Curing Reaction of Diglycidylesters Containing Alicyclic Imide Structures with Anhydrides and Amines as Hardeners

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SYNOPSIS

The cure reaction of diglycidyl esters containing bicyclo[2.2.2]oct-7-ene units with phthalic anhydride, hexahydrophthalic anhydride, bis(4-aminophenyl)methane, and bis(4-aminophenyl)ethane as hardeners was studied by differential scanning calorimetry. The use of 4-dimethylaminopyridine as a catalyst agent for the anhydride–epoxide reaction was also investigated. Depending on the curing agent, anhydride or amine, and the concentration of the catalyst, differences in activation energies were found, but negligible changes are observed between both anhydrides and the two primary amines. Thermal properties of the final product were unaltered by the hardener used. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins have been widely used in order to obtain tridimensional polymers. Some polyfunctional compounds capable of reacting with groups in the polymer have been used for this purpose. Several types of curing agents such as aromatic and aliphatic primary diamines, acid anhydrides, borine derivatives, and tertiary amines have been described[1] with the aim of achieving materials having good properties.

Borine derivatives and tertiary amines belong to the catalyst hardener type, while anhydrides and primary amines remain in the backbone of the polymer after reaction.

Anhydride curing agents find use in most of the important applications of epoxy resins, particularly in casting and laminates. Chemical reactions that take place during cure determine the resin morphology which, in turn, determines the properties of the cured thermoset.

The uncatalyzed cure of epoxy resins with cyclic anhydrides is well understood.[2,3] The mechanism in-
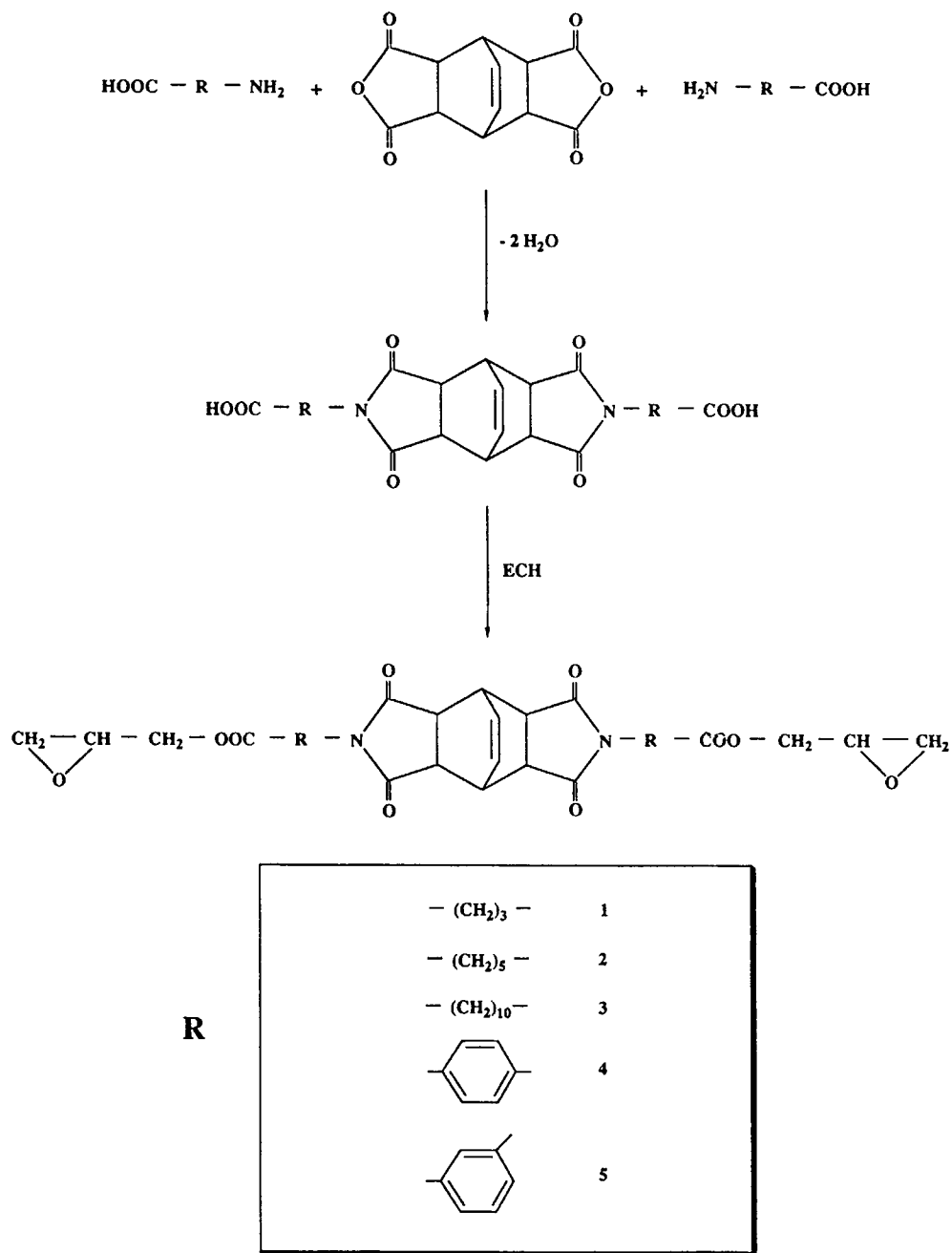
volves the attack of hydroxyl groups of the epoxy resin on the anhydride molecules to form a monoester having a free carboxyl group. The monoester then reacts with the epoxide to yield a diester and a new secondary hydroxyl group, thus perpetuating cure. The epoxide–anhydride reaction can be catalyzed by strong bases, such as tertiary amines. In this case, the reaction mechanism has not been elucidated.

On the other hand, it is well known that epoxy resins can be cured with amine compounds. Among various amine curing agents, aromatic primary amines are known to impart high glass transition temperature (T_g) to cured resins. This is a characteristic effect of the aromatic ring.[4]

Much work has been done on anhydride or amine curing of commercial epoxy resins, but very little is known about the curing of diglycidylesters.[5,6] In this article we report the cure of diglycidyl esters containing alicyclic imide units that have been introduced in order to improve thermal stability and enhance processability.

We have used polyfunctional hardeners, phthalic acid anhydride (PAA), hexahydrophthalic acid anhydride (HHPA), and 4,4'-diaminodiphenylethane (DDE). A tertiary amine, 4-dimethylaminopyridine (DMAP), also was added as a catalyst when the anhydrides were used as hardeners.

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HOOC — R — NH₂ + [anhydride structure] + H₂N — R — COOH

-2 H₂O

HOOC — R — N [imide structure] N — R — COOH

ECH

CH₂—CH — CH₂—OOC — R — N [imide structure] N — R — COO — CH₂ — CH —CH₂

R

| — (CH₂)₃ — | 1 |
— (CH₂)₅ —	2
— (CH₂)₁₀—	3
[para-phenylene]	4
[meta-phenylene]	5

Scheme 1

EXPERIMENTAL

Materials and Procedure

Bicyclo[2.2.2]oct-7-ene-tetracarboxylic dianhydride (Aldrich), 4-aminobenzoic acid (Fluka), 3-aminobenzoic acid (Merck), 11-amino-undecanoic acid (Aldrich), 6-aminohexanoic acid (Fluka), 4-aminobutanoic acid (Fluka), epichlorohydrin (ECH, Scharlau), and benzyltrimethylammonium bromide (BTMA, Fluka), were used without further purification. All solvents were purified by standard procedures.

The diimide-diacids were obtained from bicyclo[2.2.2]oct-7-ene-tetracarboxylic dianhydride and the corresponding amino acid (Scheme 1). The glycidyl compounds were synthesized by reacting the

PPA   **HHPA**

DDM   **DDE**
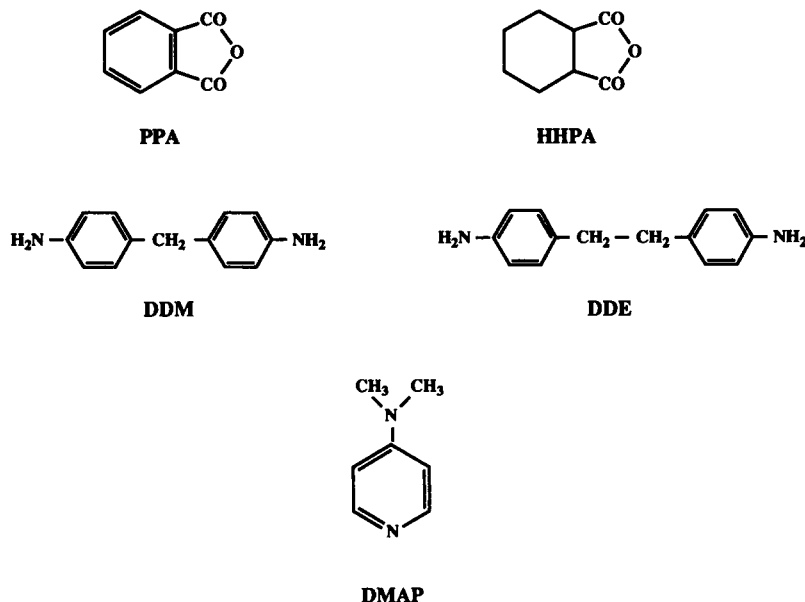
DMAP

Scheme 2

corresponding diimide-diacid, with an excess of epi-chlorohydrin, as previously reported.[7] Phthalic anhydride (PAA), hexahydrophthalic anhydride (HHPA), bis(4-aminophenyl)-methane (DDM), and 4-dimethylaminopyridine (DMAP) were used as received. 4,4'-Diaminodiphenylethane (DDE) was synthesized as previously described[8] (Scheme 2).

The diglycidylic compounds and the corresponding anhydride were mixed at room temperature in a 1 : 1 equivalent ratio and dissolved in the smallest possible amount of dichloromethane. An appropriate quantity of dichloromethane solution of DMAP was then transferred and mixed in a dry chamber. The concentrations of DMAP used were 0.5, 2, and 5 parts per hundred of resin (phr). Approximately 5 mg samples of the mixture were weighted accurately into an aluminum DSC sample pan.

In the same way, mixtures from diglycidylic compound and primary diamines (DDM or DDE) were prepared, but no catalyst was added.
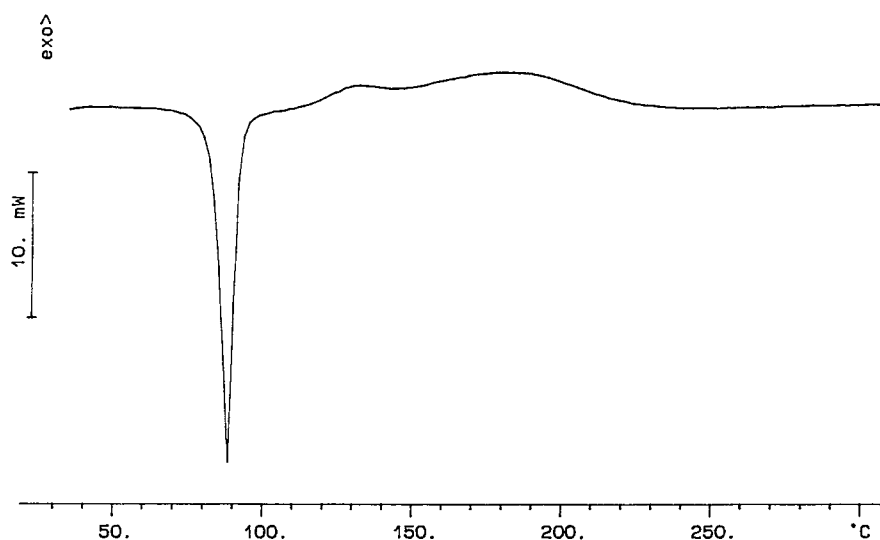

Figure 1   DSC plot of dynamic cure of 3/PAA system (epoxide groups/anhydride groups 1 : 1; 20°C/min).

Instrumentation

Calorimetric studies were carried out on a Mettler DSC-30 thermal analyzer in covered Al pans under N_2, at various heating rates (5–20°C/min). Cross-linking experiments were carried out at several temperatures for 15 min. After the isothermal treatment was complete, the sample was cooled to room temperature and cured polymer T_g and residual enthalpy of curing (if present) were tested in a dynamic experiment. Thermogravimetric analyses were carried out with a Perkin Elmer TGA-7 system in N_2.

RESULTS AND DISCUSSION

Curing of Diglycidyl Compounds with PAA

DSC was employed to obtain data on the exothermic curing reactions of diglycidylcompounds (Scheme 1) with a common curing agent PAA. This hardener was used in the ratio of epoxy groups/anhydride groups = 1 : 1. This ratio can be considered as favorable for the curing reaction between epoxy resins and anhydrides without catalyst.[9] Figure 1 shows the DSC thermogram obtained at 20°C/min for dynamic cure of the 3/PAA system. Both melt in the range 80–89°C, while the curing reaction takes place at 115–225°C, depending on the heating rate, but in all cases after the baseline is recovered. The total area under the thermogram based on the extrapolated base line at the end of reaction was used to calculate the total heat of reaction (ΔH). As can be

Table I   Crosslinking of Diglycidyl Compounds Using PAA as a Hardener

Compound[1]	1	2	3	4	5
T_{max} (°C)[2]	180	168	180	178	178
E_a (KJ/mol)[3]	82	63	85	79	42
T_g (°C)[1]	106	72	57	181	184
Crosslinking T. (°C)	T_g	T_g	T_g	T_g	T_g
120		18	17	83	83
130	14	7	34	95	
140	29	21	44	102	
150	34	22	42		113
160					116
170					115
180					115

[1] See Scheme 1.
[2] 20°C/min.
[3] Ozawa method.

seen, two exothermic peaks appear that could be due to the esterification and etherification of epoxy groups.

As has been mentioned above, the curing mechanism involves the formation of a diester and a hydroxyl group, which perpetuates the curing. These reactions are confirmed by the observation that there is no significant difference in the consumption of epoxide and anhydride. However, at higher conversions, the epoxy groups decrease faster than the diester groups increase. This fact is attributed to
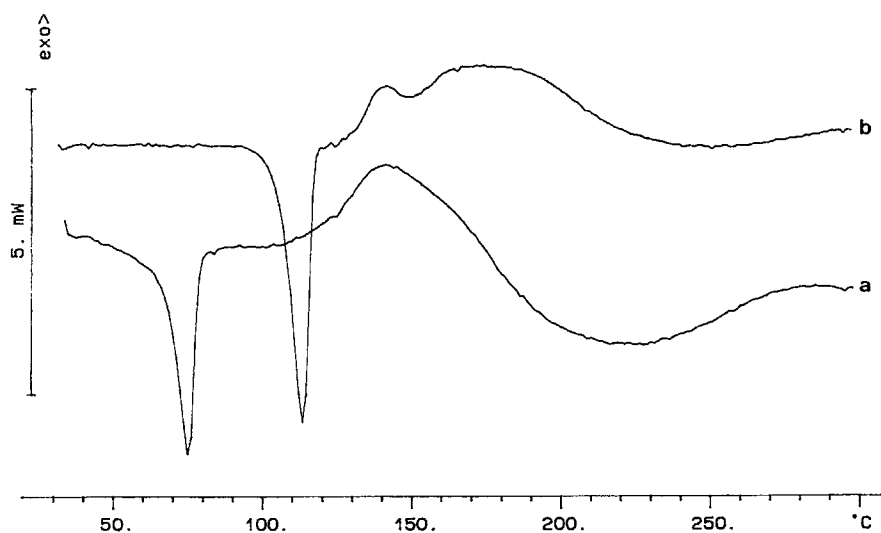

Figure 2   DSC plots of dynamic cure of 4/PAA system (epoxide groups/anhydride groups: (a) 4 : 1; (b) 1 : 1; 20°C/min).

**Table II   TGA Data of the Diglycidylesters Crosslinked
Using PAA as Hardener[1]**

Compound[2]	1	2	3	4	5
T_{onset} (°C)	328	318	337	318	328
$T_{10\%}$ (°C)	368	366	367	350	356
T_{max} (°C)	381, 442	373, 444	381, 442	346, 435	375, 440
dW/dt (%/min)	7, 8	5, 7	4, 11	3, 8	6, 10
$Y_{700°C}$ (%)	5	3	6	15	11

[1] Obtained at 20°C/min.
[2] See Scheme 1.

the etherification reaction between the epoxy and hydroxyl groups and indicates that there is more than one curing mechanism. When the ratio of epoxy/anhydride groups is 4 : 1, only the first exothermic peak can be observed [Fig. 2(a)], which confirms that the main process at lower conversions is esterification and the etherification is negligible when there is not enough anhydride to react.

Dynamic method A uses the ability of DSC to record simultaneously the rate and the enthalpy of reaction. As the temperature increases continuously, a series of rate constants at different temperatures can be obtained by determining dH/dt and the corresponding value of ΔH at each temperature. From these rate constants, the activation energy can be obtained. Thus, only one exotherm is analyzed.

However, this method led to inconsistent results, probably due to the coexistence of more than one curing mechanism. The dynamic method B, based on the fact that the peak exotherm temperature varies in a predictable way with the heating rate, allows calculation of the activation energy without previous knowledge of the reaction order. Moreover, this method is valuable as a precursor for the isothermal studies and is often the only means of analyzing the curing kinetics of systems with multiple exotherms or unreliable baselines. From the plot of ln v vs. the reciprocal temperature of the exotherm peak for different series of experiments, the values of activation energy were obtained. These values, as well as the maximum temperature of the curing exotherm for all glycidyl compounds, are collected in
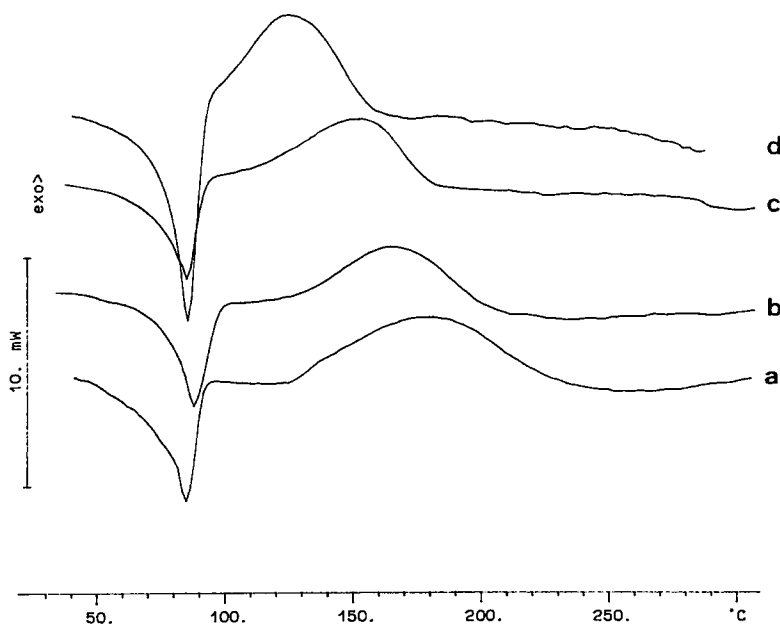

Figure 3   DSC plots of 3/HHPA system using DMAP as catalyst: (a) without catalyst; (b) 0.5 phr; (c) 2 phr; and (d) 5 phr.

Table III Crosslinking of Diglycidyl Compound 3 Using HHPA as a Hardener and DMAP as a Catalyst[1]

DMAP (phr)	—	0.5	2	5
T_m (°C)[2]	84	86	85	87
T_{max} (°C)[3]	181	165	152	126
ΔH (J/g)	154	110	108	101
E_a (KJ/mol)	60	82	82	83
T_g (°C)	29	39	41	39

[1] Values obtained at 20°C/min.
[2] Maximum temperature of the melting endotherm.
[3] Maximum temperature of the crosslinking exotherm.

Table I, and results are very close to the ones reported for hexahydrophthalic diglycidylester[5] and for diglycidylimides.[10]

The inflection corresponding to the glass transition (T_g) was clearly observed for all crosslinked polymers in a second dynamic DSC run. From the data of Table I, it was confirmed that the T_gs reflect the higher flexibility and lower chain stiffness of the tridimensional networks from the glycidyl compounds with aliphatic moieties.

From the dynamic experiments, several temperatures from 120 to 180°C were selected to perform isothermal studies. The data acquisition was started after the DSC cell temperature equilibrated and the signal was recorded for 30 min, when a steady baseline was obtained for all cases. In a second dynamic DSC run, the T_g of the isothermally crosslinked polymer and the residual enthalpy of curing, if existing, were determined. Because the total heat of reaction (heat of isothermal reaction at temperature T + residual heat of isothermal reaction) was quite different from the values obtained in the aforesaid dynamic experiments, it seems unreasonable to assume experimental error, due to an unrecorded heat of reaction, was negligible. Thus, isothermal data were not useful to evaluate kinetic parameters. At any rate, T_g increase can be observed as the curing temperature increases, as expected for higher degrees of crosslinking; but even when high crosslinking temperatures were used, the T_g values of the polymers crosslinked in the dynamic experiments were not reached.

The thermal analysis data obtained by TGA are summarized in Table II. Decomposition temperatures (T_{onset}, onset of the curve weight loss vs. temperature) and the temperature corresponding to the 10% weight loss ($T_{10\%}$) do not show great dependence on the chemical structure of the crosslinked diglycidyl compound. The recorded thermogravimetric plots for all samples show two degradation steps, suggesting the coexistence of more than one degradation process. The maximum weight loss temperatures (T_{max}) for both steps and the rate of weight loss at these temperatures (dW/dt), obtained from the differential thermogravimetric traces (DTG), are collected in Table II. As can be seen, in all cases the first weight loss is observed above 350°C, while the second one occurs about 440°C. It was proposed that the bicyclo [2.2,2] oct-7-ene structure may undergo a retrodegradative Diels–Alder reaction that begins around 360°C in nitrogen, leading to the formation of the corresponding maleimide and diene derivatives.[11] Thus, the first weight loss may be related to this reaction. The char yields at 700°C ($Y_{700°C}$) are higher for resin formulations containing aromatic moieties.

Curing of Diglycidyl Compound 3 with HHPA as a Hardener and DMAP as a Catalyst

In order to test how the structure of acid anhydride influences both the kinetics and mechanism of curing and the properties of the cured thermoset, the hexahydrophthalic acid anhydride (HHPA) was also used as a hardener. As has already been noted, this HHAP is less reactive than PAA, and for this reason the use of an accelerator was necessary.[12] This accelerator can be either acidic, which favors etherification, or basic, which favors esterification.[13]

When the epoxide–anhydride reaction is catalyzed by strong bases, such as tertiary amines, it appears the mechanism in either case represents an anionic living polymerization.[14]

As can be seen in Figure 3(a), only one exotherm is observed in contrast to the ones monitored when PAA is used. Moreover, we have tested how the addition of catalytic amounts of DMAP influences the crosslinking behavior in order to improve the processability of epoxide–anhydride systems. The study was carried out using diglycidyl compound 3, HHPA, and several concentrations of DMAP. The DSC curves are shown in Figure 3. The higher the amine concentration, the lower is the peak temperature of the curing reactions and the lower is the curing enthalpy, as can be seen in Table III. The activation energies, collected in the same table, are higher when DMPA is added but no influence of the amine concentration is observed. This fact confirms the different reaction pathway, depending on the presence or absence of amine.

In a second dynamic DSC run the T_gs of the crosslinked polymers were monitored. As can be seen in Table III, similar T_gs were obtained when different amounts of amine were used in contrast to the higher values obtained with PAA as hardener, showing the influence of the aromatic or aliphatic nature of the hardener used, since it remains in the backbone of the polymer after reaction.

TGA measurements were performed to assess the thermal stability of the crosslinked polymers using anhydrides as hardeners. Differences can be scarcely found between both anhydride hardeners. The results obtained for HHPA are summarized in Table IV.

Curing of Diglycidyl Compounds with DDM and DDE as Hardeners

The mobility and reactivity of the growing network are affected by the structural features of the reactants. Thus, bulky structures in curing agents can be of substantial advantage, and for this reason diaminodiphenylmethane (DDM) has been widely used as a hardener. The influence of bulky structures, especially at the center of the molecule, is of both theoretical and practical interest because many new and recently commercialized resins belong to this class. In a recent article[15] the introduction of alkyl substituents in DDM as well as the influence of the size of these substituents was investigated, and it was concluded that the substitutions lead to a restriction in the mobility and, therefore, affect the curing process. Moreover, the degree of substitution is more important than the size of the introduced substituents.

DDM has a methylene unit that acts as hinge function giving some mobility to the network. DDE contains an additional methylene unit, which may enhance this mobility. So, it seems that the length of this hinge function could have an influence on

Table IV   TGA Data of the Crosslinked Diglycidylester 3 Using HHPA as a Hardener and DMPA as a Catalyst[1]

DMAP (phr)	—	0.5	2	5
T_{onset} (°C)	330	338	349	260
$T_{10\%}$ (°C)	405	399	400	288
T_{max} (°C)	462	459	310, 451	318, 456
dW/dt (%/min)	11	10	2, 11	5, 11
$Y_{700°C}$ (%)	2	1	1	1

[1] Obtained at 20°C/min.

Table V   DSC[1] and TGA[2] Data of the Crosslinked Diglycidylester 3 Using DDM and DDE as Hardeners

	DDM	DDE
T_{max} (°C)[3]	223	224
ΔH (J/g)	93	120
E_a (J/g)[4]	66	68
T_g (°C)	49	40
T_i (°C)	360	375
$T_{10\%}$ (°C)	385	393
T_{max} (°C)[5]	410	413
dW/dt (%/min)	9	7
$Y_{700°C}$ (%)	4	3

[1] Data obtained at 20°C/min.
[2] Data obtained at 10°C/min.
[3] Maximum temperature of the crosslinking exotherm.
[4] Ozawa method.
[5] Maximum decomposition temperature from DTG plot.

the mobility and, therefore, on the cure kinetics. However, the differences in the initial reactivity of these amines, as well as in the activation energy found, are negligible (Table V). These energy values are comparable to the ones previously reported for DGEBA[16] and for N,N'-diglycidylimides.[10] The T_gs of the polymers crosslinked with the two diamines are similar and compare well with the ones obtained when anhydride is used as a hardener. This demonstrates that the influence of the monomer structure is substantial. The effects are much more pronounced as compared to the negligible changes observed when the hardener is either anhydride or diamine. Moreover, the thermal stability assessed by TGA (see Table V) did not show noteworthy differences for the two diamines used as hardeners.

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