Evaluation of processing temperature in the production of fibre reinforced epoxy composites

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Abstract A group of cyanoethylated amine (CEA) has been synthesized by carefully reacting triethylenetetramine with varying proportions of acrylonitrile. Such CEAs were utilized as hardener for the curing of epoxy resin. The effect of cyanoethylation of amine on their curing reaction with epoxy resin has been studied by differential scanning calorimeter (DSC). The processing temperature for the fabrication of composite is estimated from the DSC analysis with an approach to satisfy the logical selection of temperature for application of pressure during processing of a composite structure. The exotherm of such curing reaction (ΔH_{ex}) and the degree of cyanoethylation (CEt) of the amine follow the relation $\Delta H_{ex} = (324–68.40 \text{ CEt}) \text{ J g}^{-1}$.

Keywords FRP · Epoxy · Heat of reaction · Temperature

Introduction

Epoxy resin, one of the most coveted resins used in the manufacture of composite materials, undergoes curing reaction exothermically [1–14]. The very exothermic nature of epoxy curing system makes it difficult to handle bulk quantities of resin mix for fabrication of thick and large composite laminates because such composite systems consisting of resins are basically poor conductor of heat [3, 4, 6], causing accumulation of large amount of liberated

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heat which leads to the development of hot spots, non-uniformity in distribution of internal stresses and degradation of properties [1, 3, 9, 10, 13–15]. For example, composites based on ultrahigh molecular weight polyethylene (UHMWPE) fabric [3, 16] may loose their dimensional stability under the processing condition of temperature and pressure if the evolution of such heat exotherm is excessively high. Therefore, from the practical viewpoint, the quantity of epoxy resin in bulk to be handled during curing is determined by the degree of exotherm (ΔH_{ex}). Therefore, prior knowledge of the magnitude of exothermic heat is an essential requirement before taking up the job of actual processing of polymer composites.

The matrix resin may be characterized according to the curing temperature in a DSC thermogram. Selection of such temperature depends upon the desired speed of operation and resin content to be maintained in the composite laminate [4, 17–19]. But during the fabrication of composite by compression moulding there is some confusion about the selection of processing temperature (i.e., the temperature at which pressure to be applied) because of the fact that there are three prominent temperatures [18, 19] in the DSC curing thermogram such as onset curing temperature (T_o), peak temperature (T_p) and final curing temperature (T_f) [18, 19]. So at what temperature the pressure needs to be applied during processing requires some justification based on DSC analysis. Therefore, such temperature is a process control parameter and it provides the proper temperature data for application of full pressure on the resin-impregnated substrate or laminates in a compression or matched die mould [1].

In this communication the logical approach for the selection of processing temperature and evaluation of curing exotherm of a family of epoxy system based on the diglycidyl ether of bisphenol-A (DGEBA) resin and

different cyanoethylated aliphatic amines synthesized are reported.

Experimental

Epoxy resin, DGEBA (Hindustan Ciba-Geigy) was used to prepare matrix resin composition. The epoxy equivalent as determined by the pyridinium chloride method [9] was 189 g/equivalent. Triethylenetetramine (TETA) (B.D.H.) was purified by keeping it in KOH beads overnight followed by distillation under vacuum before use. Acrylonitrile (AN) was distilled under reduced pressure and the fresh stock of distillate was used to carry out the reaction with TETA. Three homologous derivatives of TETA, such as mono-, di- and tricyanoethylated TETAs were synthesized by Michael reaction [20] by reacting, respectively, 1, 2 and 3 mol of acrylonitrile (AN) with TETA at 40 °C in the nitrogen atmosphere as per Fig. 1.

Typically, TETA (225 ml) was taken in a 500 ml three necked flask fitted with nitrogen inlet. For the preparation of monocyanoethylated-TETA, AN (101.5 ml) was added gradually to the well-stirred stock of the reactant such that the temperature of the overall mixture was allowed to mature until the viscosity of the system became stationary. Subsequently, the volatiles were removed by applying

vacuum at 50 °C and the viscous stock of monocyanoethylated-TETA was collected. Similarly, the di- and tricyanoethylated-TETA were prepared using desired quantities of AN proportionately. TETA and their cyanoethyl derivatives were used for curing DGEBA epoxy resin. A typical crosslinking reaction is shown in Fig. 2.

The products were characterized by FTIR and NMR spectral analytical information. FTIR spectra of each of the cyanoethylated amines showed sharp absorption near 2,261 cm^{-1} due to CN group [20]. The ^{1}H NMR spectra of TETA and the cyanoethylated amines showed the presence of required number of methylene hydrogen atoms. And correspondingly, the spectra showed 6, 5, 4, and 3 hydrogen atoms attached to nitrogen atoms in amines. TETA : ^{1}H NMR δ (CDCl$_3$) 2.71–2.85 (12H, m, 6× CH$_2$), 1.34 (6H, s, NH and NH$_2$, exchangeable with D$_2$O): monocyanoethylated-TETA : δ (CDCl$_3$) 2.3–2.8 (16H, m 8× CH$_2$), 1.34 (6H, s, NH and NH$_2$, exchangeable with D$_2$O); dicyanoethylated-TETA : δ (CDCl$_3$) 2.53–2.94 (20H, m, 10× CH$_2$) 1.7 (5H, s, NH and NH$_2$, exchangeable with D$_2$O); tricyanoethylated-TETA : δ (CDCl$_3$) 2.2–2.86 (24H, m, 12× CH$_2$), 1.76 (3H, s, NH and NH$_2$, exchangeable with D$_2$O).

A Du Pont DSC instrument with 910 module was used for thermal analysis. A nitrogen stream of 40 ml min^{-1} was maintained through the cell during the measurement. The scan was performed at a rate of 10 K min^{-1}.

Results and discussion

A family of hardeners was synthesized by cyanoethylation of triethylene tetramine (TETA). Curing of DGEBA epoxy resin was carried out at a particular heating rate in the presence of stoichiometric proportion of hardeners endowed with progressively increasing proportions of cyanoethyl group in the constituent amine hardener. The characteristic curing temperatures [17–19], such as T_o, T_p, as well as T_f and the exotherm developed (ΔH_{ex}) during the curing of the selected resin compositions in the DSC experiment are shown in Table 1. A typical set of DSC record is shown in Fig. 3.

The thermogram of the resin systems showed that the exotherm profile is broadened with the incorporation of

H$_2$N CH$_2$CH$_2$ HN CH$_2$CH$_2$ NH CH$_2$CH$_2$ NH$_2$ + nCH$_2$ = CHCN

    (TETA)   (AN), n = 1, equation (a)

               n = 2, equation (b)

               n = 3, equation (c)

(a) For n = 1, the product is monocyanoethylated triethylenetetramine (MCTETA)

H$_2$N CH$_2$CH$_2$ HN CH$_2$CH$_2$ NH CH$_2$CH$_2$ NH CH$_2$CH$_2$CN,

(b) For n = 2, the product is dicyanoethylated triethylenetetramine (DCTETA)

NCCH$_2$CH$_2$HNCH$_2$CH$_2$HNCH$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CH$_2$CN,

(c) For n = 3, the product is tricyanoethylated triethylenetetramine (TCTETA)

NCCH$_2$CH$_2$HNCH$_2$CH$_2$HNCH$_2$CH$_2$NHCH$_2$CH$_2$N(CH$_2$CH$_2$CN)$_2$

Fig. 1 Reaction between TETA and different proportions of AN

Fig. 2 A typical reaction between amine (e.g. TETA) and DGEBA resin through opening up of the oxirane group

Table 1 Results of heat exotherm and the characteristic temperatures of different curing systems

System	Matrix constituents[a]	$\Delta H_{ex}/J\ g^{-1}$	$T_o/°C$	$T_p/°C$	$T_f/°C$
I	DGEBA + TETA	316	66	99.2	133
II	DGEBA + monocyanoethylated-TETA	268	70.5	104.5	144
III	DGEBA + dicyanoethylated-TETA	190	71.7	118.0	189.5
IV	DGEBA + tricyanoethylated-TETA	114	87.3	143.3	195

ΔH_{ex} Heat evolved in the exothermic reaction of DGEBA and the hardener, T_o onset temperature of curing reaction, T_p peak temperature appeared during curing reaction, T_f final temperature of curing reaction

[a] Matrix is prepared by curing the mixture of DGEBA epoxy resin (DGEBA) and stoichiometric proportion of a given hardener based on triethylene tetramine (TETA) and different molar proportions of acrlylonitrile (AN)
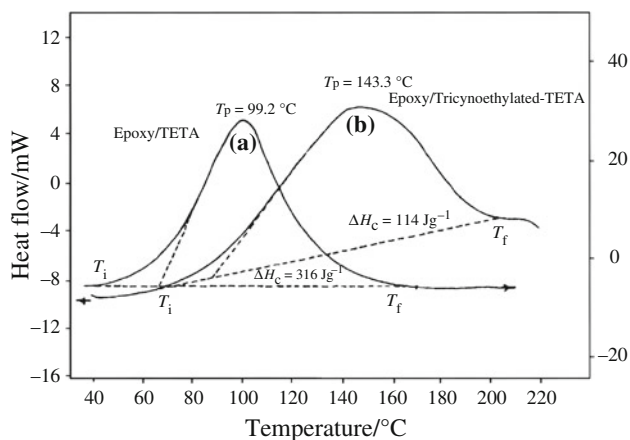
Fig. 3 Calorimetric evaluation of temperature and evolution of heat during curing of epoxy resin at a heating rate of 10 K min^{-1} with (a) TETA and (b) tricyanoethylated-TETA

cyanoethyl moiety into the constituent hardener used for curing. The position and the pattern of the exothermal peak give valuable information on the systems reactivity [17–19]. Functionality (f) is the average number of reactive centres [21] which has great influence on the curing pattern. The DSC scan indicates that the reactivity for the curing is slowed down with decreasing functionality (f) of the constituent hardener amine. It was found that the temperature for curing was increased while the exotherm was decreased with decreasing functionality of the constituent amine in the curing system. Moreover, interestingly, the DSC thermograms in question are appreciably symmetrical which implies that the distribution of networks in the matrices should be more or less uniform in all the systems. More importantly, a linear relationship between the exotherm (ΔH_{ex}) and the degree of cyanoethylation (CEt) of the amine is apparent in accordance with the Eq. (1)

$$\Delta H_{ex} = (324 - 68.40\ CEt)\ J\ g^{-1} \qquad (1)$$

as derived by regression analysis. The coefficient of correlation (R) for the relationship was found to be 0.9948. The calculated value of t for testing the significance of

correlation coefficient is 9.92 which is, therefore, highly significant [22].

This order of enthalpy relates to the progressive deactivation effect of the cyano group in the amine. The presence of electron withdrawing CN group in the amine reduces the electron donating ability towards opening the oxirane group ($H_2C\underset{}{\overset{O}{\diagup\!\diagdown}}\overset{}{\underset{H}{C}}$) of DGEBA epoxy resin; thus it makes the system less active towards crosslinking reaction in presence of amine hardener [20].

The ΔH_{ex} value indicates that the evolution of heat decreases with the use of hardener having increasing level of cyanoethylated group. It is clear from the ΔH_{ex} analytical data that among all compositions, System I is more prone towards scorching [23] than the rest of the systems. Thus, it would be easier and convenient to use System IV rather than other systems (Table 1) when bulk quantities of resin are to be handled, say in a production unit, for the fabrication of very large laminates or big composite [1, 4, 6] structures. Curing of epoxy resin with the tricyanoethylated amine showed the highest temperature (in respect of T_o, T_p, or T_f of Table 1) for curing. Based on the assumption that the heat developed is proportional to the formation of network [17–19], then the analysis of DSC data imply that the crosslink density of the matrix decreases with the lowering of functionality of the amine used for the curing of epoxy resin.

In the field of plastics technology, prepreg [1, 3, 9, 16] is generally defined as a resin-impregnated substrate—usually woven fabrics—prepared mainly for storage with desired shelf-life before fabrication of laminates or fibre reinforced plastics composite items under applied pressure. Processing technology through prepregging provides several advantages to the composites [1, 2, 10, 12]. As a matter of fact, chemical technology of prepreg demands a long shelf-life. And that is rather possible with a resin system which cures slowly. The enthalpy data, curing temperatures and the pattern of DSC record implies that the reaction rate of System IV is the slowest. Therefore, among all the systems (Table 1), System IV may be considered more

suitable resin for prepregging purpose because this composition is the most sluggish towards crosslinking.

It is well known that with the progress of crosslinking the viscosity of the resin increases [1, 16–18, 21] which is likely to allow better retention and consolidation of resin within the composite system during processing. In the early stage of the region between T_o and T_p (close towards T_o) the chance of bonding the 'fabric interlayers' is likely to be less because of the lack of enough development of viscosity or tack. Therefore, the application of pressure at an early stage may lead to immediate removal of resin from the system before the inter-layers could get sufficient chance to be bonded properly. On the other hand, in the region between T_p, and T_f, especially at the later stage near T_f the system looses its fluidity substantially which prevents it from penetrating into the 'intertices' of the fabrics of the laminate because of the excessive increase in viscosity of the curing medium. Obviously, during fabrication of laminates, say, from the prepregs in a moulding process, the pressure should be applied just beyond but near the peak temperature (T_p) of curing. Therefore, with the resin System IV during processing, the limiting temperature before application of pressure on the intended prepreg should preferably be around 143.3 °C plus (Table 1).

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