

Lifetime Assessment of Epoxies by the Kinetics of Thermal Degradation

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ABSTRACT: The kinetics of thermal degradation of 4,4'-diaminodiphenylsulfone (DDS)-cured glycidylethers (DGBA) and glycidylamines (TGDDM) have been studied by isothermal annealing. Thermal degradation proceeds via first-order kinetics with activation energies of 138 (DGBA/DDS) and 95 kJ/mol (TGDDM/DDS). From these data the temperature-dependent lifetime can be calculated. Based on the heat distortion temperature and 20 years' service as criteria, the upper service temperature is found to be around 115–120°C.

In spite of the different activation energies and bond stabilities, only marginal differences in the upper allowed service temperatures between these resins were found. Only slight improvements can be expected by optimizing the cure conditions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1881–1886, 2004

Key words: epoxies; service temperature; lifetime; thermal degradation; kinetics

INTRODUCTION

The question of durability and lifetime of polymers and polymer composites especially at higher service temperatures is a major problem both in research and applications. To characterize the durability of polymers, it is common practice to follow some important properties with time within the temperature range of interest, until a certain preselected limit is attained.¹ In that way reliable data are obtained, but it is tedious and requires lots of experiments. In addition, these data are only valid for the actual temperature under consideration and cannot be transformed to other service temperatures.

This unsatisfactory situation could be overcome, if the changes would not be followed via a certain property, but by a molecular process. Reactions related to degradation also obey Arrhenius kinetics. Thus, when the kinetics of thermal degradation is known, the data can be transformed over the whole temperature range and the temperature-dependent service lifetime can be calculated from these data.

The disintegration of the network itself could provide a reliable basis for this problem. As outlined in Figure 1, in curing epoxies by amines, the four amine protons are alkylated subsequently such that a tetrafunctional crosslink is obtained. The most important degradation reactions are dehydration with subse-

quent homolytic cleavage between the N and the adjacent C atom and nucleophilic cleavage, which generates aldehydes. Because degradation occurs at the same aliphatic structures, which were before generated by curing, degradation can be considered as a reversal of curing. In fully cured resins the properties are dominated by the crosslink density and the statistical network theories represent always the actual state of the network. Since the theory is valid both for formation and degradation,^{2–4} the changes of the network can be used to characterize the kinetics of thermal degradation.

The best way to follow the degradation of the network is the glass temperature. Since at high degrees of cure the glass temperature is governed by the crosslink density and the influence of the end groups being small and representing primarily the change in mobility,⁵ the different nature of the initial epoxy groups and the new end groups generated by degradation is negligible. Thus the glass temperature is a unique function of the degree of cure representing always the actual state of the network, such that the same incremental change of the glass temperature can be caused either by curing in the positive or degradation in the negative direction. In addition, the glass temperature is one of the most important properties of the polymer, because it determines the upper limit of the service temperature.

Although the mechanisms of thermal,^{6,7} oxidative,⁸ and photooxidative degradation^{9,10} and their products are well known, studies on the kinetics are rarely reported. Kinetic data were only reported from thermogravimetric studies of diglycidyl-bisphenol A/4,4'-

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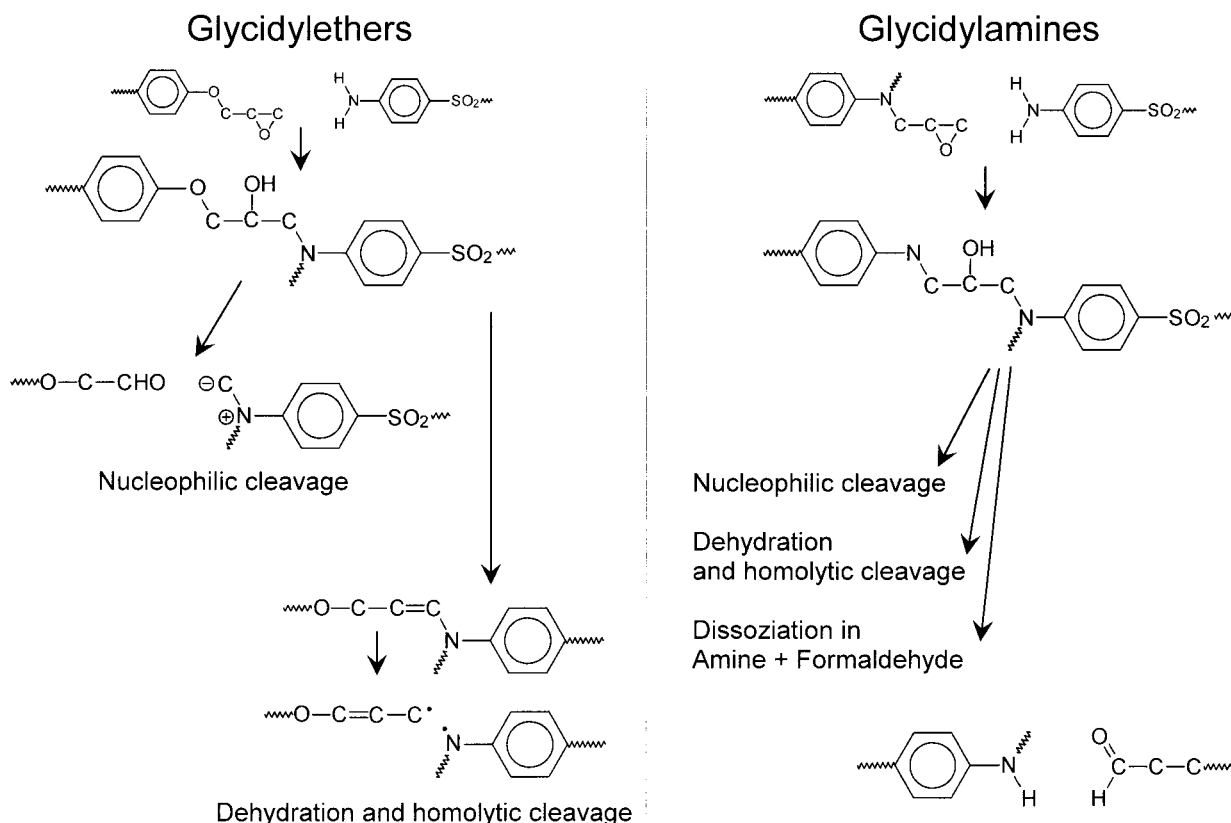


Figure 1 Curing and major thermal degradation reactions of glycidylethers and glycidylamines.

diaminodiphenylsulfone,¹¹ and the generation of acrolein during thermal decomposition.¹²

The present article summarizes studies on the thermal degradation of glycidylethers (diglycidyl-bisphenol A = DGBA) and glycidylamines (tetraglycidyl-diaminodiphenylmethane = TGDDM) cured by 4,4'-diaminodiphenylsulfone (DDS), their kinetics of thermal degradation, stability, and the resulting lifetimes and service temperatures.

EXPERIMENTAL

Materials

Commercial resins (Epikote® 828, Shell, and MY® 720, Ciba Geigy) were used as received. Both resins were cured by DDS at stoichiometric equivalent ratios. To avoid interference between postcuring reactions and degradation, the resins were cured to equilibrium. After mixing at 120°C the samples were cured in ~5 mm thick layers in sealed Al pans under nitrogen to avoid oxidative degradation. The DGBA resin was cured by heating with a heating rate of 1°C/min up to 215°C followed by a 12 h hold at this temperature. The TGDDM resin was cured by the following cure cycle:

2 h isothermal cure at 120°C,
heating with 1°C/min to 180°C,

4 h isothermal cure at 180°C,
heating with 1°C/min to 250°C,
30 min isothermal cure at 250°C,
cooling to room temperature.

The cured resins were degraded by isothermal annealing under nitrogen at preselected temperatures; the samples for analysis were cut from the center of the material. The glass temperatures were measured by differential scanning calorimetry (DSC) (Perkin Elmer DSC4) at a heating rate of 20°C/min; the corresponding degrees of cure were obtained from the theoretical T_g -cure conversion curves in Figure 2. These curves were obtained from the literature.⁵

Kinetics of thermal degradation

If we assume first-order kinetics for thermal degradation, then the rate of bond cleavage is proportional to the actual concentration of intact bonds or to the difference between the initial concentration and that already broken; hence,

$$\frac{p_i - \Delta p}{p_i} = \frac{p_i - (p_i - p_t)}{p_i} = e^{-k_d t} \quad (1)$$

or

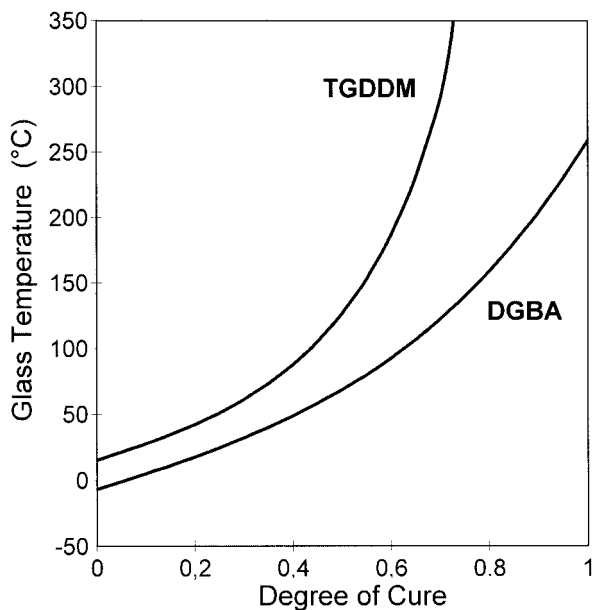


Figure 2 Dependence of the glass temperature on degree of cure of DGBA and TGDDM epoxies cured by DDS at stoichiometrically equivalent ratios.

$$p_t = p_i e^{-k_d t} \tag{2}$$

where p_i is the initial degree of cure, p_t that at time t , and k_d the rate constant for thermal degradation.

The DGBA/DDS resin cured to equilibrium at 215°C had a glass temperature of 216°C corresponding to a degree of cure of 0.927, and exhibited no indications of further curing and no residual heat. This glass temperature is somewhat higher than those reported

in the literature (around 210–212°C), but it is reproducible and due to the special cure cycle with the slow heating rate used here.

This resin was degraded isothermally under nitrogen at 220–260°C; the results are shown in Figure 3.

Figure 3 shows, that over the whole temperature range a linear decrease of $\ln p/p_i$ with time is observed. So the thermal degradation follows a first-order kinetics with a preexponential factor of 6.89E9 [min^{-1}] and an activation energy of 138 kJ/mol.

The same study was performed with TGDDM/DDS. Here the initial glass temperature after curing was 250°C, which corresponds to an effective degree of cure of 0.67. Degradation was performed between 180 and 240°C; the results are shown in Figure 4.

Again, a reasonable linear decrease is obtained at least in the initial stages indicating also a first-order kinetics with a preexponential factor of 4.34E4 [min^{-1}] and an activation energy of 95 kJ/mol. Here only the initial linear part was used for fitting. The deviations in the later stages may be due to secondary reactions of the degradation products, because TGDDM generates highly reactive amines by degradation (Fig. 1).

These results are in good agreement with literature data; most polymers follow first-order kinetics in thermal degradation, when no other mechanisms are interfering. For DGBA/DDS an activation energy of 172 kJ/mol has been reported from thermogravimetric studies.¹¹ From other studies 91 kJ/mol were reported for TGDDM/DDS,¹³ and 122 kJ/mol for triglycidylaminophenol/DDS.¹⁴ A somewhat lower activation energy of 67 kJ/mol was reported from the generation of acrolein during thermal decomposition of

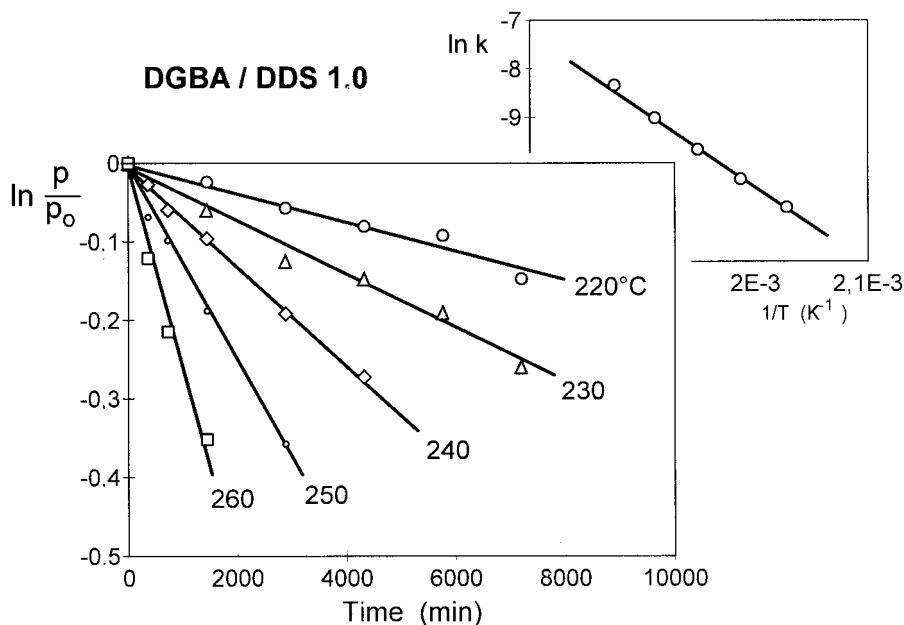


Figure 3 Kinetics of thermal degradation of DDS-cured DGBA.

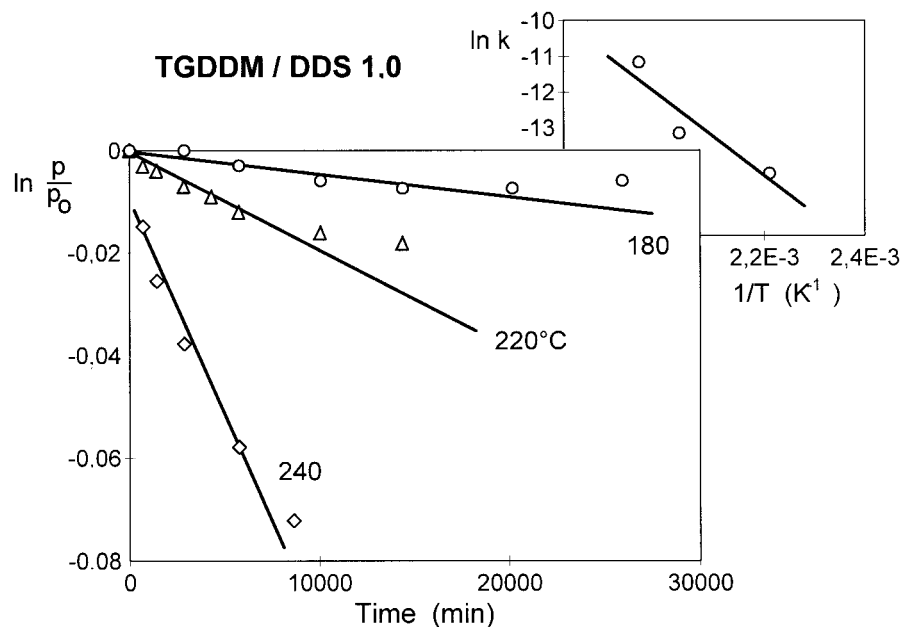


Figure 4 Kinetics of thermal degradation of DDS-cured TGDDM.

TGDDM/DDS.¹² Obviously the degradation is only dependent on the stability of the polymer itself, but not affected by the curing mechanism, because a similar activation energy was found for a cationically cured DGBA resin.¹⁵

Of special interest are the results of the DGBA/DDS resin. Although degradation was performed here in the vicinity of the glass transition, a clear first-order kinetics was observed. This shows clearly, that in contrast to cure kinetics,^{16,17} the degradation reaction is not related to chain mobility (and therefore not dependent on the difference between annealing temperature and actual glass temperature), but controlled only by the absolute temperature. Obviously the bond breakage in a polymer is only dependent on the thermal activation of the bond and independent of segmental mobility.

Lifetime assessment

If we consider as service lifetime the span in time for the glass temperature to drop from the initial value to the service temperature, then these data can be used for an assessment of the lifetime at any temperature. This can be achieved by calculating the time required for the glass temperature to decrease from the initial value after curing $T_{g(i)}$ to that of any storage temperature. The corresponding degrees of cure were obtained from the T_g -cure conversion curves in Fig. 2. Experimental data for isothermal degradation of DGBA resins between 200 and 170°C are reported in ref. 19.

Since the high temperature epoxies used for composites are cured always at 180°C, their actual glass temperatures after curing are always around 195–200°C depending on cure time. Therefore the calculation was based in both cases on an initial glass temperature of 200°C. The results are shown in Figure 5.

According to Figure 5, in a semilogarithmic plot both resins exhibit an almost linear decrease of the lifetime with temperature. Both curves cross over around 160°C; below that, DGBA shows better resistance to degradation. Based on a suggested lifetime of 20 years, the upper allowed service temperatures would be 137°C for the DGBA/DDS resin and 129°C for TGDDM/DDS when cured to an initial glass tem-

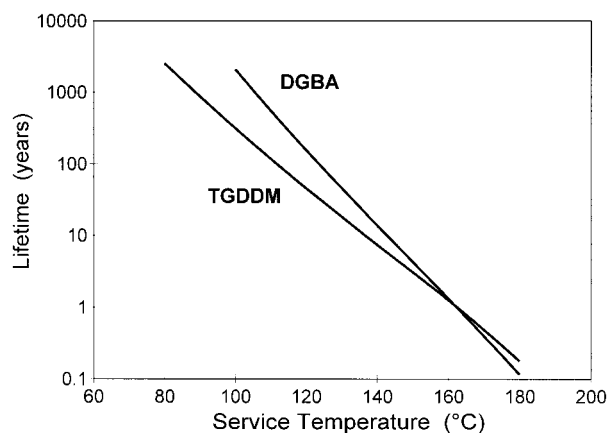


Figure 5 Suggested temperature-dependent service lifetime of epoxy resins.

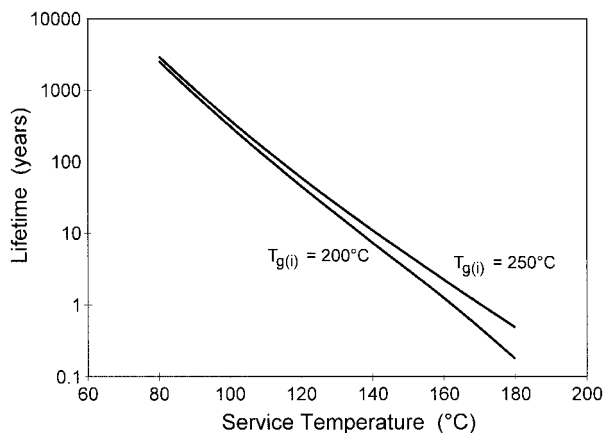


Figure 6 Influence of the initial glass temperature of TGDDM/DDS on the suggested lifetime.

perature of 200°C. This difference reflects the differences on bond stabilities of these resins.

These service temperatures seem somewhat too high, because it is known from practice that the allowed service temperatures of epoxies are somewhat lower, around 110–120°C.¹⁸ However, the glass temperature is not the correct criterion here; in general the heat distortion temperature (HDT) must be used for that purpose, since a structural part loses its usability already when it begins to deform under load, not when it is already flexible. The HDT, of course, is about 15°C above the glass temperature, and this might explain the difference. Using the HDT as criterion brings the upper service temperature down to 115–120°C, as known from practice.

Finally, the effect of different degrees of cure should be discussed. Although in practice the cured resins have glass temperatures around 200°C depending on their cure conditions, they could in principle be cured to considerably higher glass temperatures by using appropriate cure cycles. Here 216°C was obtained for DGBA/DDS and 250°C for TGDDM/DDS, which should also shift the service temperatures to higher levels.

Figure 6 shows the results of the expected lifetimes of TGDDM/DDS epoxies calculated for initial glass temperatures of 200 and 250°C. As mentioned earlier, 200°C is usually obtained by curing as usual at 177°C (350°F); 250°C would be the highest possible glass temperature of this resin (irrespective whether or not such high glass temperatures would be possible in practice).

However, only marginal differences are obtained. Even a shift in the initial glass temperature from 200 to 250°C would shift the service temperature of the TGDDM/DDS resin only from 129 to 133°C. This disappointing result is due to the steep increase of the glass temperature curve in Figure 2, where this rather large difference in the glass temperature corresponds only

to a rather small difference in the degree of cure (or degree of degradation respectively). So, only few broken bonds are required to bring the glass temperature down. This, however, is not caused by the inherent instability of glycidylamines, but primarily characteristic for highly crosslinked resins.⁵

So it may be concluded that the service temperatures at least of high functional epoxies cannot significantly be improved by appropriate cure cycles leading to higher initial glass temperatures. Somewhat better prospects may be expected from low functional epoxies such as DGBA/DDS resins. Here an improvement of almost 10°C seems to be possible by appropriate curing.

CONCLUSIONS

A study was performed to characterize the kinetics of thermal degradation of DGBA and TGDDM epoxies by following the disintegration of the network.

The thermal degradation of epoxies follows first-order kinetics with activation energies reflecting the bond stabilities, so 138 kJ/mol for DGBA/DDS and 95 kJ/mol for TGDDM/DDS were found. In contrast to cure kinetics, the thermal degradation is only dependent on the thermal activation of the bond itself, but not affected by the segmental mobility.

These kinetic data were used to calculate the lifetimes depending on the service temperature. Based on the HDT as criterion and an initial glass temperature of 200°C, the upper allowed service temperatures are found to be around 115–120°C as known from practice.

Glycidylethers such as DGBA exhibit somewhat better thermal stability than glycidylamines (TGDDM); however, the difference in the upper service temperature is less than 10°C.

Although appreciable differences in the initial glass temperatures can be obtained depending on cure conditions, this is only slightly reflected in the service temperature. This is due to the steep increase of the glass temperature curves in the final cure stages, because only a few broken bonds are required to bring the glass temperature down. So at least for highly crosslinked resins it cannot be expected to improve lifetime and allowed service temperature by optimizing the cure path and initial glass temperature.

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