Crosslinking of Trimellitimide Glycidyl Ester Derivatives

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ABSTRACT: The cure reaction of diglycidyl trimellitimide esters with 4-dimethylaminopyridine, diaminodiphenylmethane, and dicyandiamide as hardener was studied by differential scanning calorimetry (DSC). Isoconversional kinetic analysis was applied to nonisothermal DSC data and the dependences of activation energies on conversion degrees were obtained. Differences in the shape of these plots were found in accordance to the different kinetic schemes of the curing agents. The thermal properties of the final products evaluated by thermogravimetry do not show noteworthy differences. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 537–542, 1999

Key words: glycidyl imides; epoxy resins; DSC; isoconversional kinetic analysis

INTRODUCTION

Owing to their extreme versatility, epoxy resins are used extensively in industrial applications in which they are required to cure quickly and be readily formulated as one-pot compositions. In particular, we have focused on epoxide-imide resins due to their high heat resistance. Imide groups were introduced to modify the backbone structure of epoxy resins,[1] or a curing agent containing imide groups[2] was used with the aim of improving the thermal properties.

Linear epoxy resins are converted into three-dimensional thermoset networks by different chemical reactions. For this purpose, some polyfunctional compounds capable of reacting with epoxide groups were used. Several types of curing agents—such as aromatic primary diamines,[3] acid anhydrides,[4,5] tertiary amines,[6] as well as diisocyanates[7] and dicyandiamide,[8]—have been described. The mechanism of these reactions dictates the processing conditions and influences the morphology of the network. Of the many techniques available, differential scanning calorimetry (DSC) is the most valuable for investigating cure reaction kinetics and storage stability in one-pot formulations.

The results reported here are the continuation of our earlier work, aimed at obtaining new epoxy resins with greater thermal stability. Previously, we reported the synthesis, characterization,[9] and crosslinking with aromatic diamines[10] of several trimellitimide diglydcidyl ester derivatives. In the present work, we have studied the curing of some of these epoxy-imide compounds with several crosslinking agents. The process was monitored by DSC, and isoconversional kinetic analysis of nonisothermal data was applied to determine the dependence of the process's activation energy on the degree of conversion.

EXPERIMENTAL

Reagents

Solvents were purified by standard methods. Diglycidylesters were obtained as described previously.[9] 4-Dimethylaminopyridine (DMAP), hexamethylene-diisocyanate (HMDI) (Fluka), bis(4-

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Scheme 1

aminophenyl)methane (DDM), *p*-phenylenediamine, and dyciandiamide (Aldrich) were used as received.

Diglycidylesters were kept under vacuum at 60°C for about 24 h to remove moisture. Then they were mixed with the corresponding amount of hardener at room temperature, dissolved in the smallest possible amount of dichloromethane or ethanol to homogenize the mixture, and, finally, the solvent was evaporated under vacuum.

Characterization and Measurements

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). The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration). A known weight of about 5 mg of epoxy resin or mixture with a suitable amount of hardener was put into an aluminium pan. The curing kinetics of the epoxy resins were evaluated using the Mettler–Toledo TA 8000 kinetic software. Thermogravimetric analyses were carried out with a Perkin Elmer TGA-7 system in N_2.

RESULTS AND DISCUSSION

As has been mentioned above, diglycidylic compounds with imide rings in their structure were obtained with a high degree of purity from the corresponding salt of the diimide-diacids and epichlorohydrin in excess and a quaternary ammonium halide as catalyst.[9] The curing behavior of these compounds with *m*-phenylenediamine and diaminodiphenylmethane was investigated using infrared (IR) and ^{13}C-NMR spectroscopy.[10] Of these compounds, the ones containing aliphatic moieties have lower melting points and therefore facilitate the crosslinking process. So the aliphatic compound shown in Scheme 1 was selected for the present study because it was previously observed that the maximum temperature of the

curing exotherm seems to be independent of the aliphatic chain length.

Glycidylester derivatives can be cured thermally or by using several crosslinking agents as was reported previously.[6,10] DSC study was carried out and thermograms of the rate of heat evolution as a function of the temperature for the diglycidylic compound are shown in Figure 1. The endothermic melting peak appears at 149°C and the curing reaction begins at about 250°C. Results reported for the crosslinking of diglycidylesters with an alicyclic imide structure[6] show that the thermally initiated cure takes place at similar temperatures, whereas for the epoxycycloaliphatic compounds[11] the thermal crosslinking is observed at higher temperatures (400°C). In the proposed curing mechanism, the reaction begins through the opening of the oxirane ring with the attack by imide nitrogen or more probably by hydroxylic or carboxylic impurities which act as catalysts. The above-mentioned epoxy compounds behave differently because of the different chemical structure of the glycidylic and cycloapliphatic oxirane rings or because of the absence of protic impurities in the latter.

From the TGA measurements it can be concluded that the thermally initiated cure takes place at temperatures at which significant weight

Figure 1   DSC plot of diglycidylic compound (20°C min^{-1}).

Figure 2 DSC plot of epoxy compound crosslinked with 1 phr of DMAP [5 (a), 10 (b), 15 (c), and 20°C min^{-1} (d)].

loss is observed, so the diglycidylic compounds have to be cured at lower temperatures to ensure that no degradation takes place.

As is well documented,[12] the addition of catalyst or hardener decreases the crosslinking temperature, preventing polymers from degrading and improving their processability. In this way, tertiary amines were found to initiate the crosslinking process by a mechanism that depends on the catalyst concentration.[13] At low concentrations, the first step is the opening of the oxirane ring by the amine, followed by a homopolymerization reaction. At high concentrations, the epoxies may isomerize, thus leading to an allylic alcohol that acts as a proton donor.

We have previously tested how the addition of catalytic amounts of tertiary amine influences the crosslinking behaviour of diglycidylesters, and we found variations in the curing temperatures and activation energies of the process.[6] In the present case, an overall study was carried out using 4-dimethylaminopyridine (1 phr). The DSC curves at different scanning rates are shown in Figure 2. As can be seen, the amine-catalyzed curing takes place at lower temperatures (150–180°C) than the thermal curing. As a first approach, the Ozawa method[14] was used to calculate the activation energies of the process. The obtained value of 70 kcal/mol is lower than the value reported for the crosslinking of diglycidylesters with an alicyclic imide structure.[6]

As is evident, the curing process involves several reactions. Therefore Arrhenius parameters (E_a and A) should be considered as effective values that can vary with changing temperature and conversion. The shape of this dependence is conditioned by the change in the contributions of single chemical reactions to the overall rate during the process. The change in these contributions depends on the process mechanism. Therefore, by analyzing the conversion dependence of the effective activation energy of the process, it is possible to understand the process kinetics without knowing the real rates of the single chemical reactions. Isoconversional kinetic analysis is based on the idea that the reaction rate at a constant conversion depends only on the temperature. For a single step process, E_a is independent of the degree of conversion and may have the meaning of the intrinsic activation energy. Multistep processes reveal that E_a depends on the degree of conversion, the analysis of which helps not only to disclose the complexity of a process, but also to identify its kinetic scheme.[15]

In the present study, isoconversional kinetic analysis was applied to nonisothermal DSC data of the curing of diglycidylimide compounds with tertiary amines as curing initiators. Figure 3 shows the plot of E_a versus conversion. The process starts with the reaction of the highest E_a. This E_a can be associated to the attack of the tertiary amine on the oxirane ring. The dependence of E_a on conversion has a decreasing shape. This suggests that the homopolymerization reaction, with the smallest E_a, makes a constantly increasing contribution to the total heat release

Figure 3 Dependence of the activation energy on conversion for the curing of epoxy resin with 1 phr of DMAP.

up to conversions of 30–40%. At this point, small variations in the dependence can be observed, indicating that the polyetherification has become the main process. The fact that the tertiary amine concentration is low implies that side-reactions leading to autoacceleration are negligible. As the reaction proceeds, the viscosity increases and diffusion effects should be taken into account. However, only at very high degrees of conversion can deviations from the asymptotic E_a value be appreciated, attributable to diffusion phenomena.

Epoxy resins can also be cured with primary amine compounds. Of the various amine curing agents, aromatic primary amines are known to impart high thermal stability to cured resins. Thus, curing was carried out with equimolecular amounts of phenylenediamine and diaminediphenylmethane. The crosslinking takes place at approximately 150°C and the activation energy for the process, calculated by Ozawa's method,[15] is approximately 60 kJ/mol. Differences in the reactivity and activation energy of both amines are negligible. These energy values are comparable to the ones previously reported for DGEBA[16] and diglycidylesters with an alicyclic imide structure.[6]

The application of isoconversional kinetic analysis to this curing process gives the dependence of E_a on the degree of conversion that is shown in Figure 4. As is described,[17] decreasing dependences are observed. The primary amine addition to the epoxide ring controls the overall heat release at lower conversions. So the $E_a = 85$ kJ/mol

is ascribed to this process, being higher than the value obtained by Ozawa's method that considers the addition of the primary amine as a single step and the activation energy constant throughout the process. Because the hydroxyl groups formed during the cure facilitate ring opening, the activation energy is lower than the nonautocatalyzed reaction at the beginning of the process. As has been previously described for epoxy-amine curing systems,[17] a change from kinetic to diffusion controlled curing was observed in conversions of about 40%, and the dependence of E_a on conversion takes a convex shape.

Dicyandiamide (DICY) is one of the most widely used latent hardeners for epoxy resins. Extensive studies on the mechanism of curing epoxides with DICY were carried out[18] and several possible reaction pathways were proposed. In addition to the usual amine/epoxide reaction, the consumption of cyano and hydroxyl groups was observed according to some recent investigations that show DICY to have a functionality higher than four toward epoxides, although a functionality of four would be expected because of the presence of four NH bonds.[19] A mechanism has been proposed in which the initial epoxy/DICY reaction leads to the formation of N-alkyl dicyandiamides, which in turn may cyclize to form 2-amino-1,3-oxazolines[20] and 2-imino-1,3-oxazolidines.[21] In accordance with this mechanism, the minimum concentrations of reactive groups was found to be close to molar ratio of 7 mol of epoxy per 1 mol of DICY.

Figure 4 Dependence of the activation energy on conversion for the curing of epoxy resin with diaminediphenylmethane.

Figure 5 DSC plots of the crosslinking of epoxy compound with dicyandiamide [molar ratio epoxy/DICY 3 : 1 (a) and 7 : 1 (b)].

In the present study, the diglycidylic compound was cured using epoxy/DICY molar ratios 3 : 1 and 7 : 1 to elucidate the behavior of the system. As can be seen in Figure 5, DSC scans showed melting endotherms at approximately 140°C and exotherms attributed to the crosslinking process at higher temperatures. The onset temperature of the exotherm (at ca. 160°C) is lower than the one described for the diglycidylether of bisphenol A[22] and is similar for both epoxy/DICY molar ratios. The maximum temperature of the crosslinking exotherm increases with the amount of epoxy compound in the mixture (epoxy/DICY ratios: 3 : 1 T_{max} = 177°C and 7 : 1 T_{max} = 201°C).

Isoconversional kinetic analysis of nonisothermal DSC data of curing of the diglycidylester with both molar ratios showed different shapes for dependences of E_a on conversions (Fig. 6). This indicates that the kinetic scheme of the reaction depends on the epoxy/DICY ratio, in accordance with the mechanism mentioned above. When 3 mol of epoxy per 1 mol of DICY are used, the plot obtained for E_a versus conversion percentage is similar to the one obtained previously for the crosslinking using primary amines as hardeners: E_a decreases with conversion, the higher E_a being associated with the primary amine addition.

For the epoxy/DICY molar ratio of 7 : 1, E_a is seen to increasingly depend on conversion. The shape of this plot is related to a process which starts with the reaction with the lowest activation energy. As conversion increases, the contribution

of the intramolecular cyclizations causes an increase in E_a, and the maximum value of activation energy can be considered as an estimation of the activation energy of the cyclization reactions. As can be seen, at low conversion degree very different activation energies were found for the two different molar ratios of DICY to epoxy compound. However, when almost none of the curing agent present reacted, the initial activation energies are expected to be similar. This difference could be attributable to the existence of a differ-

Figure 6 Dependence of the activation energy on conversion for epoxy resin and DICY [molar ratio epoxy/DICY 3 : 1 (a) and 7 : 1 (b)].

Table I   Thermal Data of the Crosslinked Materials Obtained by TGA

Crosslinking Agent	T_{onset} (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	$Y_{600°C}$ (%)
DMAP	310	393	420	27
DDM	270	349	305, 395, 475	32
DICY 1/3	260	335	300, 410	28
DICY 1/7	260	385	423	29

ent reaction pathway at the first stages of reaction or to the inaccuracy of the method at low conversion degree.

In a second dynamic DSC run, none of the completely crosslinked materials obtained show baseline inflections attributable to the glass transitions, due to the low c_p differences. It seems to support a crosslinking reaction that has progressed to such a degree that it immobilizes the polymer chains within a three-dimensional network, as a consequence of the high crosslinking density.

To determine the thermal stability of the materials obtained using the above hardeners, thermogravimetric analyses were performed. The thermal data are shown in Table 1. Decomposition temperatures (T_{onset}, onset of the curve weight loss versus temperature) and the temperature corresponding to the 10 wt % loss ($T_{10\%}$) do not show a great dependence on the curing agent. The shape of the recorded thermogravimetric plots suggests the coexistence of more than one degradation process. The maximum weight loss temperatures (T_{max}) for the different steps are collected in Table 1. However, the epoxy resin crosslinked with DMAP as a catalyst began its degradation at slightly higher temperatures. Finally, the char yields at 600°C are similar in all cases.

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