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Networks by fast epoxy polymerization

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SUMMARY

A fast curing epoxy system, suitable for reactive processing, was investigated. The reaction of epoxy resin (Epon 815, Shell), comprising 85% diglycidyl ether of bisphenol-A and 15% butyl glycidyl ether with boron trifluoride etherate was extremely fast and uncontrollable at room temperature. The reaction rate could be controlled by complexing boron trifluoride with a polyether triol (Voranol 2070, Dow). The new system was ideal for reactive processing. It exhibited an induction time at an initial temperature of 40°C before undergoing very rapid curing. The induction time decreased from 55 to 2 seconds with increasing ratio of boron trifluoride to epoxy and with reactant temperature. The triol was fully incorporated in the network, affecting the final properties of the polymer network. Thus, it was possible to manipulate the gel times and material properties by varying the reactant ratios. A model system comprising phenyl glycidyl ether and octanol was used to investigate the mechanism. The incorporation of triol and the presence of cyclic oligomer indicates that both activated monomer and active chain end mechanisms were operating during the curing of these systems. The low molecular weights of the polymers made from the model system indicated the presence of chain transfer and termination reactions.

INTRODUCTION

Epoxy resins are one of the most commonly used class of resins in electrical moldings, encapsulations, adhesives, sealants and coatings. These resins have epoxy groups at the end of the polymer chains and the resins are cured through the reaction of these epoxy groups. Curing is by either step growth reactions with amines, anhydrides and other similar compounds [1,2] or by chain growth reactions with Lewis acids [3-5]. Curing by step growth reactions is generally slow and the resins used exhibit high initial viscosities. High mold temperatures (> 130°C) are required to cure these systems [6,7]. On the other hand, cationic reactions with Lewis acids proceed at a fast rate. Their low initial viscosities and fast curing make them good candidates for fast reactive processing.

In this paper, we report our investigations on the curing of commercially available epoxy resin by micro RIM (reaction injection molding). Boron trifluoride was used as the Lewis acid. Boron trifluoride is normally complexed with a Lewis base. The most readily available complex is boron trifluoride etherate [$BF_3 \cdot O(Et)_2$]. When boron trifluoride etherate was used as a catalyst to cure the epoxy resin, the reaction was so fast that the polymer formed turned dark brown and degraded because of the high exothermic heat generated during the reaction. On the other hand the boron trifluoride monoethyl amine complex is known to cure epoxy resin over a long period of time (24 hours) even at high temperatures (140°C) [8].

Thus, boron trifluoride when complexed with Lewis bases of increasing strength, e.g. hydroxyl, thiol and amine, takes longer times and higher temperatures to generate the active species that initiate polymerization. This fact motivated us to synthesize a complex of BF_3 with a polyether triol made from ethylene and propylene oxide. The complex readily reacted with the epoxy resin to give crosslinked networks. These systems were slower than

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$BF_3 \cdot O(Et)_2$ but much faster than $BF_3 \cdot RNH_2$ and thus appeared ideal for fast reactive processing. Here, we report those results as well as an attempt to investigate the mechanism of the reaction.

EXPERIMENTAL

Materials: Epon 815 (Shell Chemical), which is a mixture of 85% diglycidyl ether of bisphenol-A and 15% butyl glycidyl ether was dried under vacuum at 70 °C for 5 hours and stored over molecular sieves. Voranol 2070 (Dow Chemical), which is a polyether triol made from ethylene and propylene oxide (MW-700) was dried under vacuum at 70 °C for 5 hours and stored over molecular sieves. Boron trifluoride etherate (Aldrich) was used as received from the Sure/Seal™ bottle. Phenyl glycidyl ether (Fluka) was dried over molecular sieves and distilled under vacuum before use. Isobutanol (Aldrich) was dried over calcium chloride and distilled. It was stored over molecular sieves and distilled again before use.

Synthesis of boron trifluoride complex: Boron trifluoride etherate was reacted with the triol at BF_3 : hydroxyl ratio of 1:10. The reaction was carried out at 45°C under vacuum in a dry atmosphere. The ether liberated was distilled out under vacuum. The BF_3-triol complex was stored under nitrogen in an air-tight container. The complex was further diluted by adding calculated amounts of triol to obtain various BF_3 : hydroxyl ratios. Similar complexes were formed by reacting boron trifluoride etherate and isobutanol (IBA).

Micro reaction injection molding of epoxy resin: The micro RIM machine used for the studies was developed at the University of Minnesota. The machine has a lance style chemical cylinder and a fixed cross arm driven pneumatically. The mixing of the chemicals occured in a self cleaning mix head with crosshead recycle. The details of the machine are reported by Mikkelsen and Macosko [9]. The tank temperatures were varied between room temperature and 65°C. The viscosities of the epoxy resin and the BF_3-polyol complex, at room temperature, were 750cps and 315cps, respectively. At this temperature the nozzle Reynolds numbers [10] in the impingement mixhead were 120 and 100 for epoxy and polyol, respectively, and mixing was poor. When the temperatures were raised to 40°C, the Reynolds number increased to 250 and 220, respectively, and mixing was good. The two components were stored under dry nitrogen gas in the tanks of the machine. We changed the chemical ratio by changing the cylinders and by diluting the initiator complex with additional polyol. The shot size could be varied between 5 to 120cc. The reactants were shot into the insulated cylindrical reactor, fitted with a thermocouple. The thermocouple was linked to a digital data acquisition system and the adiabatic temperature rise (ATR) was recorded.

Experiments for mechanistic study: Phenyl glycidyl ether (PGE) was reacted with BF_3-isobutanol complex in clean, dry test tubes. Bulk reactions were carried out under nitrogen in an oil bath at 21°C, 40°C and 200°C. Solution polymerizations were conducted at 40°C using carbon tetrachloride and methylene chloride.

Differential scanning calorimetry (DSC): The crosslinked polymers were analyzed on a Mettler TA3000 system. About 10 to 15 mg of each sample were scanned from -100 to 250°C at the rate of 10°C/minute in air. The samples were subjected to a second heating cycle to check the irreversible changes during the first heating.

Gel permeation chromatography (GPC): The low molecular weight polymers were analyzed using a Beckman 100A GPC. Two Zorbax bimodal columns were used in series. Columns were at room temperature. Tetrahydrofuran was used as the solvent at a flow rate of 1ml/min. Standard polystyrene samples were used for the calibration.

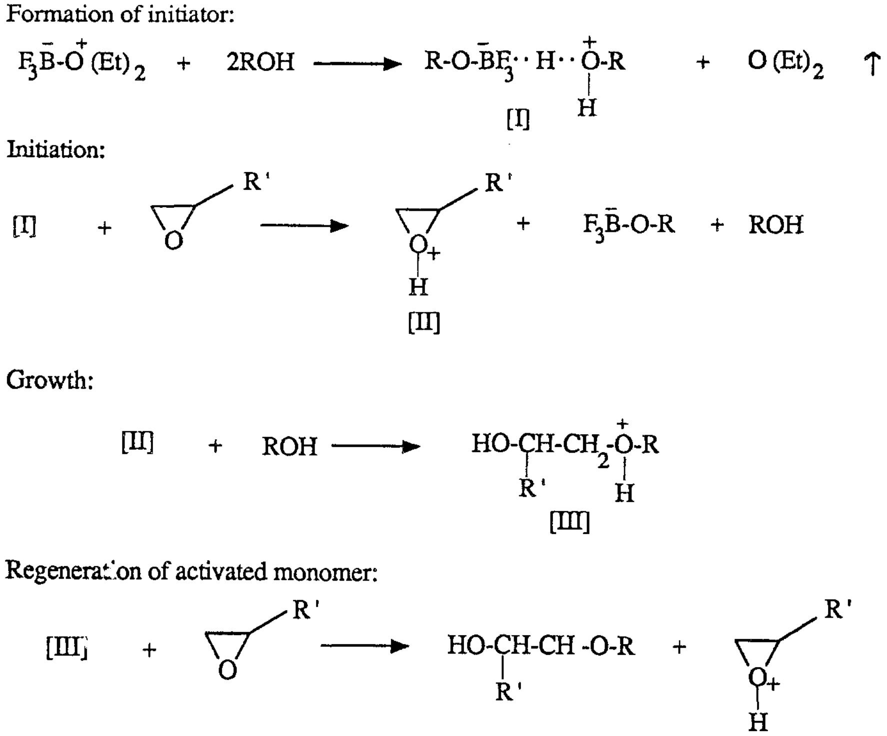
Gas chromatography / mass spectrometry (GC/MS): The low molecular weight polymers were injected into a VG 7070E - HF GC/MS manufactured by VG Instruments, UK. The injector temperature was 250°C and the column temperature was 300°C. The nonvolatile fraction of the sample remained at the injector. The separated fractions coming out of the column were fed to mass spectrometer.

RESULTS AND DISCUSSION

Epon 815 and the BF_3-Voranol complex were reacted by micro RIM. The adiabatic temperature rise (ATR) plots reveal interesting information about the curing reactions.

Figure-1 shows the effect of the amount of BF_3 on the ATR at a constant epoxy : hydroxyl ratio of 6 : 1. The reaction exhibited an induction time which decreased with the amount of BF_3. The rate of temperature rise and the maximum exothermic temperature also increased with the amount of BF_3 in the reaction. The decrease in the ultimate temperature in ATR with the decreasing amount of BF_3 indicated a decrease in the extent of reaction. The DSC of the polymers did not show the glass transition of the triol (-55°C) which indicated that the triol was completely incorporated into the polymer network. The reaction mixture gels at as high an epoxy : hydroxyl ratio as 1:1.3. However, the reaction does not gel above the ratio 1:2. This observation supports the latent chain/activated monomer mechanism as per scheme I [11], wherein a proton is first transferred from the catalyst complex to the monomer. The activated monomer then reacts with the the hydroxyl containing compound to open the ring. The activated monomer could be regenerated by proton transfer from the oxonium ion in the chain.

Scheme I- Activated Monomer Mechanism:



Thus the active center is always on the monomer.

Termination:
There is no classical termination step involved but the low extents of reactions observed from ATR plots indicate occurrence of termination which could be due to vitrification or deactivation of the growing chain due to some side reactions (dead end polymerization).

ATR experiments were conducted with reactants at varying initial temperatures in order to investigate the origin of the induction time. These ATR plots (Figure-2) clearly indicate the reduction in the induction time with increasing initial temperatures of the reactants. The reaction started almost instantaneously when the starting materials were preheated to 65°C. In order to check if the formation of activated monomer was a slow step and caused the induction time, we added a stoichiometric amount of phenyl glycidyl ether to the initiator complex to preform the activated species. The induction times were unchanged (Figure-3). Thus, the induction time seems to be due to initial slow reaction of the activated monomer with the hydroxyl compound which is then accelerated due to the exotherm of the reaction.

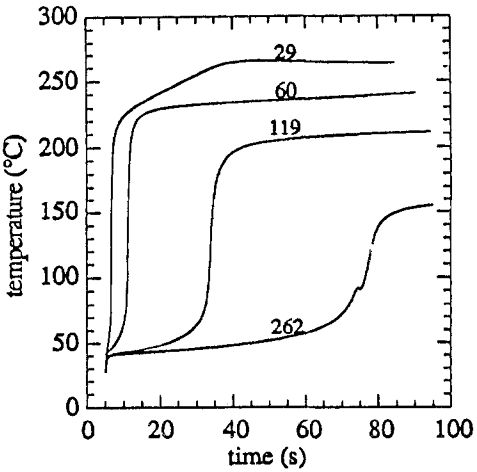


Figure-1 Effect of amount of boron trifluoride on the adiabatic temperature rise. The numbers in the plot represent the epoxy : BF_3 ratio.

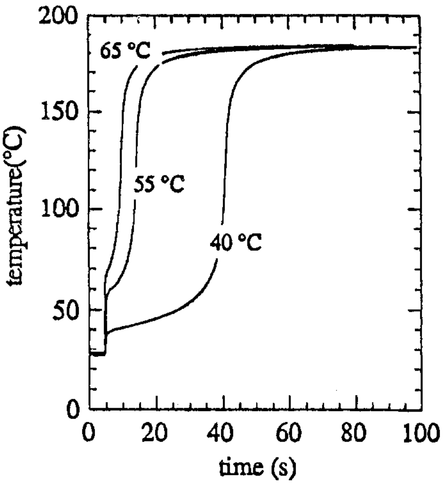


Figure-2 Effect of initial temperature on the reactants on the adiabatic temperature rise at a fixed epoxy : polyol : BF_3 ratio of 128 : 22 : 1.

In Figure-1, the ATR results for epoxy : BF_3 ratio of 29 showed a two stage temperature rise. The second stage is believed to be degradation. The sample discolored and emitted fumes due to the high reaction exotherm. If we assume that epoxy : BF_3 = 60 (Figure-1) represents complete conversion, we can calculate a heat of reaction of of 89 kJ/mol [10]. Thus, the heat of reaction could be ≥ 89 kJ/mol. A higher value of 110 kJ/mol is reported by Bidstrup for an epoxy and amine reaction [12]. Based on this value , the calculated extent of reaction varied between 80% to 45% for epoxy : BF_3 ratios of 60 and 262 respectively. The conversion decreased as the starting temperature was increased from 40°C to 60°C (Figure-2)

In an ideal situation, as per the activated monomer mechanism, the degree of polymerization should be dependent on the ratio of the epoxy and hydroxyl compound. Since the monomers used in our RIM experiments were multifunctional, polymers formed were in network form and did not dissolve in solvents to allow characterization. Hence, we decided to continue our mechanistic investigations with a model system comprising phenyl glycidyl ether and isobutanol as the hydroxyl compound which would enable us to carry out solution characterization. Boron trifluoride etherate was reacted with isobutanol at molar ratios between 1:1 and 1:10. It was necessary to react a minimum two moles of isobutanol per mole of BF_3-etherate to remove the ether completely. The probable structure of the complex is given in scheme I.

The polymerization reactions were carried out in test tubes under an inert and dry atmosphere to eliminate any reactions with water or oxygen. The model system was reacted at different epoxy : hydroxy : BF_3 ratios in bulk as well as in solutions at both high (200°C) and low (40°C) temperatures. However, the resultant polymer always had a low molecular weight and a MWD broader than expected from a purely living polymerization (Table-1). The molecular weight, instead of increasing, decreased marginally, with decreasing amount of BF_3. It was also observed that the extent of reaction decreased (from 98% to 80%)with decreasing amount of BF_3. The epoxy contents were determined during the reaction by quenching the samples in a dry ice / acetone mixture and reacting with pyridinium chloride / pyridine reagent [13]. It was found that the reactions stopped in 4-5 minutes. Thus, the reaction is terminated by some side reactions of the reactants and at the lower concentrations of BF_3, the active centers are being deactivated before they form polymer.

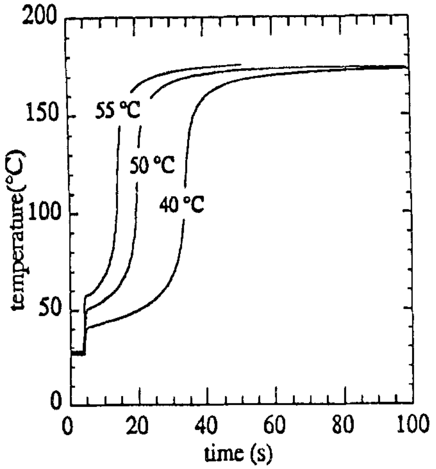


Figure-3 Effect of initial temperature of reactants on the adiabatic temperature rise at an epoxy : polyol : BF_3 ratio of 132 : 22 : 1. One mole of PEG was added to the initiator complex of the material in Figure-2.

Table-1 Effect of molar ratios of reactants on molecular weights of polymers.

molar ratio PGE	:	IBA	:	BF_3	Mw*	Mn*	MWD*
100	:	2	:	1	1944	1105	1.76
100	:	3	:	1	1719	1079	1.59
100	:	5	:	1	1573	1057	1.49
100	:	5	:	1	1563	923	1.69
200	:	2	:	1	1472	767	1.92
400	:	2	:	1	1420	752	1.89

* relative to polystyrene standards.

Penczek showed that independent of the activated monomer mechanism, the active chain end mechanism with tertiary oxonium ion may also operate [14-16]. However, with a large excess of hydroxyl groups the activated monomer mechanism is predominant.

It is known that the epoxides cyclize to a considerable extent during cationic polymerization [17-19]. In fact a number of references are found in the literature wherein the molecular weight of the polymer was limited to low values during the polymerization of ethylene oxide and tetrahydrofuran, irrespective of reaction conditions. The lower values of molecular weight were attributed to an equilibrium between monomer and polymer [18-22]. The excess of the monomer, however, keeps reacting to form dioxanes.

A similar kind of equilibrium seemed to be operating during the polymerization of phenyl glycidyl ether which limited the molecular weight in our experiments. However, not all the monomer was consumed, indicating the deactivation of the active centers. The GC/MS of the low molecular weight polymers showed the presence of the cyclic dimer with molecular weight of 300, which is mainly produced by the active chain end mechanism. Thus, the extremely fast rate of initiation and propagation, involvement of two mechanisms and the occurrence of the side reactions via the active chain end mechanism, prevented the reaction from being a living polymerization and gave low molecular weights with broader MWD.

Since the polymers made from the monofunctional epoxy (phenyl glycidyl ether) and the monofunctional alcohol (isobutanol) were linear and low molecular weight compounds, they were not of any practical use. However, the polymers made from Epon 815 and Voranol 2070 formed highly crosslinked networks due to their higher functionalities. In fact, even the cyclization of more than two oxirane moieties would give rise to crosslinking between polymer chains in such high functionality systems.

The DSC analysis of the crosslinked polymers showed an exothermic peak at high temperatures (>150°C). This peak shifted to higher temperatures with the increasing ratio of BF_3 : epoxy (Table-2). The exothermic peaks disappear in the second heating as depicted in Figure-4. The polymers displayed glass transitions near room temperature (Table-2). These lower values of glass transition temperatures (Tg) could be due to the presence of polyether blocks. The degree of crosslinking increased with increasing BF_3, which was evident from the increasing Tg. In fact, the exothermic peak in the first DSC run could be due to the residual reaction of the epoxy groups which remained after the material had cooled down from the adiabatic reaction temperature, the post gel reaction being diffusion controlled. The peaks shifted to higher temperatures with increasing amount of BF_3.

Table-2 Effect of molar ratio of reactants on Tg and exotherm onset temperatures of the epoxy resins measured by DSC.

epoxy *	:	hydroxyl†	:	BF_3	Tg, °C	exotherm onset,°C
29	:	5	:	1	38	235
60	:	10	:	1	32	190
119	:	20	:	1	30	170
237	:	40	:	1	9	170
45	:	18	:	1	-5	
32	:	27	:	1	-12	
26	:	34	:	1	-22	

* Epon 815 , † Voranol 2070

Table-3 Effect of initial temperature of reactants (T_o) on Tg and exotherm onset at fixed molar ratio of reactants.

T_o °C	Tg °C	exotherm onset °C
35	34	155
55	12	105
60	0	—

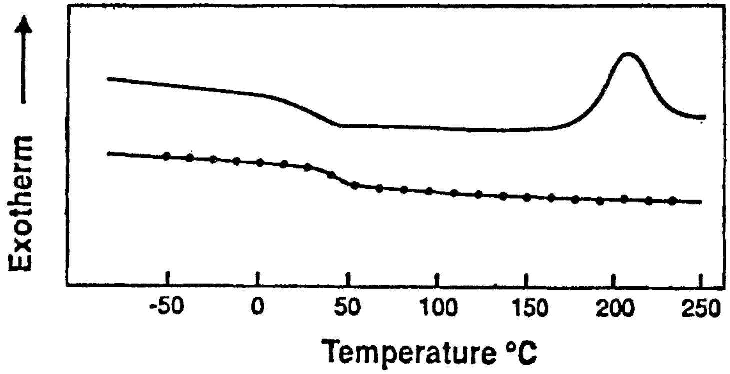


Figure-4 Representative DSC plot at an epoxy (Epon 815) : hydroxyl (Voranol) : BF_3 ratios of 60 : 10 : 1. The solid line represents first heating and dotted line indicates the second heating.

The lowering of Tg with increasing initial temperature of the reactants (Table-3) may be attributed to the lower extent of reaction observed from Figure-2 wherein the plots practically end at the same temperatures but start at different values.

Thus, these systems allowed the manipulation of gel times and material properties by changing the reactant ratio and temperature. The polymers were highly crosslinked even in the case of incomplete conversions. The polymers were insoluble in THF, toluene and acetone and did not not show any exotherm up to 250°C.

CONCLUSIONS

A fast curing epoxy system could be developed by reacting a commercially available epoxy resin, Epon 815, with a complex of BF_3 and a triol, Voranol 2070. This system allows the manipulation of gel time by changing the reactant ratio. The triol is incorporated into the network and modifies the material properties. Thus, various epoxy systems can be developed by changing the nature of the triol. The polymers exhibited a wide range of Tg values varying between -25 and 40°C. The presence of both the activated monomer and the active chain end mechanisms lead to various reactions. The activated monomer mechanism involves reaction of epoxy and hydroxyl functionalities and can form living polymerization system. However, the active chain end mechanism gives rise to various possibilities like self polymerization of epoxy, cyclization and transfer to hydroxyl which prevents the reaction from being a living system.

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