Development of Nanocomposite from Epoxy/PDMS-Cyanate/Nanoclay for Materials with Enhanced Thermal Stability for Engineering Applications

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Abstract: *Dicyanate monomer viz bis-4-cyanato-polydimethylsiloxane(PDMS-CY) containing siloxane known as thermally stable structural unit was prepared. The PDMS-CY/DGEBA-Epoxy/Nanoclay were prepared. They were analysed for their properties such as thermal stability, thermal degradation kinetics and microstructures.*
Keywords: *Cyanate ester; Resins; Nanoclay; Nanocomposite; Flame retardance; Degradation kinetics;*

I. Introduction

Cyanate ester resins have stimulated substantial interest due to their exclusive combination of properties, *e.g.* low water absorption, low dielectric constant, heat release rate, superior strength, excellent bonding towards metals, glass and carbon matrices, low volatility curing, and high resistance towards high heat and high humid environments. Owing to their excellent final properties they find applications as structural adhesives and matrices in high temperature resistant and light weight advanced composites [1, 2]. Cyanate ester resins are primarily used in the field of aerospace materials, in dielectric components, printed circuit boards, coatings and other applications that require high temperature resistant and moisture resistant materials. These applications follow logically from their high mechanical strength, high moisture resistance, low dielectric loss, and low volatility during cure and low toxicity properties [3, 4]. These attributes are reflected in relatively high fracture toughness when incorporated into epoxy resins [5].Conventional epoxies are not suitable to satisfy many high performance applications due to inherent brittleness. Hence, the incorporation of cyanate esters to the diglycidylether of bisphenol A (DGEBA) resin has definite advantages due to the lower crosslink density and higher flexibility in the final polymer due to the high percentage oxygen linkages present [6].Furthermore, the search to achieve superior performance and reduction in cost was never ending. The relatively high price of the cyanate esters was one of the important issues to be considered for development of cyanate modified epoxy resins [7]. This issue could be surmounted by further formulating them with nanoclays, which are relatively cheaper in cost and are expect to yield competitive performance characteristics. Hence, the objective of the work involves the preparation of PDMS-Cyanate blended Epoxy/Clay nanocomposite using *bis*-4-cyanato-polydimethylsiloxane and to assess their thermal properties and their thermokinetic behaviours[8].

II. Experimental

2.2. Materials

The diglycidylether of bisphenol A resin (DGEBA, LY556, EEW 180-185, Density 1.23, Refractive Index 1.57 and viscosity 10,000 cP) was supplied by Ciba Speciality Chemicals PVT Ltd., India, Diaminodiphenyl sulphone was procured from Fluka Company and triethylenetetramine, cyanogen bromide (99%), Nanomer 1.30E (MMT-Clay surface modified with octadecylammonium halide) from Aldrich Company. were purchased from Aldrich Chemical Company. Triethylamine, acetone and methanol (Analytical Reagent grade) were purchased from *S.D.Fine Chemicals* Pvt. *Ltd.*, Mumbai, India. The thermal stabilities of the prepared composites were determined using TGA, Netzsch, Jupiter, STA 449, F3 thermal analyzer.

2.3. Synthesis of Cyanate esters

Cyanate ester was synthesized at 0°C by the reaction of cyanogen bromide (2.2 moles (19.41 g).) and hydroxyl terminated polydimethyl siloxane (PDMS-OH) of 1.1 mole (50.41 g). Triethylamine (90g, 0.89 mol.) was added to catalyse the reaction and as well to absorb the evolved HCl gas to obtain as salts of *triethylamine* hydrochloride. The product, PDMS-Cyanate (Figure 1) was a white crystalline with 76g yield

(80%) and m.p. 75–78°C.The product was characterized and confirmed the product formation by FT-IR and $^1H/^{13}C$-NMR techniques.
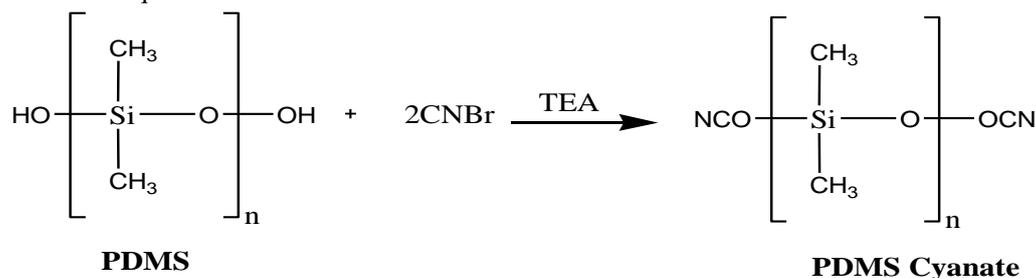

Fig.1. Preparation of PDMS-Cyanate Monomer

2.3.1. Preparation of PDMS-CY/DGEBA/Clay Nanocomposite

The DGEBA/DDS blends were considered as 100 wt % and to that 10wt % PDMS-CY was added. A 5wt % MMT-clay was taken separately in a 250ml beaker and dispersed in the required amount of acetone (100ml.). The obtained nanoclay dispersion was added to the DGEBA/DDS/PDMS-CY mixture. The resulting prepolymer was poured into a stainless steel mould that was preheated at 140°C and cured at 180°C. The nanocomposite synthesized was characterized using several techniques. These blends were denoted here as modified systems.

III. Results And Discussion

3.1. Thermogravimetic Analysis
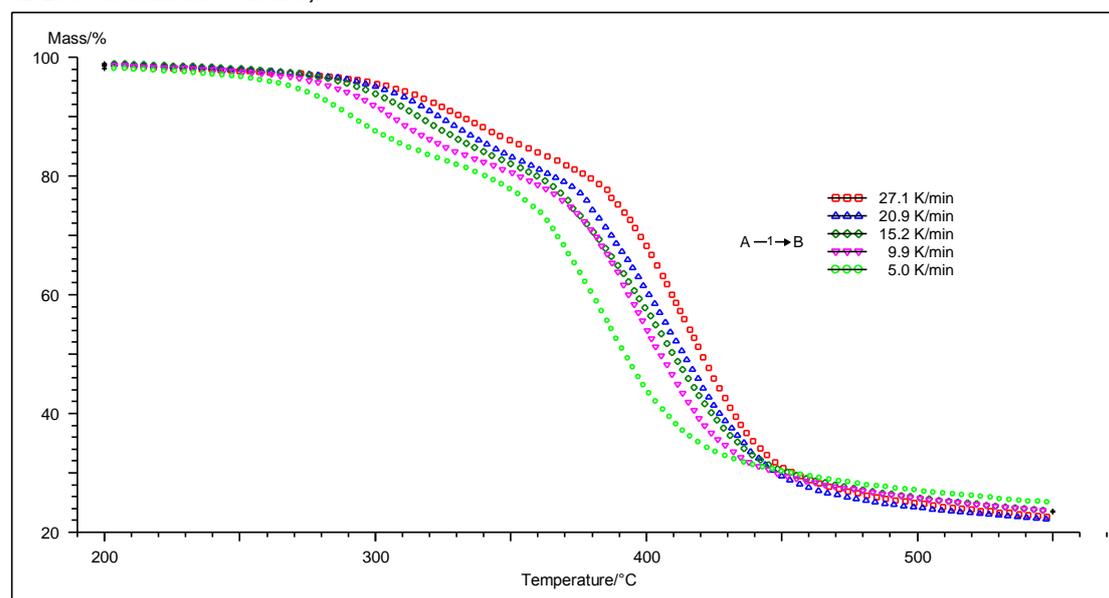### 3.1.1. Thermal Property

Fig.2. Non-linear regression plots of nanocomposite conducted by varying the heating rate using Thermogravimetric analysis (TGA)

The thermal stabilities of the cured resin systems were examined using the TGA technique. The thermal stability was evaluated by estimating the initial decomposition temperature (IDT), at which approximately 5% of the sample starts to degrade and where the detectable quantity of heat was evolved. The onset degradation temperature at which the maximum rate of mass loss (T_{max}) begins and the final decomposition temperature (FDT) at which the degradation of entire sample was complete. The TGA curves of nanocomposite are shown in Figure 2. The IDT values were high in nanocomposite because of the presence of oxazolidione rings and hard nanoclay layers. The maximum decomposition temperature occurred at two stages. The first stage of decomposition started around 300°C was due to the epoxy chain scissions. The second stage of decomposition observed around 400°C was due to the synergistic effect of thermally stable siloxane linkages and a s well due to the inorganic minerals of the clay particles. The excellent thermal stabilities was due to the incorporation of the PDMS-Cyanate into the DGEBA epoxy.

3.4.4. Determination of activation energy

Thermogravimetric analysis was used for the determination of the kinetics of thermal degradation of polymers. The thermal degradation of the cured system was carried out in multiple heating rate method under a flowing nitrogen atmosphere. The activation energy and order of reaction (n) were predicted by the integral methods of using equations derived from the Arrhenius equation.

$$kA \exp\left(\frac{-E}{RT}\right) \tag{1}$$

The estimation of activation energy and the conversion rate with respect to their functions are key factors in analyzing the degradation mechanisms. The models such as the Ozawa and Friedman equations are considered as model free kinetic methods are comparatively more reliable than the mono heating rate kinetic data. These kinetic equations employed are useful in analyzing dynamic degradation process, inorder to determine the activation energy and the relative kinetic parameters such as α, the conversion degree, $f(\alpha)$ – the differential conversion function, $g(\alpha)$ – the integral conversion function dynamically. Furthermore, the results obtained from the multiple heating rate degradation kinetics data are comparatively more reliable than the mono heating rate kinetic data. Several heating rate was employed to study the extent of rate of mass loss with respect to the kinetic parameters. The Friedman lines obtained by plotting the conversion rate $d\alpha/dt$ Vs reciprocal temperature exhibit a slope which is proportional to the activation energy

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \tag{2}$$

$$\frac{dx}{dt} = \frac{A}{B} \exp\left(-\frac{E}{RT}\right) f(x) \tag{3}$$

$$g(X) = \int_{X_o}^{X_p} \exp\left(-\frac{E}{RT}\right) dt = \frac{AE}{\beta T} P(x) \tag{4}$$

$$\frac{A}{\beta} = \int_{X_o}^{X_p} \exp\left(-\frac{E}{RT}\right) dt \tag{5}$$

$$\log\beta = \log\frac{AB}{G(X)R} + \log P(x) \tag{6}$$

Thus Ozawa equation gives a straight line by plotting $\ln\beta$ vs 1000/T. The Ea value could be obtained from the slope which is -0.1.0516 X slope. The Firedman and ozawa analysis agrees that the activation energy is dependent on the degree of conversions. β = heating rate, α= Conversion. The regression co-efficient of the plot is >0.9.

Thus the Ozawa kinetic analysis was done using Netzch thermokinetic multivariate non-linear regression analysis. The prepared nanocomposite are exhibiting highest thermal properties in comparison with the other systems was used to obtain the ozawa plot by the iso-conversion method. Several heating rate was employed to study the extent of rate of mass loss with respect to the kinetic parameters. The Friedman lines obtained by plotting the conversion rate $d\alpha/dt$ Vs reciprocal temperature exhibit a slope which is proportional to the activation energy

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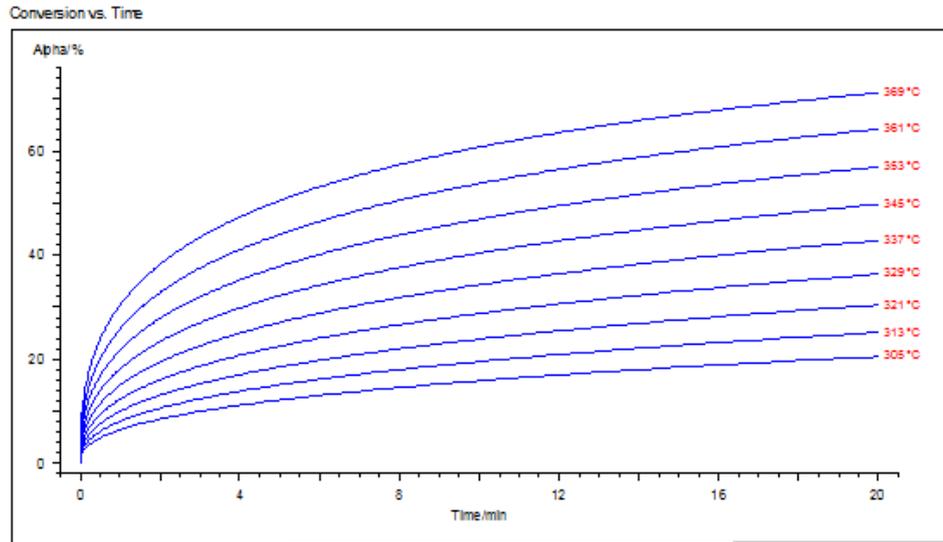
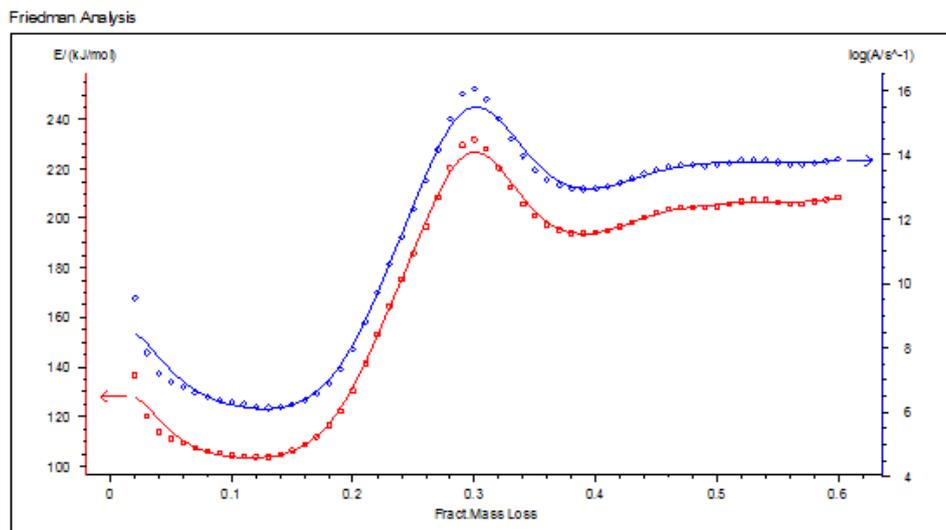**Fig. 3.** Mass loss temperature Vs Time study of nanocomposite

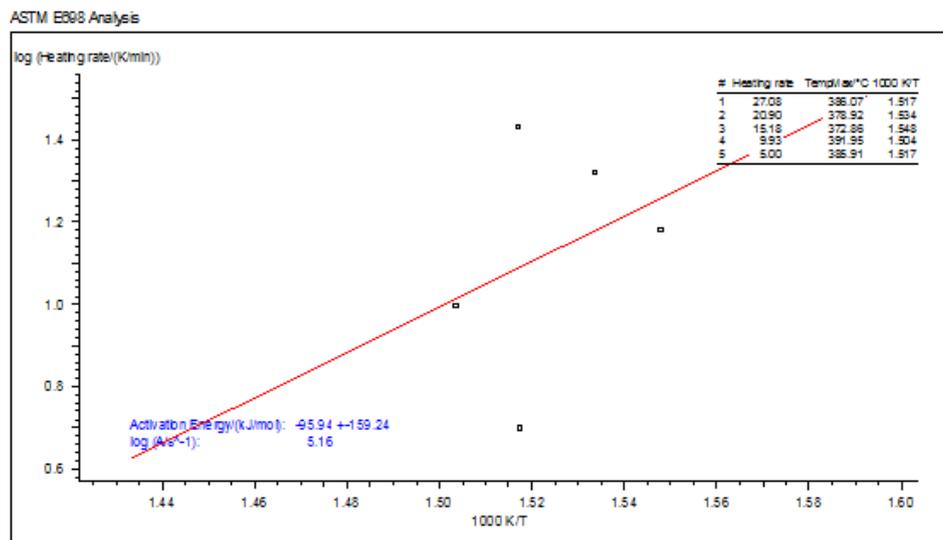**Fig. 4.** Activation energies Vs Degree of conversion of nanocomposite

Fig.5. The plots of lnβ Vs 1000/T of nanocomposite

The correlation between Ea with fractional mass loss showed 2 step degradations. During the 1st stage 0- 25% conversion took place and the Ea involved were 120-160kJ/Mole. During the 2nd stage 25-75% conversion took place and the Ea values were upto 300kJ/Mole **(Fig.3).** The 1st stage decomposition took place between the temperatures 280 to 340C. While the 2nd stage conversion though it took less Ea and Low F(α), the temperature range was broad, ie., from 340 to 400C. The second stage decomposition was due to the inorganic clay layers acted as a barrier to the degradation of the polymers. The rate of degradation is dependent on the heating rate was confirmed from the plot of degree of conversion vs Time. The higher the heating rate, the quicker the mass loss irrespective the time was noticed **(Fig.4).** This is in accordance with the ASTM kinetic plots obtained by plotting inverse of time versus heating rate to obtain the constant activation energy **(Fig. 5)**

IV. Conclusions

A dicyanate with siloxane (PDMS) as a backbone was successfully prepared in good yield and fully characterized before being polymerized to form thermoset nanocomposite by adding with DGEBA-Epoxy and Nanoclay. The cured polycyanurates undergo thermal degradation in a broad range with the rate of maximum decomposition being observed at around 400°C. The activation energy values of multiple heating rated degradations have exhibited higher values. The Ea values of nanocomposite are higher than the conventional composite is in agreement with the two types of degradation kinetic mechanisms. Siloxane molecules present in the PDMS-CY possess high heat resistance and electrical insulation characteristics. The degradation kinetics study carried out by varying the heating rate helps to understand that the variation in the heating rate decreases the degradation time which was due to the hardening effect of the materials reflected in excellent thermal stability Therefore the nanocomposite prepared comprising of PDMS-CY/DGEBA-Epoxy/Nanoclay has promising applications in the printed circuit boards and it the similar environment as an adhesives and fibre reinforcing resin component.

Acknowledgements

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