

Effect of Prereaction on Curing of Elastomer-Modified Epoxy Resins

A. PADMA,¹ R. M. V. G. K. RAO,¹ G. NAGENDRAPPA²

¹ F. R. P Pilot Plant, Material Science Division, National Aerospace Laboratories, Bangalore 560 017, India

² Department of Chemistry, Bangalore University, Bangalore, India

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ABSTRACT: Three multifunctional epoxy resins novolac epoxy (EPN), triglycidyl para-aminophenol (TGPAP), and tetraglycidyl diaminodiphenylmethane (TGDDM) were modified with a carboxy-terminated acrylate-based liquid elastomer (PnBA). The effect of prereaction of the epoxy groups in the resin and carboxyl group in the elastomer on curing parameters, such as the cure reaction conversions; processing parameters, such as gel times and vitrification times; initial cure temperatures, and activation energy values were evaluated. Fourier transform infrared spectrometry (FTIR), dynamic mechanical spectrometry (DMS), and differential scanning calorimetry (DSC) were used for the study. The results indicated that while the cure reactions were slightly retarded in the presence of elastomer, they were slightly accelerated when certain prereaction catalysts were used. The gel times and vitrification times decreased due to the prereaction. The physical properties such as fracture toughness and modulus of neat resin castings and flexural strength properties of carbon cloth-reinforced laminates were evaluated. Results indicated that the toughness property increased and the modulus decreased with elastomer addition. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1751–1757, 1997

Key words: multifunctional epoxy; PnBA elastomer; prereaction; effect on cure; physical properties

INTRODUCTION

Toughening of thermoset matrix materials such as epoxies has received much attention in the area of polymer composites as it improves the fracture toughness, impact strength, and delamination resistance of such materials.^{1–3} Chemical linking between the elastomer and the epoxy matrix results in maximum improvement in toughness in thermoset matrices.^{4,5} The elastomer and the epoxy form a single phase when prereacted. When a curing agent is added to this the elastomeric portion separates out into a second phase due to

changes in solubility parameters, molecular weights, densities, and many other factors. The presence of crosslinked elastomer as a discrete, well-dispersed discontinuous phase in epoxy resin was found to be an essential requirement for improving the above properties of the matrix.^{6,7} This second-phase formation may result in changes in curing characteristics of the resin matrix; hence, there is a necessity to monitor the cure parameters of the modified epoxy matrices. Chan and Gillham⁸ reported that the prereaction of CTBN-epoxy resulted in no change in cure kinetics of the resin. In another report⁹ a decrease in gelation and vitrification times of the epoxy resin was reported in the presence of amino terminated butadiene acrylonitrile (ATBN) elastomer. However, the effect of prereaction of PnBA elastomer on

Correspondence to: R. M. V. G. K. Rao.

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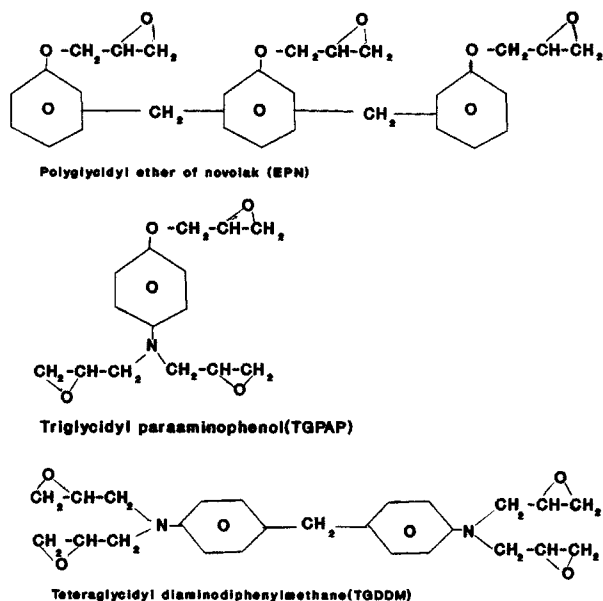
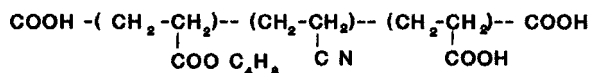
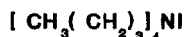


Figure 1 Structure of epoxy resins used.

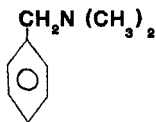
the curing of multifunctional epoxy resin is not reported in the literature. In our earlier publications^{10,11} the evidence of a prereaction of epoxy resin with elastomer, effect of different prereaction catalysts, their concentration, and reaction temperature were reported. In the present article,



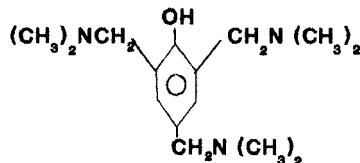
PnBA liquid elastomer



Tetra n-butyl ammonium iodide



N,N-Dimethylbenzylamine



2,4,6-Tris(dimethylaminomethyl)-phenol

Figure 2 Structure of elastomer and prereaction catalysts.

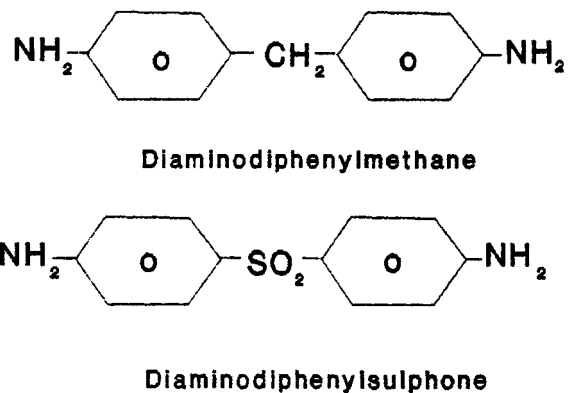


Figure 3 Structure of hardeners.

variations in the cure reactions kinetics with carboxy-epoxy prereaction were evaluated using different techniques such as FTIR, DMA, and DSC. Some of the physical properties such as fracture toughness of castings and flexural modulus of carbon cloth-reinforced laminates are presented. A detailed presentation on the mechanical properties of the other systems will be presented in our future publications.

EXPERIMENTAL

Materials

Resins

Epoxy novolac (functionality 2.6 and epoxy equivalent weight 176 g/eq) was obtained from Hindu-

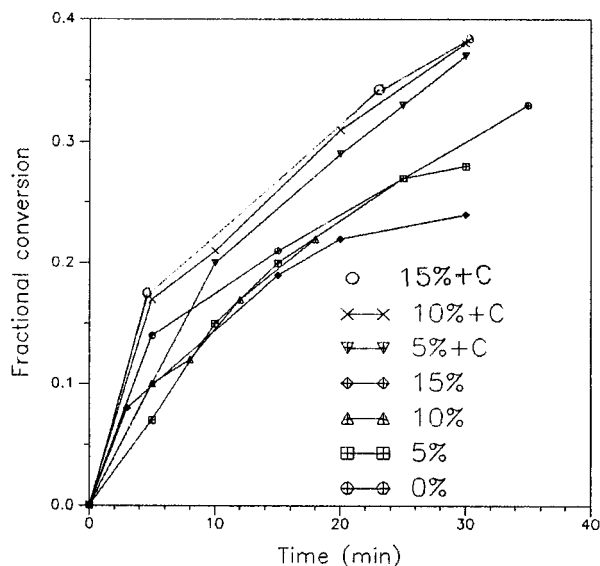


Figure 4 Epoxy conversion versus time in EPN/DDM with different percentages of PnBA elastomer. C, prereaction catalyst.

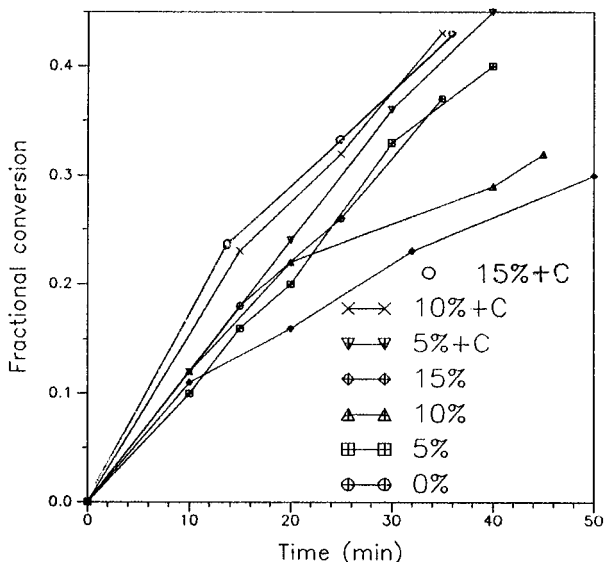


Figure 5 Epoxy conversion versus time in TGPAP/DDS with different percentages of PnBA elastomer. C, prereaction catalyst.

stan Ciba Geigy, India. TGPAP (functionality 3 and epoxy equivalent weight 115 g/eq) was synthesized in-house, and TGDDM (functionality 4 and epoxy equivalent weight 135 g/eq) was synthesized in-house. Figure 1 presents the structure of the resins.

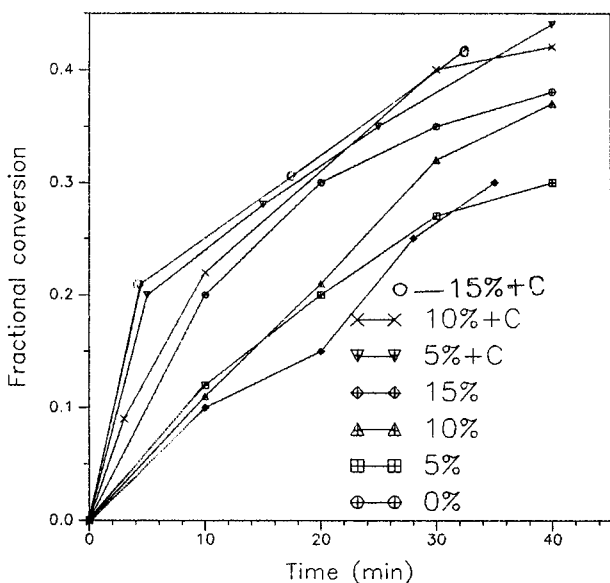


Figure 6 Epoxy conversion versus time in TGDDM/DDS with different percentages of PnBA elastomer. C, prereaction catalyst.

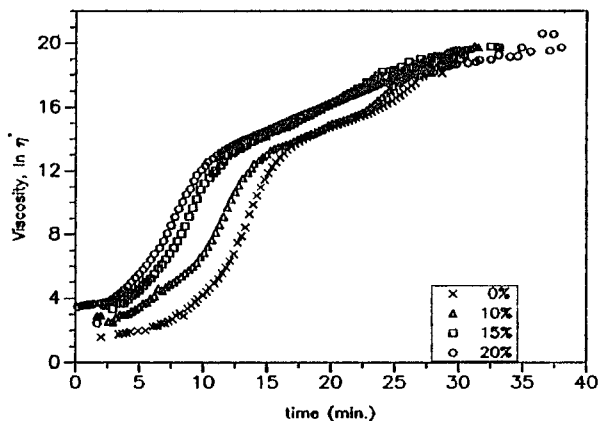


Figure 7 Viscosity profiles of EPN/DDM resin system with different percentages of acrylic elastomer.

Elastomer

Carboxy-terminated poly(*n*-butyl) acrylate acrylonitril acrylic acid (PnBA) (molecular weight M_n 10000 and M_w 30000) was synthesized in-house.⁸

Catalysts

Catalysts used were tetrabutyl ammonium iodide mp 145–147°C (BDH limited, London) (for EPN resin), and 2,4,6 tris (dimethylaminomethyl) phenol (DMP 30, bp 130–135°C, Merck-Darmstadt) for TGPAP and TGDDM. Figure 2 represents the structure of the elastomer and catalyst.

Hardeners

Hardeners used were diaminodiphenyl methane (DDM) 97% from Merck-Schuchardt for EPN resin, and diaminodiphenyl sulfone (DDS) 98% from Merck-Schuchardt for TGPAP and TGDDM resins. The structures of the hardeners are given in Figure 3.

Table I Effect of Elastomer on Cure Characteristics of EPN/DDM at 100°C as Obtained by RDS Analysis

Sl. No.	% Elastomer	T_{gel} (min)	T_{vitri} (min)	n_{max} (p)
01	0.0	13.9	29.3	7.8e + 07
02	5.0	11.3	26.7	9.6e + 07
03	10.0	12.2	27.6	3.6e + 08
04	15.0	9.8	25.4	3.9e + 08
05	20.0	9.0	20.1	8.8e + 08

Table II Effect of 10% PnBA on EPN/DDM Curing at Different Isothermal Conditions as Obtained by RDS Analysis

Sl. No.	Temperature (°C)	T_{gel} (min)		T_{vitri} (min)	
		Control	10% PnBA	Control	10% PnBA
01	80	—	—	58	56
02	100	13.9	12.2	29.3	27.6
03	120	6.6	6.4	14.9	13.1
04	130	5.5	5	12	6.7

Preparation of Samples

The resins were blended with 5, 10, and 15% by weights of the elastomer at $\sim 50^\circ\text{C}$. In another batch 1% by weight of the respective catalysts were added to the resin elastomer mixture and blended. The resin, elastomer, and catalyst mixtures were reacted at $100^\circ\text{C}/10$ min. Stoichiometric quantities of the respective hardeners were added to these prereacted resins. The cure reactions of the prereacted epoxy/hardener blends were monitored by IR, DSC, and DMA techniques.

Infrared Spectra Analysis

A Bruker IFS 48 Fourier transform spectrometer was used to record the spectra. A resolution of four was used and the spectra were averaged over 32 scans. The prereacted resins and stoichiometric amounts of hardeners were mixed and the mixtures were coated as a thin film on the KBr pellet and heated in the heat cell, and IR spectra were recorded at different intervals of time under isothermal conditions of 120°C for EPN and 135°C for TGPAP and TGDDM resin systems. The changes in intensities of epoxy groups were monitored with time.

Dynamic Mechanical Spectroscopic Analysis

An RDS 7700 spectrometer was used for DMS analysis. The DMS analysis was done using the

parallel plate method. The gel times, vitrification times, and viscosity changes were monitored.

DSC Analysis

A TA instruments DSC model 1 was used for DSC analysis. The prereacted resin–hardener mixtures were used in the DSC cell and the dynamic thermograms were recorded. Various temperatures such as T_i (initial kickoff temperature), T_p (peak exothermal temperature), and T_f (final temperature) were recorded. Activation energies E were obtained using a Borchardt–Daniel kinetics software package. Neat resin castings and carbon cloth-reinforced ($V_f 50 \pm 8\%$) laminates were prepared and cured with a cured cycle as given below:

Cure Cycle for Different Resins

Resin System	Hour (°C)
EDN/DDM	2(120) + 2(175) + 1(200)
TGPAP/DDS	1(135) + 2(150) + 2(175) + 1(200)
TGDDM/DDS	2(135) + 2(150) + 4(175) + 1(220)

The fracture toughness of the neat resin castings was determined as per the ASTM E-399 method.

Table III Effect of 10% PnBA on Cure Characteristics in TGDDM/DDS at Different Temperatures as Obtained by RDS Analysis

Sl. No.	Temperature (°C)	T_{gel} (min)		T_{vitri} (min)	
		Control	10% PnBA	Control	10% PnBA
01	155	18.4	16.1	26.6	23.4
02	177	7.9	7.8	13.7	12.0
03	210	2.9	2.3	11.0	8.4
04	230	1.4	1.1	11.3	6.2

Table IV Cure Characteristics of EPN/DDM with Different Percentages of PnBA by Dynamic DSC Analysis

Sample	T_i (°C)	T_p (°C)	T_f (°C)	E_a (kJ/mol)
Control	66.4	132	231	68.3
5% PnBA	68.5	144	241	70.1
5% PnBA + C	65.3	133	207	70.1
10% PnBA	64.1	125	228	74.1
10% PnBA + C	63.8	129	215	72.2
15% PnBA	69.5	126	220	71.8
15% PnBA + C	64.8	140	220	70.5

C, prereaction catalyst TBAl.

The flexural module of the carbon cloth-reinforced laminates was determined using the ASTM D-790 test method.

RESULTS AND DISCUSSION

The results obtained in the above experiments are presented below.

Results Obtained from IR Spectral Analysis

The intensities of the epoxy groups at $\sim 914 \text{ cm}^{-1}$ in EPN and 905 cm^{-1} in TGPAP and TGDDM were monitored as a function of time. The changes in absorbance ratio between these groups and alkyl groups $\sim 2923 \text{ cm}^{-1}$ were followed with time. From the IR results obtained it was seen that addition of liquid elastomer did not affect the ep-

Table V Cure Characteristics of TGPAP/DDS with Different Percentages of Elastomer by Dynamic DSC Analysis

Sample	T_i (°C)	T_p (°C)	T_f (°C)	E_a (kJ/mol)
Control	135	204	223	112
5% PnBA	136	197	217	117
5% PnBA + C	142	214	238	108
10% PnBA	138	197	217	120
10% PnBA + C	137	195	213	111
15% PnBA	151	212	236	123
15% PnBA + C	136	214	235	112

oxy conversion during cure to a large extent. It was observed that the initial conversions were slightly reduced with the elastomer, probably because of the viscosity constraints. In the presence of the prereaction catalyst the epoxy conversions were slightly enhanced. This may be because of the presence of the catalyst which not only enhanced the resin elastomer reaction but also enhanced the curing of the resin. Figures 4–6 represent an epoxy conversion versus time plots in the presence of different percentages of elastomers in EPN, TGPAP, and TGDDM resin systems, respectively.

Results Obtained from DM Analysis

From the RDS spectra of viscosity versus time plots it was seen that the viscosity of the resins during cure reaction increases with PnBA percentage (Fig. 7). EPN resin was studied extensively to monitor the effect of elastomer on the cure reaction. The gel time and the vitrification times were also studied. It was found that with addition of elastomer gel times and vitrification times decreased significantly. Table I presents the changes in gelation and vitrification times with addition of different percentages of elastomer at 100°C isothermal mode. It was observed that these changes were more prominent at higher temperatures (Table II). In TGDDM/DDS the same trend was observed. Table III presents the changes in gelation and vitrification times with 10% elastomer at different temperature in this system. From Tables II and III it can be seen that the changes in time for vitrification (diffusion control reaction) are more prominent with elastomer modification com-

Table VI Cure Characteristics of TGDDM/DDS with Different Percentages of PnBA Elastomer by Dynamic DSC Analysis

Sample	T_i (°C)	T_p (°C)	T_f (°C)	E_a (kJ/mol)
Control	169	258	271	147
5% PnBA	173	257	273	149
5% PnBA + C	142	255	272	105
10% PnBA	176	260	272	150
10% PnBA + C	142	255	272	96
15% PnBA	178	259	272	150
15% PnBA + C	143	270	285	78

C, prereaction catalyst DMP30.

Table VII Fracture Toughness (Mpm^{1/2}) of Neat Resin Castings of Different Resin Systems

% Elastomer	EPN/DDM	TGPAP/DDS	TGDDM/DDS
0	2.1	1.78	0.60
5	2.9	1.93	0.40
10	3.0	2.30	0.69
15	2.4	2.00	0.78
5 + C	3.3	1.20	0.53
10 + C	3.5	2.20	0.88
15 + C	3.1	1.80	0.71

pared to changes in gelation times (chemical control reaction). This may be because of the high viscosity buildup due to curing coupled with the phase separation or precipitation of the second elastomeric phase.

Results Obtained from DSC Analysis

The dynamic DSC exotherms were studied extensively for all three systems with 0, 5%, 10%, and 15% PnBA with the prereaction catalysts. From the thermograms it was seen that there were no major changes in cure kinetic parameters. However, it was observed that T_i slightly decreased. The activation energy as calculated using Borchardt–Daniel kinetics also increased with the addition of elastomer but decreased in the presence of the prereaction catalyst. This trend is very clearly observed in the TGDDM/DDS system. The effect of the prereaction catalyst on the epoxy/amine reaction is very predominantly seen in this system. Tables IV–VI present the data obtained in EPN/DDM, TGPAP/DDS, and TGDDM/DDS, respectively, for first-order reaction.

Results Obtained from Physical Property Evaluation

Tables VII and VIII present the results obtained from preliminary physical characterization of the three resin systems. The fracture toughness increased and in general a maximum improvement was observed at 10% elastomer both in catalyzed and uncatalyzed systems. The flexural modulus of CFRP laminate decreased with elastomer addition as the strain increased due to the flexibility of the matrix by the elastomer.

CONCLUSIONS

The effect of prereaction of epoxy groups (in the resin) and the carboxy (in elastomer) on epoxy/amine hardener curing reaction was studied. It was observed that the cure reaction was affected to a very small extent due to prereaction of epoxy/elastomer. IR spectral results have shown that the epoxy group conversions were lowered slightly with the addition of elastomer, but increased conversions were observed in the presence of prereac-

Table VIII Flexural Modulus of Carbon Reinforced Laminates

% Elastomer	EPN/DDM (kg/m ² × 10 ⁴)	TGPAP/DDS (kg/m ² × 10 ⁴)	TGDDM/DDS (kg/m ² × 10 ⁴)
0	7.4	7.7	6.3
5	7.5	6.2	4.6
10	7.1	7.3	5.8
15	7.0	4.8	4.9
5 + C	6.6	6.9	5.0
10 + C	6.4	6.5	5.2
15 + C	7.0	6.0	5.0

tion catalysts. The DSC also has shown similar results. The initial kickoff temperature and the activation energies were lowered slightly in the presence of prereaction catalysts. The trend is very predominant in the TGDDM/DDS system. This may be due to the prereaction catalysts which not only enhanced the epoxy elastomer reaction but also catalyzed the epoxy amine reactions. However, dynamic mechanical analysis showed that the presence of elastomer reduced the time for gelation and vitrification. The reductions were higher at higher temperatures. More extensive RDS analysis is under progress. Fracture toughness of the neat resin castings increased and modulus decreased with elastomer addition. A detailed mechanical characterization of the other systems and SEM studies will be presented in future publications.

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