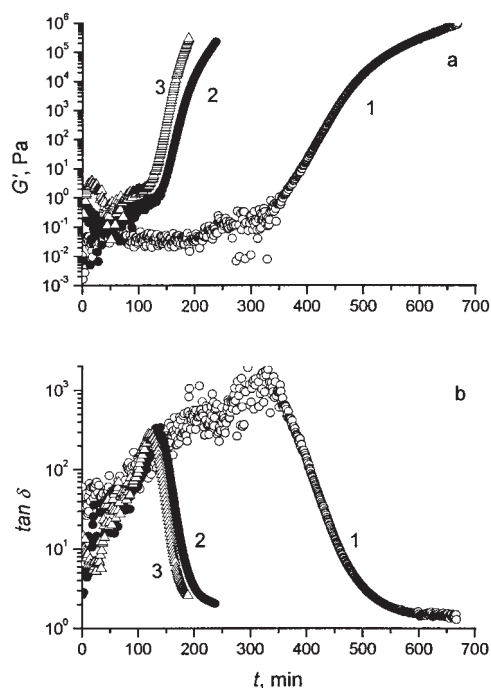


Figure 2 Evolution of the storage modulus (a) and loss factor $\tan \delta$ (b) during cure of the epoxide systems at $T_C = 30^\circ\text{C}$ (1) Epoxy 513-DETA, (2) Epoxy 521-DETA, (3) Epoxy 531-DETA.

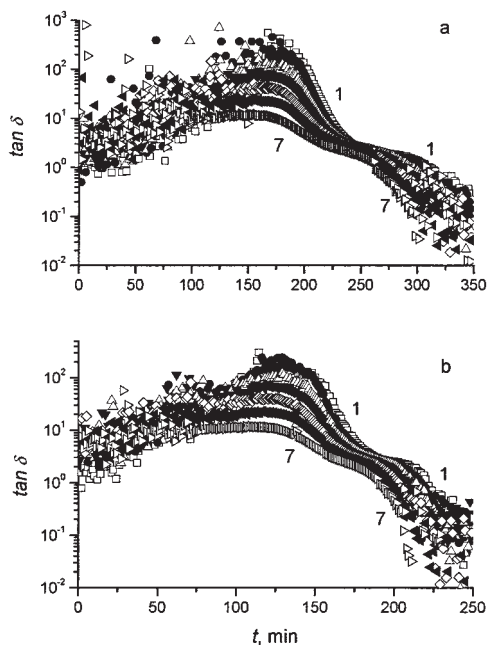


Figure 3 Evolution of the loss factor $\tan \delta$ during cure of Epoxy 521-DETA (a) and Epoxy 531-DETA (b) at $T_C = 30^\circ\text{C}$. Multifrequency sweep, $\omega = 1\text{--}64$ rad/s, (1) 1 rad/s, (7) 64 rad/s.

the loss factor show the smallest frequency dependence in the region close to the gel point at $(\tan \delta)_C = 2.3$, however, they are not frequency-independent, and crossover does not occur. This rheological behavior as well as deceleration of the drop in $\tan \delta$ around the gel point in Figure 2b are the result of vitrification of the system. Both processes, gelation and vitrification, interfere and rheological behavior in the gel point is not independent.

Effect of vitrification on kinetics of the curing

Vitrification of the system and its influence on the reaction kinetics were followed by DSC. The kinetics of the cure Epoxy 531-DETA at $T_C = 30^\circ\text{C}$ is depicted in Figure 4. The reaction is decelerated after the gel point and the final conversion reaches only 85%. During the cure the gradual growth of the glass transition temperature of the reacting systems takes place (see Fig. 5) as a result of the growth of the molecular structure and network crosslinking density. The glass transition temperature increases from the value of the initial composition, $T_{g0} = -46^\circ\text{C}$, up to the value of the cure temperature $T_C = 30^\circ\text{C}$. At this moment vitrification of the system occurs. The reaction rate is no longer kinetically controlled but the rate of diffusion of the reagents becomes crucial. Figures 4 and 5 show that the reaction is slowed down when T_g reaches T_C . Glass transition temperature at the gel point is $(T_g)_{\text{gel}} = 20^\circ\text{C}$, and the vitrification sets in

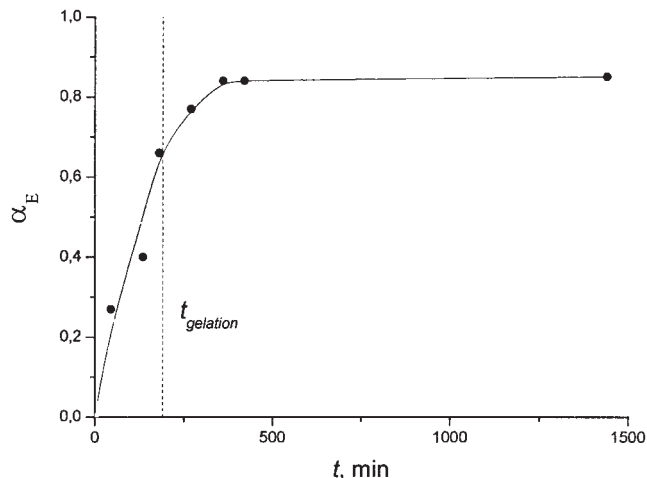


Figure 4 Conversion of the epoxy groups during Epoxy 531-DETA cure at $T_C = 30^\circ\text{C}$.

closely after the gel point. It is probable that during cure at $T_C = 30^\circ\text{C}$, the reaction is affected by vitrification already at the gel point. The structure could be partly immobilized and diffusion control operates. Hence, the rheology close to the gel point of the studied epoxy system is interfered by vitrification and rheological determination of the gel point is complicated.

Rheological behavior of the epoxides at the critical point severely differs in the reaction at a higher temperature. Figure 6 illustrates the chemorheology of the Epoxy 521-DETA crosslinking at $T_C = 60^\circ\text{C}$. The reaction at 60°C is not only much faster, but at the same time, the drop of $\tan \delta$ around the gel point does not decelerate. The loss factor in Figure 6 decreases smoothly well below unity, characterizing a crosslinked elastic material. Only later in the postgel stage, the de-

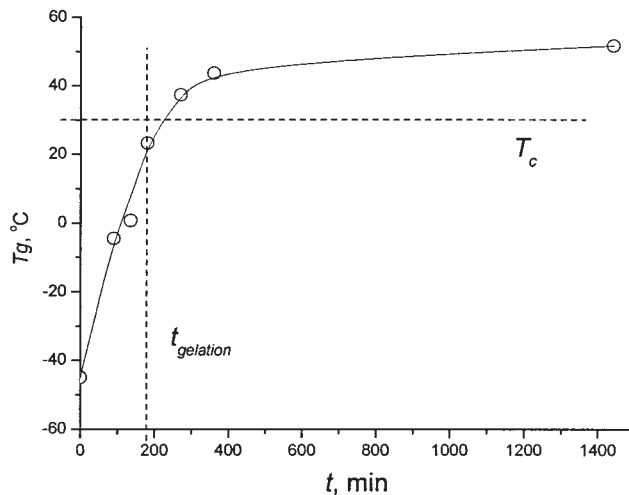


Figure 5 Growth of glass transition temperature T_g during Epoxy 531-DETA cure at $T_C = 30^\circ\text{C}$.

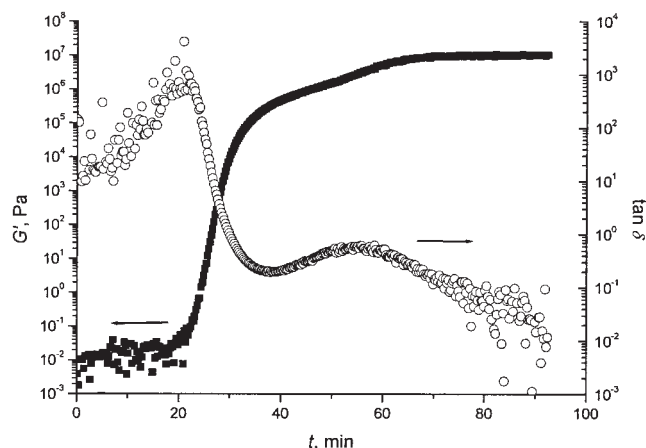


Figure 6 Evolution of the storage modulus G' and loss factor $\tan \delta$ during cure of Epoxy 521-DETA at $T_C = 60^\circ\text{C}$.

crease is slowed down, $\tan \delta$ reaches a local minimum, and becomes growing because of vitrification. The dynamic storage modulus (Fig. 6) shows a short plateau followed by another increase corresponding to the vitrification. The multifrequency sweep in Figure 7 reveals that $\tan \delta$ is frequency-independent at the gel point. Crossover of the curves for different frequencies occurs. Because of a larger interval of vitrification after gelation, the rheological behavior at the gel point is not affected by vitrification and the power law holds.

Vitrification manifests itself by the local minimum (Figs. 6 and 7) and by the second, frequency-dependent crossover of the loss factor curves (Fig. 7). During vitrification, i.e., transition of the system to the glassy state, strong viscoelastic effects operate, characterizing chain immobilization. As a result, the loss factor increases during the cure. Moreover, because of slow

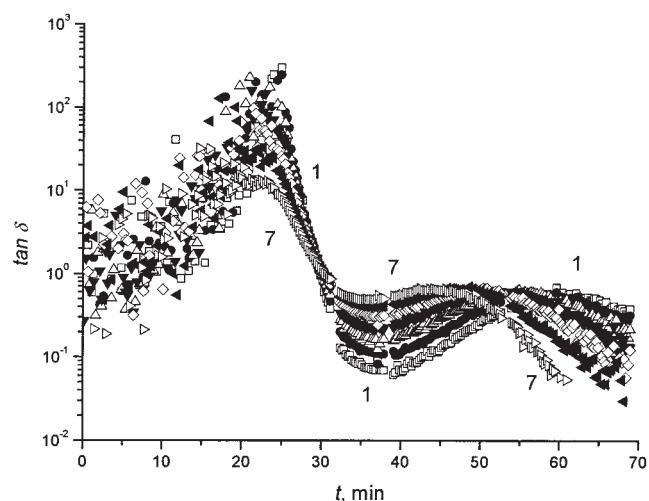


Figure 7 Evolution of the loss factor $\tan \delta$ during cure of Epoxy 521-DETA at the temperature $T_C = 60^\circ\text{C}$. Multifrequency sweep, $\omega = 1\text{--}64$ rad/s, (1) 1 rad/s, (7) 64 rad/s.

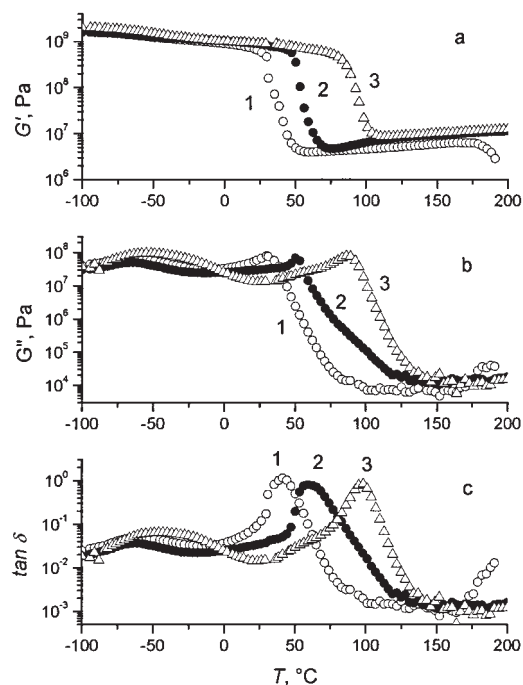


Figure 8 Components of the complex dynamic shear modulus and loss factor $\tan \delta$ as a function of temperature for the epoxy systems cured at $T_C = 20^\circ\text{C}$. (a) G' , (b) G'' , (c) $\tan \delta$. (○) Epoxy 513-DETA, (●) Epoxy 521-DETA, (Δ) Epoxy 531-DETA. Thickness of the samples during cure, $d = 9$ mm.

relaxation modes and broad relaxation spectrum in the glass transition region, the loss factor decreases with increasing frequency in a similar way as in the viscous liquid state and in contrast to the elastic solid state.

Thermomechanical behavior of the cured epoxy systems

We have determined the thermomechanical behavior of the epoxy systems cured both at low sub- T_g temperatures, $T_C = 8^\circ\text{C}$ and 20°C , and at a high temperature, $T_C > T_g$. The network prepared at the high temperature, $T_C > T_g$. The network prepared at the high temperature serves as the fully cured reference system. The samples are characterized by glass transition temperature T_α , defined as a temperature at which the shear loss modulus G'' attains maximum, and by storage modulus in the rubbery state G' (at $T = T_\alpha + 30^\circ\text{C}$). The rubbery modulus is determined by the crosslink density of a network ν according to the theory of elasticity, $G = A\nu RT$, where A is a front factor defined by the model.¹² Figure 8 illustrates the temperature dependence of the components of the dynamic complex shear modulus and loss factor $\tan \delta$ of the epoxy systems cured at $T_C = 20^\circ\text{C}$. The samples were cured in a 9-mm thick layer.

The results given in Table I reveal that T_α values and the rubbery modulus of the samples fully cured at

TABLE I
Thermomechanical Characteristics of the Epoxy Systems
Cured at Various Temperatures

System	T_c (°C)	T_α (°C)	$G'_{T_\alpha+30^\circ\text{C}}$ MPa
Epoxy 513-DETA	150 ^a	30	4.0
	20	30	4.0
	8	20	0.8
Epoxy 521-DETA	150 ^a	72	10.7
	20	51	4.8
	8	29	0.9
Epoxy 531-DETA	150 ^a	95	13.6
	20	87	8.7
	8	40	3.0

Thickness d of the cured samples was 9 mm.

^a $d = 1.5$ mm.

temperature $T_C = 150^\circ\text{C}$ ($>T_g$) increase in the series Epoxy 513-DETA < Epoxy 521-DETA < Epoxy 531-DETA. This is a result of the presence of a flexible epoxyacrylate resin in Epoxy 513 and of a monofunctional epoxy diluent in Epoxy 521. Whereas the cured Epoxy 531-DETA is a relatively high- T_g material, the Epoxy 513-DETA network shows much lower crosslinking density and occurs in the main glass transition region at ambient temperature.

Table I shows that the decreasing cure temperature T_C results in decrease both in T_α and rubbery modulus. The significant drop was observed mainly in Epoxy 521-DETA and Epoxy 531-DETA networks. The modulus and corresponding crosslink density decreased by an order of the magnitude when Epoxy 521-DETA was cured at $T_C = 8^\circ\text{C}$. On the contrary, in the case of low- T_g Epoxy 513-DETA, the network is completely cured even at a temperature slightly below T_g , at $T_C = T_\alpha - 10^\circ\text{C}$. The modulus and T_α of the sample cured at $T_C = 20^\circ\text{C}$ reach the values of the sample fully cured at $T_C = 150^\circ\text{C}$. Surprising is the high glass transition temperature of the system Epoxy 531-DETA ($T_\alpha = 87^\circ\text{C}$), cured at $T_C = 20^\circ\text{C}$, which is only 8°C lower than that of the fully cured network. DSC measurement in Figure 5 shows the reaction retardation at $T_g = T_C$ and the stop of T_g growth. However, the determined T_α is 70°C higher than T_C . This apparent disagreement is given by the exothermic course of the reaction, and by different cure conditions of the small sample during DSC measurement and in the thick mold used for preparation of samples for mechanical measurements.

The curing epoxide-amine is a highly exothermic reaction. The heat of the reaction Epoxy 531-DETA was determined to be $\Delta H = -506.7$ J/g. Under adiabatic conditions the heat evolution results in a temperature rise $\Delta T_{\text{ad}} = \alpha (-\Delta H)/c_p$, where c_p and α are isobaric heat capacity and reaction conversion, respec-

tively. The maximum temperature of the reaction mixture for the adiabatic cure is $T = T_0 + \Delta T_{\text{ad}}$, where T_0 is the initial temperature. The system is changing during the reaction and also the c_p value is changing. In the case of Epoxy 531-DETA, $c_p = 1.26$ J/g K for an amorphous reaction mixture of monomers at $T = -40^\circ\text{C}$. During the reaction at cure temperatures, the heat capacity of the reaction mixture ranges between 1.3–1.5 J/gK because of structure changes and temperature dependence of c_p . The calculation shows that the corresponding ΔT_{ad} for an ideal adiabatic process and full conversion in the system Epoxy 531-DETA reaches the values $\Delta T_{\text{ad}} = 338\text{--}390^\circ\text{C}$.

The difference between T_g and T_C for the three epoxy networks cured at sub- T_g temperatures decreases with diminishing rate of the cure. In the slowly reacting systems, e.g., Epoxy 513-DETA, or at a low cure temperature, the heat generation is slow compared to its dissipation. The reaction proceeds under almost isothermal conditions at $T_C \approx 20^\circ\text{C}$, and at the condition $T_g = T_C$ it becomes retarded and finally stops. In contrast, in the fast-reacting system the heat generation is quicker than its dissipation and the temperature of the reaction medium grows. As a result of the higher cure temperature, also T_g of the final material increases. Moreover, the volume of the reaction mixture or the surface/volume ratio is an important factor governing the reaction heat dissipation.

The effect of the reaction rate and sample volume on growth of temperature of reaction mixture is depicted in Figure 9. The curves 1, 3, and 4 characterize the temperature evolution during cure of the fast-reacting mixture Epoxy 531-DETA in the center of the layer of various thicknesses; 50 mm, 12 mm, and 1.5 mm, respectively. Because of low polymer thermal conductivity the heat transfer from the thick layer (50 mm), is

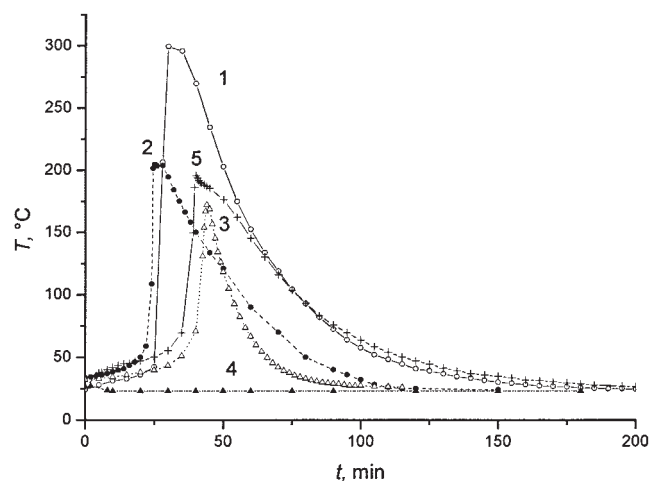


Figure 9 Temperature evolution during Epoxy 531-DETA cure for samples of various thickness: (1) 50 mm center, (2) 50 mm surface, (3) 12 mm center, (4) 1.5 mm, (5) Epoxy 531-DETA 50 mm center.

TABLE II
Thermomechanical Characteristics of Epoxy Systems
Cured at 20°C at Various Layer Thicknesses

System	T_c (°C)	T_α (°C)	$G'_{T_\alpha+30^\circ\text{C}}$ (MPa)
Epoxy 513-DETA			
thickness $d = 1.5$ mm	20	31	3.6
$d = 9$ mm	20	30	4.0
$d = 12$ mm	20	29	2.9
$d = 50$ mm	20	29	2.2
	150 ^a	30	4.0
Epoxy 531-DETA			
thickness $d=1.5$ mm	20	48	6.5
$d = 9$ mm	20	87	8.7
$d = 12$ mm	20	86	10.8
$d = 50$ mm surface	20	97	8.7
Center	20	73	3.6
	150 ^a	95	13.6

^a fully cured network.

much slower than the heat generation.⁴ The temperature rise is very dramatic and temperature reaches 300°C (curve 1). The theoretical value for an adiabatic process and full conversion could attain ~ 360 – 410°C ($= T_0 + \Delta T_{\text{ad}}$) (see above). The lower experimental temperature is a result of nonadiabatic conditions. Moreover, there is a significant temperature gradient across the sample. At the sample surface, the maximum temperature is only 205°C because of a fast heat transfer (curve 2). Also an increase in the surface/volume ratio in thinner layers results in a better heat dissipation, and a slower and smaller temperature increase (curve 3). The reaction in 1.5-mm thin layer proceeds without any temperature rise (curve 4) because of a very efficient heat transfer from the sample. The slow reaction in Epoxy 513-DETA produces an exotherm in the center of the 50-mm thick layer (curve 5), which is smaller compared to that of the fast Epoxy 531 system. The temperature grows only up to 195°C. While the heat transfer is the same in both systems because of similar polymer structure and the same sample geometry, the heat generation is much slower in the Epoxy 513-DETA.

The influence of the cure rate and of the reaction mixture volume on the thermomechanical properties of the epoxide networks cured at 20°C is given in Table II.

The low- T_g , slowly-reacting system Epoxy 513-DETA is fully cured at ambient temperature independently of layer thickness as follows from a comparison with the network cured at 150°C. In the 1.5-mm thin layer the slow reaction proceeds at $T_c = 20^\circ\text{C}$ without any exothermal heating. The final $T_\alpha = 30^\circ\text{C}$ implies that the full conversion was achieved in this case by the cure occurring in the glassy state in the last reaction stage.

In the case of the fast-reacting system with a relatively high- T_g Epoxy 531-DETA, the effect of the reaction mixture volume on thermomechanical properties is very strong. The sample cured in a 1.5-mm thin layer shows a low glass transition temperature ($T_\alpha = 48^\circ\text{C}$) and a low modulus in such a sample geometry (see Fig. 9, curve 4). The reaction proceeds under isothermal conditions at $T_c = 20$ – 25°C and early vitrification sets in thus quenching the reaction at a low conversion. In the sample cured in 9–12-mm thick layer, the glass transition temperature increases by 40°C and modulus is higher by 35–80% due to an exothermal temperature rise in the thick layer. The maximum temperature within the sample attains 172°C. However, the temperature exceeds the glass transition temperature only for 15 min during the reaction (see Fig. 9). This time interval is not sufficient to reach the complete cure. Further enhancement of the sample volume led to deterioration of mechanical properties. The temperature rise up to 300°C in the center of the 50-mm thick layer resulted in thermal degradation of the epoxy network. Both T_α and modulus in rubbery state significantly drop. However, because of temperature gradient across the sample (see Fig. 9), also the final material behavior depends on the position within the sample. The specimen taken from the surface of the cured sample shows much higher T_α and modulus (Tab. II) as a result of a better heat dissipation and a lower exothermic temperature rise, which avoid thermal degradation.

Thermal degradation of a polymer network proceeds in consecutive steps. Scission of a polymer chain resulting in: (a) a decrease in concentration of elastically active chains and the corresponding drop of modulus. Further chain splitting leads to (b) formation of a sol fraction, (c) a decrease in chain length, (d) formation of low-molecular-weight degradation products, which evaporate and thus cause mass loss.

(a) The results show that the drop of crosslinking density in the center of the 50-mm layer of the Epoxy 531-DETA is very strong. The concentration of elastically active network chains, determined from rubbery modulus, decreased by $\sim 70\%$. (b) The sol-fraction is not very high, 2.4%, in the center of 50-mm layer, compared to 1.3% at the sample surface and 1.2% in the reference network cured at 150°C. (c) Information on chain degradation is provided also by mechanical secondary relaxation below the glass transition temperature at $T = -50^\circ\text{C}$, characterizing segmental and group motions. By comparing the samples cured up to various conversions, depending on the layer thickness, it was found that the secondary maximum broadens during the cure. This implies a broadening distribution of the relaxation times corresponding to relaxation of longer chain sequences. Thermal degradation in the center of 50-mm thick layer manifests itself by narrowing the secondary relaxation, which

can be ascribed to motion of shorter sequences formed by chain scission. (d) Thermal stability of the Epoxy 531–DETA system was determined independently by thermal gravimetric analysis (TGA). In the TGA scan at a heating rate of 10°C/min, the mass loss at 300°C reached only 1.4% because of the thermal degradation in nitrogen and 4.4% because of thermal oxidation degradation in air. No mass loss occurs at $T < 250^\circ\text{C}$.

Analysis of thermal degradation of the network Epoxy 531–DETA in the center of the 50-mm layer provides the following conclusions. The exothermal temperature rise (cf. Fig. 9) results in a very strong decrease in crosslinking density. However, the thermal conditions are not severe enough to promote appearance of a high sol fraction of split chains, only 2.4%, or formation of a high amount of low-molecular weight degradation products.

CONCLUSIONS

Curing of the epoxy resins Epoxy 513, Epoxy 521, and Epoxy 531 with DETA at temperatures below T_g results both in low- and relatively high- T_g material depending on the particular system and reaction conditions. Cure kinetics, structure evolution and gelation are affected by vitrification leading to an undercured material. Chemorheology of the cure process reveals an interference of gelation and vitrification thus making determination of the gelation point difficult.

The final thermomechanical properties depend on the reaction kinetics and the reaction mixture volume governing the exotherm formed during the cure. Hence, optimization of the sample volume for a particular system is necessary to achieve required properties. The fast reacting, high- T_g Epoxy 531–DETA

system was cured to a high conversion at ambient temperature and the optimized volume of the reaction mixture. The network with T_g exceeding by 70–80°C the cure temperature was prepared in a 12-mm thick layer due to the exothermal heating. Even larger reaction volume (50 mm layer thickness) resulted in a too high exothermal temperature rise, up to 300°C, leading to thermal degradation of the network and deterioration of its thermomechanical properties. However, thin layers (1.5 mm) were undercured because of the absence of an exotherm. A slower reaction in Epoxy 521–DETA results in a smaller exothermal heating and a lower- T_g material compared to the Epoxy 531–DETA when cured at ambient temperature. The low- T_g Epoxy 513–DETA system was fully cured at the temperature 10°C below the glass transition temperature despite the absence of an exothermal temperature rise.

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