Cure Kinetics Studies of Cyanate Ester and Bisphenol-F Epoxy Blend

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ABSTRACT: Cyanate ester and Bisphenol-F blends with manganese acetylacetonate in nonylphenol as catalyst and cocatalysts respectively is an attractive candidate as the insulation impregnation materials for fusion grade magnets winding packs that is required to be operating in moderate irradiated environments in fusion devices like Tokamaks. The curing kinetics of this blend system as a thermosetting polymer has been investigated in this paper in detail for 60 : 40 (epoxy:ester) composition strongly driven from application interests. The order of reactions in both chemical kinetics controlled region as well as diffusion controlled regimes have been experimentally found out using Differential Scanning Calorimetric (DSC) studies. Corresponding rate constants and associated cure kinetics have been consequently determined. The second order kinetic model, as it is found, does not fit in to the epoxy-cyanate ester reaction mechanism. The results, therefore,

INTRODUCTION

In recent times, cyanate ester-epoxy blends together with kapton have become an attractive candidate as an insulation system for fusion grade magnet winding packs such as International Thermonuclear Experimental Reactor (ITER) and DEMO reactors.^{1,2} Fusion relevant magnets winding packs are envisaged to experience fast neutron fluence up to $1 \times 10^{22} \text{ m}^{-2}$ (*E* > 0.1 MeV) in ITER and even more in case of DEMO reactor. Conventional glass-fiber/kapton insulations impregnated with diglycidyl ether bisphenol F (DGEBF) epoxy resins shows tremendous disintegration and degradation of its electro-mechanical and thermomechanical characterization. Cyanate ester (CE) as an alternate insulation resin candidate on the contrary does not show any measurable degradation.^{2,3} However, this material is quite expensive and delicate in its application due to possible high exothermic reactions. Also the bonding to the kapton surhave been discussed in the context of widely used autocatalytic models and variable "*n*" kinetics models appropriate for chemical controlled region. The reaction conversion rate $d\alpha/dt$ of the cyanate ester-epoxy blend is more rapid in chemical controlled regime compared to that in the diffusion controlled regime. The order of reaction is not constant throughout the reaction and is higher in chemical controlled regime. The variable "*n*" kinetic model has been employed to determine the hypothetical temperature (350.81 K) below which no more curing reaction would occur. The activation energy and the pre-exponential factors have been determined in the chemical controlled regime using Arrhenius reaction. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1068–1076, 2012

Key words: kinetics (polym); polymer blends; resins; fibers

face is not that good when the adhesiveness is compared with either CE system or a blend of DGEBF and CE blend. Investigations have established that the blend of CE with DGEBF resins in the range of 60 : 40 do not manifest any measurable irradiation induced degradation in thermomechanical and electrical characterization.⁴ Further such blends show excellent bonding with the kapton surfaces. There blends are suitable for the impregnation of large volumes (typical of fusion magnets winding packs) over long distances as their viscosity is typically below 100 mPa s. These blends do have a pot life of several hours for the impregnation to be feasible too.

In one of the study, the insulation samples following 60 : 40 (DGEBF:CE) ratio in manganese Acetyl Acetonate in Nonylphenol as catalyst and cocatalysts respectively, have been made and the products being systematically characterized as per the applicable ASME and DIN standards with and without neutron irradiations, however, a systematic study on the order of the reaction in the chemical kinetics of this blend has not been carried that extensively. The primary objective of this article is focused on the studies related to the order of reactions in the chemical kinetics of this blend in 60 : 40 proportions as a

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thermosetting polymer starting from the chemical controlled regime till the end of the diffusion controlled regime.^{5,6} Kinetic aspects of the cure reactions can be explained through the complex changes in morphology and structure of the polymer during its processing operations which helps at comprehending and curing the processes towards achieving the tailor made optimum properties.

The curing reactions between cyanate ester and epoxy resin proceeds with cyanurate formation through trimerization of cyanate ester followed by insertion of glycidyl ether epoxide into aryl cyanurate. Next the realignment of aryl cyanurate into alkyl isocyanurate occurs followed by oxazoline formation through epoxy resin and cyanate ester as shown in Figure 2. All these intermediate reactions take place in chemical kinetics domain as well as in diffusion kinetics domain as per autocatalytic models and nth order model⁷ as shown below.

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

Where " α " is the curing conversion, "n" is the order of reaction and is constant with respect to temperature of reaction and conversion, " $\frac{d\alpha}{dt}$ " is the reaction rate and "k" being the apparent rate constant. The reaction rate constant "k" is governed by Arrhanius relationship

$$k(T) = Ae^{-E/RT}$$
(2)

"*E*" being the activation energy, "*R*" as the universal gas constant (8.314 J/K), "*T*" is the absolute temperature and "*A*" being the frequency factor.

The epoxy-ester thermosetting reactions may be conveniently described by a two-step plateau kinetic model where the steps correspond to chemical controlled regime and diffusion controlled regimes respectively.⁸ These two steps are indicated as two *n*th order reactions as,

$$\frac{d\alpha}{dt} = k_1 (1 - \alpha)^{n_1} \quad (\alpha < \alpha_{\text{onset}})$$
(3)

$$\frac{d\alpha}{dt} = k_2 (\alpha_{max} - \alpha)^{n_2} \quad (\alpha \ge \alpha_{onset})$$
(4)

Where " k_1 " and " k_2 " are the rate constant in chemically controlled regime and diffusion controlled regimes respectively, " n_1 " and " n_2 " are the order of the reaction in the above regimes. " α_{max} " is the saturated plateau conversion and " α_{onset} " is the transition of " α " between chemical kinetic regime to that of the diffusion controlled regime. In these reaction order models appropriate definition to physical parameters of " k_2 " and " n_2 " in diffusion controlled region is a must. Alternatively, these thermosetting reaction can also be narrated from *ab initio* by considering the overall rate constant of the reaction to be comprising of two rate constants i.e., one rate constant referring to that of chemical kinetics domain and other rate constant referring to that of diffusion kinetic domain^{5,6} as follows.

$$\frac{1}{k_{overall}} = \frac{1}{k_{chem}} + \frac{1}{k_{Diff}}$$
(5)

" k_{chem} " is chemical controlled regime rate constant obeying Arrhenius equation (prior to vitrification) and k_{Diff} is the diffusion regime rate constant as a function of curing temperature and conversion (α).

In this article, an experimental investigation has been carried out for the 60 : 40 (epoxy:ester) blend system focused at determining the order of reaction in the cyclotrimerization towards the polycyanurate network in the run up to the final thermosetting. Order of reaction have been attempted to be determined from both autocatalytic model as well as by "n" kinetic models.

EXPERIMENTAL

Material

Araldite PY 306 is a bisphenol F diglycidyl ether with exceptionally low viscosity. Bisphenol F Epoxy monomer-a mixture of para/para, ortho/para and ortho/ ortho strereoisomers. Arocy L-10 is a low viscosity liquid dicyanate monomer which derives its liquid physical state from an asymmetric linkage in the bisphenol unit. The low viscosity feature facilitates rapid online and in-mold impregnation of fibrous reinforcements in less labor-intensive processes for manufacturing structural composites. Blends of Arocy L-10 monomer and epoxy resins containing 35% or more cyanate ester will cure by a combination of epoxy insertion into the polycyanurate network and by 5-membered, oxazolidinone ring formation. Arocy L-10 and Araldite PY-306 used as an insulation system for fusion grade magnet winding packs were supplied by Huntsman. The curing agents, copper acetyl actonate, cobalt acetylacetonate, aluminum acetylacetonate, manganese acetylacetonate, and zinc acetylacetonate can be used as catalyst. Shimp and Craig presented a preferred ranking of metal ions for incorporation in cyanate/catalyst formulations to minimize moisture plasticization and thermo-oxidative degradation in the cured polycyanurate.⁹ Preferred curing catalyst is solution of manganese acetylacetonate chelates in 2 to 6 phr nonylphenol. Metal concentration ranging from 20 to 300 ppm based on resin content are typical, depending on pot life and curing requirements, metal activity and companion resins. Tables I and II show the typical chemical properties of

TABLE ITypical Properties of Araldite PY-306

Visual appearance	Clear, no contamination
Colour, Gardner, max	1
Epoxy Value, eq./kg	5.9-6.2
Epoxy Equivalent, g/eq.	159-170
Viscosity @ 25°C (77°F), mPas (cPs)	1200-1800
Density @ 25° C (77° F), g/cm ³ (lb/gal)	1.18(9.8)
Flash Point, Closed Cup, °C (°F)	>93 (>200)

Araldite PY-306 and Arocy L-10, respectively. Chemical structures of Arocy L-10, Araldite PY-306, manganese acetylacetonate and nonylphenol are shown in Figure 1.

Conversion and T_g measurement of partially cured blends

Differential scanning calorimetry (DSC) was performed at 150, 160, and 170°C using a TA instruments Model 2920 calorimeter. Before measurement, the temperature, baseline, and heat flow calibrations were carried out by the recommended procedures using pure indium with a melting point 156.4°C and heat of fusion, $\Delta H_f = 6.80$ cal/g.

Blend system comprised of epoxy resin and cyanate ester (60 : 40) was prepared. Initially, Mn-acetylacetonate was dissolved in nonylphenol at a molar ratio of 25 : 1 (nonylphenol:Mn-acetylacetonate) at 80°C for 1 h. Mn-cetylacetonate/catalyst blend was then mixed with the blend system at 60°C for 30 min. In each case the molar ratio of cyanate/epoxy blend : Mn-acetylacetonate was 1000 : 1. To measure the heat of reaction, sample around 7 mg was hermetically sealed in an aluminum pan. The sample was then cured in the DSC cell at an isothermal temperature (150, 160, and 170°C) for different periods of time. The cured sample

TABLE II Typical Properties of Arocy L-10

Visual appearance	Amber liquid
Brookfield Viscosity @ 25°C (cPs)	100
Density @ 25° C, g/cm ³ (lb/gal)	1.18 (9.83)
Refrective Index 25°C (107°C),	1.565 (1.534)
Reactivity at 110°C, % trimerization/hour	0.3
Nonvolatiles, weight %	99.5

was quenched in ice-water and scanned again from room temperature to 300°C at 5°C/min. The DSC scans yielded the T_g and residual heat of reaction, $\Delta H_{\rm res}$. The temperature corresponding to the mid point of the endothermic deflection was taken as the T_g . $\Delta H_{\rm res}$ was calculated from the exotherm area, as shown in Figure 3(a). The conversion α of each sample was calculated from the equation below:

$$\alpha = \frac{\Delta H_{total} - \Delta H_{res}}{\Delta H_{total}} \tag{6}$$

Where, ΔH_{total} is the total heat of reaction, which was calculated from the exotherm area of an uncured sample divided by the mass of the sample.

Isothermal DSC measurements

Curing kinetic study was performed using an isothermal method. Isothermal experiments were carried out at 150, 160, and 170°C in this work.

In an isothermal experiment, the sample pan was placed in the DSC cell at 50°C and nitrogen gas was used for purging at a flow rate of 60 cc/min. This is to minimize the unrecorded reaction heat during the initial heating before data collection was initiated. After holding at this isothermal temperature till there is no change in the heat flow, the experiment



Figure 1 Chemical structure of Arocy L-10, Araldite PY-306, Mn-acetylacetonate and Nonylphenol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 2 Reaction scheme for copolymerization of cyanate and epoxy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is stopped. The conversion at time t, $\alpha(t)$ can be determined from eq. (7):

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{total}} \tag{7}$$

where $\Delta H(t)$ is the enthalpy of the reaction at time *t*. For a given isothermal temperature, $\Delta H(t)$ is the accumulative heat of reaction up to curing time t and given by the area above the baseline and below the curve, as shown in Figure 3(c). The base line is a straight tangential line to the horizontal part of the isothermal DSC curing curve. A dynamic DSC scan at 0.5°C/min was taken to select the temperature range as shown in Figure 3(b).

The characteristic adsorption band at 2266 cm⁻¹ is attributed to cyanate decreasing gradually and disappearing eventually. However, the change of epoxide band at 912 cm^{-1} is observed to be very small. It can therefore be concluded that the cyanate ester monomers have reacted first and the epoxy monomers take part in the reaction processes subsequently. The epoxy band decreases simultaneously with the reduction in intensity of the isocyanurate band (1679 cm⁻¹) due to the oxazolidone formation, which is reported by the band as appearing at 1754 cm^{-1} . This feature is demonstrated in Figure 5. The 60 : 40 blend system takes a lot of time for curing below 140°C temperature. FTIR study on this blend system is carried out to preselect the temperature range for DSC isothermal measurements.

RESULTS AND DISCUSSION

Second order autocatalytic model

Experimental curves of conversion (α) against curing time (t) at isothermal curing temperatures from 150

till 170°C at an interval of 10°C for the 60 : 40 (epoxy : cyanate) blend system are shown in Figure 4. The solid line is an arbitrary line that distinguishes the chemical controlled regime and diffusion controlled regime. As expected α from energetic the conversion in the chemical regime increases with temperature



Figure 3 (a) Schematic diagram of the measurement of ΔH_{res} and T_g (b) Nonisothermal DSC curve (0.5°C/min) (c) Isothermal DSC curves for 60 : 40 (Epoxy : Cyanate) blend system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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0.7

0.6

0.5

0.4

0.3

0.2

0.1

0 + 0

5

10

Conversion, a

% Transmittance

3500

3000

starting from 150 to 170°C. The overall conversion is also increased.

15

Figure 4 Experimental data of conversion versus curing

time for epoxy: cyanate blend system. The solid line is an

arbitrary division of chemical controlled and diffusioncontrolled regions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

20

Time(min)

The rate of conversion and the reaction proceeds is then found out by differentiating the conversion (α)—time (t) curve as shown in Figure 6 at various isothermal curing temperatures in the range of 150– 170°C. In the early stages of cyclotrimerization polymerization, the rate of conversion is best describes for identical blend system as,

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha)(1 - \alpha)^2 \tag{8}$$

-150 -160

Diffusion

Chemical control

25

30

35

170

Where, " α " denotes the conversion of cyanate

Figure 5 FTIR spectra of the catalyzed 60: 40 blend system cured at 160° C. (a) 60: 40 (mix, t = 0 min) (b) 60: 40 1 (pregelation, t = 10 min) (c) 60: 40 2 (gel, t = 20 min) (d) 60: 40 cured (t = 30 min) (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2000

Wave number(cm ⁻¹)

1500

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2500



0.25

0.2

da/dt/(1-a)²

60/40 min

500

1000

0.1



Figure 6 Reaction rate $\left(\frac{d\alpha}{dt}\right)$ versus curing time at different isothermal temperatures for 60 : 40 (Epoxy:Cyanate) Blend system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups and " k_1 " and " k_2 " are empirical rate con-

stants. Reaction time and conversion characterization

in the 150-170°C temperature range have been plot-

BRAHMBHATT ET AL.



Figure 7 $\frac{d\alpha/dt}{(1-\alpha)^2}$ versus conversion α at different isothermal temperatures for 60 : 40 (Epoxy:Cyanate) Blend system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 8 Plot of α_{max} versus 1/T (K^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Variable "n" kinetics

As evident in the earlier section, the reaction conversion rate $d\alpha/dt$ of the cyanate ester-epoxy blend in rapid to begin with and gets slowed down with the gradual transition from the chemical controlled domain to diffusion controlled domain. At the end, the conversion attains a plateau, typically known as maximum conversion (α_{max}). This plateau conversion is empirically expressed as,¹⁰

$$\alpha_{max} = p_1 \left(\frac{1}{T_1} - \frac{1}{T} \right) \tag{9}$$

When " p_1 " is the fitting parameter, "*T*" is the curing temperature and " T_1 " is the theoretical critical temperature below which no more curing reaction would occur ($\alpha_{max} = 0$).

Similarly, the relationship between the onset of conversion and curing temperature is established. (Where, α_{onset} deviates the transition from chemical domain till diffusion domain).



Figure 9 Plot of α_{onset} versus 1/T (K^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 10 Maximum conversion and onset conversion versus curing temperature for 60 : 40 Blend system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Where " p_2 " is a fitting parameter, *T* is the curing temperature and T_2 is the hypothetical critical temperature below which no chemical reaction could occur as $T = T_2$ ($\alpha_{onset} = 0$). In both eqs. (9) and (10), the upper limit of α_{max} and α_{onset} is unity. Figures 8 and 9 show the plots of maximum conversion versus curing temperature and onset conversion versus curing temperature, respectively.

$$p_1 = 1050 \text{ K}, p_2 = 1251 \text{ K}, T_1$$

= 350.81 K (77.81 °C), $T_2 = 371.43 \text{ K} (98.43 °C)$

 α_{max} in practice refers to the saturated state of conversion at a particular temperature *T*. This varies from temperature to temperature. On the other hand shows the transition form the chemical kinetics domain to that of the diffusion kinetics domain in the



Figure 11 Plots of $\ln \frac{d\alpha}{dt}$ versus $\ln (1-\alpha)$ at different isothermal temperatures for 60 : 40 (Epoxy : Cyanate) Blend system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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-0.8

y = 3.274x - 0.606

-5

Figure 12 Plots of $\ln \frac{d\alpha}{dt}$ versus $\ln (1-\alpha)$ for chemical controlled region and $\ln \frac{d\alpha}{dt}$ versus $\ln(\alpha_{max}-\alpha)$ for Diffusion controlled region at 170°C isothermal temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In(amax-a)

Chemical controlled region

-0.4

-0.2

-0.5

-1

-1.5

-2.5

-3

-3.5

-0.5 -1 -1.5

-2

2.5 dt

-3

-4

-3.5

In(da

-2 -2

In(da

-0.6

In(1-a)

Diffusional controlled region

-3

y = 0.412x - 2.157

-2

experimental data as shown in Figure 4 where the conversion " α " as a function of time (*t*) is shown for T = 150, 160, and 170°C along with the variable "*n*" kinetics model. Figure 10 indicates that the reaction mechanism shifts from chemical controlled to diffusion controlled. The shift is marked at an onset con-



Figure 13 Arrhenius plots of the rate constants in chemical controlled and diffusion controlled regions as a function of 1/T (K^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 14 Plot of $\ln(d\alpha/dt)$ as a function of $\ln(1-\alpha)$ at the isothermal temperature of 170°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

version, α_{onset} which increases with increasing temperature.

The plot of $\frac{d\alpha''}{dt}$ versus time as shown in Figure 6 indicate that the reaction rate is maximum at the very beginning itself ($t \rightarrow 0$). The kinetic further bears similarity towards the *n*th order reaction kinetics. Thus the order of reaction can be determined from the slope of the curve plotted between $\ln \frac{d\alpha}{dt}$ and $\ln (1-\alpha)$. This abrupt change in the slope in Figure 11 shows the almost linear relationship between $\ln \frac{d\alpha}{dt}$ and $\ln (1-\alpha)$ at a value $\alpha = 0.54$ at the isothermal curing temperature 170°C investigated in this work. As the conversion increases, the linear relationship no longer remains linear between $\ln \frac{d\alpha}{dt}$ and ln (1- α). This abrupt change in the slope in Figure 11 indicates the transition from the chemical domain to that of the diffusion domain. This transition as described earlier is represented as α_{onset} with increasing temperature, α_{onset} increases as expected. Thus, the reaction kinetics in chemical controlled region can also be adequately described by a variable order as,

$$\frac{d\alpha}{dt} = k \left(1 - \alpha\right)^n \tag{11}$$

which signifies the fact that the variable reaction order "n" becomes a function of conversion; $n = n(\alpha)$. This is attempted and illustrated in a detailed plot of $\ln \frac{d\alpha}{dt}$ versus $\ln (1-\alpha)$ in the chemical controlled regime at $T = 170^{\circ}$ C as shown in Figure 14. This figure shows the experimental data is better explained with a variable "n" rather than a fixed "n". The order varies being lowest at the initial stage of the reaction and increasing with conversion/reaction time increase. It can be clearly seen from Figure 15(a–c) shows that the variable "n" model is notably better in the chemical controlled region and has almost perfect fitting to the experimental data at



Figure 15 Comparison of fixed "n" model and variable "n" model at isothermal temperature 150°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 TABLE III

 Parameters of Isothermal DSC Scan of 60:40 (Epoxy:Cyanate) Blend System

Temperature (K)	n_1	<i>n</i> ₂	$k_1 \; (\min^{-1})$	$k_2 ({\rm min}^{-1})$	$k_{\rm overall} \ ({\rm min}^{-1})$	$\alpha_{end}(\%)$	$\Delta H_{\rm iso}~({\rm J/gm})$	$\Delta H_{\rm res}~({\rm J/gm})$
423	2.73	0.46	0.11	0.071	0.043	51.32	125.6	1.09
433	3.15	0.62	0.16	0.092	0.058	54.15	135.8	4.40
443	3.27	0.41	0.55	0.115	0.095	63.23	153.4	1.51

early stage of the curing reaction. For different isothermal temperatures, the values of α_{max} are also different. It can be seen that the higher the isothermal temperature, the higher the onset conversion. This agrees well with eq. (10) and Figure 9 as discussed earlier.

It is natural to cast the experimental data in the chemical controlled domain by Arrhenius relationship. Figure 13 shows the plot of ln (*k*) versus 1/T and the activation energy "*E*" and the frequency factor of 62.13 KJ/mol and 1.9435×10^{6} min⁻¹ are found out for the ester epoxy blend of 60 : 40. The order of reaction and rate constant have been determined from the plots of $\ln \frac{d\alpha}{dt}$ versus ln (1- α) for chemical controlled region and ln $\frac{d\alpha}{dt}$ versus ln(α_{max} - α) for diffusion controlled region at 170°C isothermal temperature as shown in Figure 12.

CONCLUSIONS

The kinetics study of the blend system [Epoxy (60): Cyanate (40)] indicates that the reaction follows nth order kinetics model in the chemical controlled regime for particular curing temperatures. The conversion in this regime approaches a plateau. The diffusion occurs at a particular "onset conversion". This

TABLE IV Parameters of 60:40 (Epoxy:Cyanate) Blend System

E = 62.1335 (KJ/mol)	$A = 1943498 \; (\min^{-1})$	$P_1 = 1050$ (K)	$P_2 = 1251 \text{ (K)}$			
$T_1 = 350.81$ (K)	$T_2 = 371.43$ (K)	$\Delta H_{\rm non-iso} = 242.6 \; ({\rm KJ/mol})$	$T_g = 493$ (K)			

onset conversion increases with the increase of isothermal curing temperature. Results indicate that the reaction order "n" is not constant throughout the whole reaction time. The same is also true as the conversion increases. The reactivity of the functional group is observed to be increased as a function of the curing temperature. Hence, the conversion, heat of reaction, order of reaction and the overall rate constant of the blend system are strong functions of the curing temperature. Chemical reactions for the above blend system are not feasible below a critical temperature, which is around 371 K (\sim 98°C). It would be advisable not to carry out the vacuum pressure impregnation processes below the critical temperature, so that the blends involving 60 (epoxy):40(ester) curing would not occur in the fusion relevant magnets winding pack and the resin mixture could penetrate into the winding pack voids. Subsequent curing of the winding pack can then be carried out at elevated temperatures in the curing oven to attain the required mechanical rigidity and breakdown strength. Further, from Figure 7, it is evident that there is an increasing deviation from the linearity as the reaction progresses and the conversion increases. Thus, the reaction kinetics cannot be simply considered as second order. Therefore, the autocatalytic effect is very weak and can be neglected for this particular blend system. The reaction resembles more towards higher order kinetics as shown in Table III. It can be seen that, higher the isothermal temperature, higher the onset conversion. The increase in the viscosity reduces the mobility and accessibility of the reactive functional group and results in

decreasing reactivity and possibly varying the intermediate reaction mechanisms. The reaction sequences demonstrate visco-elastic behavior in diffusioncontrolled regime, where the reaction rate becomes much slower than that in the chemical controlled regime.

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