

Kinetic Studies on Cure Kinetics of DGEBA (Diglycidyl Ether of Bisphenol-A) with Terephthalamide Hardening System generated from PET waste

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Abstract: An aromatic amide system for epoxy resin based on diglycidyl ether of Bisphenol-A was developed through ammonolysis of PET waste. The ammonolysis of PET waste was carried out at ambient conditions of temperature & pressure. The end product, characterized as terephthalamide was used as hardener in epoxy resin (Diglycidyl ether of Bisphenol-A) and triethylamine and sodium hydroxide were used as catalysts. Several samples were used to study the curing kinetics having varying amounts of the catalysts by means of Differential scanning calorimetry (DSC). Isothermal and Dynamic DSC characterization of the formulations were performed. The curing kinetics of terephthalamide with epoxy resin shows high energy of activation as 50.18 KJ/mole in the absence of catalyst which was lowered towards negative values in their presence. The optimum curing of epoxy resin heated with aromatic hardener can be obtained in 28 minutes at 320 °C. The use of catalysts reduced the curing time to 2.0 minutes at 60 °C.

Keywords: Epoxy resin, terephthalamide, DSC, curing kinetics.

1. INTRODUCTION

Epoxy resins are polymer materials which are used for a wide range of applications, either unmodified or as matrix materials for composites. The advantageous properties of epoxies include good adhesion to many substrates, no emission of volatiles upon cure, enhanced mechanical properties, high electrical insulation, good chemical resistance, low shrinkage and a broad formulating range [1]. Epoxies find use as adhesives, caulking compounds, casting compounds, sealants, varnishes, paints as well as laminating resins for a variety of industrial applications. It is essential to control the degree of cure of resins in order to achieve the desired end properties corresponding to the applications. Many studies can be found in literature [2-8] in which the epoxy resins are blended with other materials in order to achieve desired end properties. Different types of hardening systems for epoxies have been developed and their curing kinetics have been studied with the help of differential scanning calorimetry [9-13]. Differential scanning calorimetry has been widely recognized as useful method to determine cure kinetics of thermoset resins. Several workers investigated the cure kinetics of DGEBA with different amine systems such as poly(oxypropylene) triamine [14], poly(oxypropylene) diamines [15], 4, 4'-

diaminodiphenylsulphone [16], 4, 4' diaminediphenylmethane [17] etc. by means of DSC.

The objective of the current research is to develop an aromatic amide hardening system for epoxy resin, through ammonolysis of PET waste with liquor ammonia [18, 19] at ambient conditions of temperature and atmospheric pressure. The end product obtained by the ammonolysis of PET waste was characterized as terephthalamide with the help of spectroscopic techniques, SEM and Differential Thermal Analysis. To our knowledge, cure kinetics of this system has not yet been investigated. Several samples were prepared using epoxy resin and terephthalamide having varying amounts of triethylamine and sodium hydroxide, which were used as catalysts. Dynamic characterization of the samples was performed at a constant heating rate within the temperature range 40 °C – 360 °C. The isothermal cure kinetics of diglycidyl ether of Bisphenol-A using terephthalamide as hardener has been investigated by means of DSC both in absence and presence of catalysts.

2. EXPERIMENTAL

2.1. Materials and Characterization

The PET waste used in this study was obtained from various post-consumer sources such as soft drink bottles, water bottles etc. The PET waste bottles were collected manually and processed before use. Liquor ammonia solution (sp. Gravity 0.91) was of A.R. grade and procured from M/s Qualigens. The ammonolysed

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end products were synthesized and characterized as per procedure given in our earlier publications [18, 19] and used in the present study. The epoxy resin used in this study is diglycidyl ether of Bisphenol A (DGEBA) procured from M/s Huntmen and it was of commercial grade (LY 556). The number average molecular weight $M_n=360$ was obtained from epoxy equivalent 180 g/eq, that was determined by chemical titration of the end groups. Triethylamine and sodium hydroxide were obtained from M/s Qualigens and used as such without further purification.

2.2. Methods

The cure of epoxy resin with aromatic amide hardening system generated from PET waste in absence and presence of catalysts was studied by means of DSC on a Mettler star SW 9.01 differential scanning calorimeter, using an empty aluminum pan as a reference. Prior to DSC runs, the temperature and heat flow were calibrated using indium and zinc standards. The measurements were conducted under nitrogen atmosphere. Dynamic DSC experiments were performed to determine the curing temperatures for each sample keeping constant heating rate of 10 °C within the temperature range of 40 °C – 360 °C. The sample mass used was kept in the 10 to 25 mg range. Since the reaction rate constant is a function of temperature, the calculation of kinetic parameters needs at least three isothermal experiments at different temperatures. For isothermal experiments samples were placed in the preheated DSC cell and scan was started when the temperature equilibrium was regained. The reactions were conducted at three different temperatures for each sample. The recorded isothermal thermograms were analyzed with the help of DSC kinetic software (STARe).

2.3. Sample Preparation

Table 1 shows composition of different samples comprising epoxy resin, terephthalamide used as

hardener and catalysts (triethylamine and sodium hydroxide). These formulations have been designated as S_0 , S_1 , S_2 , S_3 and S_4 where S_0 is the control sample without any catalyst. In these samples the epoxy resin and the hardener used were 67% and 33% respectively. The concentrations of epoxy resin and terephthalamide were kept constant and catalysts were used in the range 1g-4g in different samples. All the components were mixed thoroughly by stirring with the help of glass rod at room temperature. The thoroughly mixed solutions of epoxy resin, hardener and catalysts were used to perform the dynamic and isothermal DSC characterizations.

3. RESULTS AND DISCUSSION

3.1. Dynamic DSC Characterization

DSC curves of the investigated systems (S_0 , S_1 , S_2 , S_3 and S_4) at heating rate of 10 °C within the temperature range of 40 °C – 360 °C are shown in Figure 1. Table 2 shows the data of Dynamic characterization of all samples. All the exothermic peaks are symmetrical and give curing temperature for each reaction mixture. For S_0 formulation, which is a control sample the reaction mixture was cured between 295 – 335 °C. This curing temperature is in the absence of catalysts. The thermogram shows an exothermic peak with peak point of 320 °C. The exothermic peak is quite symmetrical and suggests that the epoxy resin cures with terephthalamide by following auto catalytic cure. S_1 formulation contains 1g of triethylamine and 1g of sodium hydroxide as catalysts. This reaction mixture was found to be cured within a temperature range of 50-88 °C with peak temperature 70 °C hence the curing temperature was markedly decreased. For S_2 sample it was observed that the reaction mixture cured between 40-75 °C with peak temperature of 64 °C and for S_3 sample the peak temperature was 76 °C. Again it was seen that S_4 sample cures between 50-80 °C with peak temperature

Table 1: Shows Composition of Different Formulations of Epoxy Resin, Terephthalamide and Catalyst Used for Dynamic and Isothermal DSC Characterizations

S. No.	Designations	Epoxy (g)	Hardener (g)	Catalysts (g)	
				Sodium hydroxide	Triethylamine
1	S_0	9.3	4.5	-	-
2	S_1	9.3	4.5	1	1
3	S_2	9.3	4.5	2	1
4	S_3	9.3	4.5	3	1
5	S_4	9.3	4.5	1	4

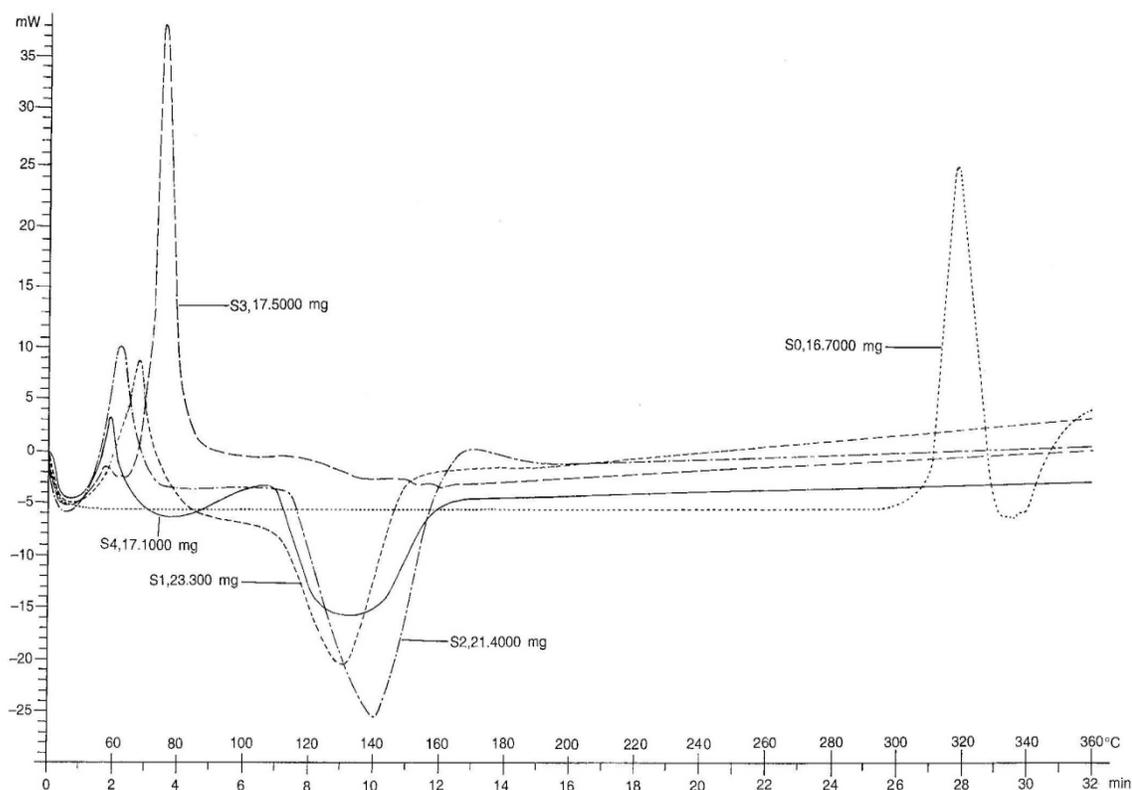


Figure 1: Dynamic DSC thermograms for investigated systems (formulations S_0 , S_1 , S_2 , S_3 & S_4) at heating rate of $10\text{ }^\circ\text{C/minute}$.

Table 2: Showing Data obtained From Dynamic DSC Characterization of Different Samples (Curing Temp. Ranges for the Samples Along with their Peak Temperatures)

S. No.	Formulation	Weight of sample (mg)	Cure temp. range ($^\circ\text{C}$)	Peak temp. ($^\circ\text{C}$)	Curing time (minutes)
1	S_0	16.7000	295-335	320	28
2	S_1	23.3000	50-88	70	2.9
3	S_2	21.4000	40-75	64	2.4
4	S_3	17.5000	65-90	76	3.9
5	S_4	17.1000	50-80	60	1.9

of $60\text{ }^\circ\text{C}$. These results emphasize that catalysts are lowering the activation energy for curing and hence the curing temperature has been decreased as the concentration of the catalyst is being increased. In S_3 formulation the amount of NaOH used is the highest among all the samples, however it possess higher peak temperature than S_2 sample. But when we increased the amount of Triethylamine in S_4 sample, a marked decrease was observed in the peak temperature.

3.2. Isothermal DSC Characterization

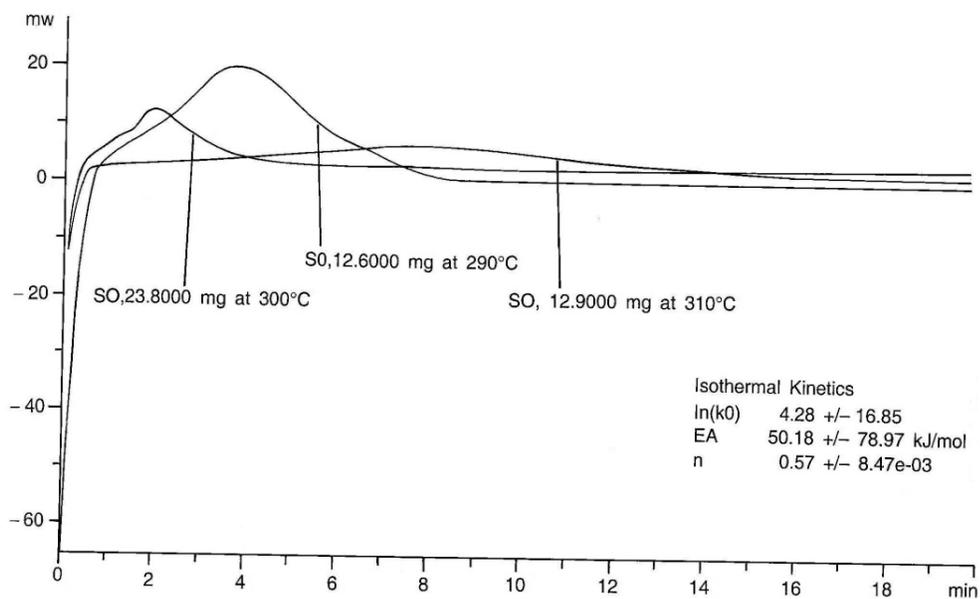
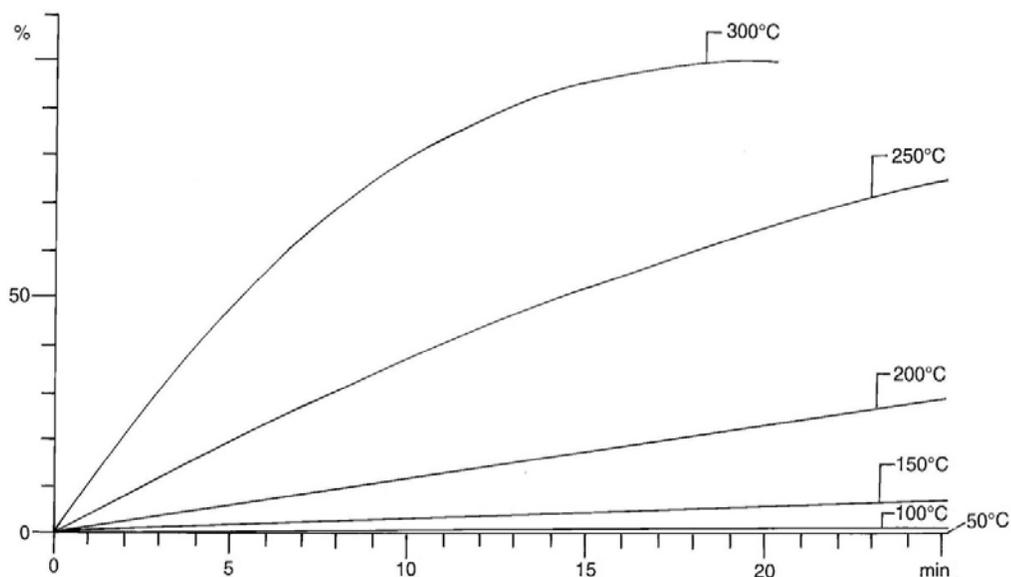
The curing kinetics of the samples was studied by DSC isothermal method keeping three constant temperatures for each sample (Table 3).

3.2.1. Curing Kinetics of Terephthalamide with Epoxy Resin in S_0 Sample

Figure 2 shows a DSC thermogram of the sample which was prepared by mixing 4.5 g terephthalamide and recorded three different iso-thermal curves at 290, 300 and $310\text{ }^\circ\text{C}$ temperatures. The curves show that on increasing the temperature the rate of reaction is increasing. These thermogram were analyzed with the help of STARe software and the analytic results show that the energy of activation was found to be quite high of the range of 50.18 kJ/mole at $320\text{ }^\circ\text{C}$ and the order of the reaction was observed near one i.e. 0.57. The Figure 3 shows conversion plot between percentage of conversion vs time at constant temperatures of 50,

Table 3: Isothermal Curing Kinetic Study Data Showing the Effect of Temperature on Curing Time

S. No.	Designations	Isothermal temp. (°C)	Weight of sample (mg)	EA (Activation energy, KJ/mol)	Order of reaction
1	S ₀	290, 300, 310	12.60, 23.80, 12.90	50.18	0.57
2	S ₁	125, 140, 150	18.30, 17.60, 11.80	2.56	0.45
3	S ₂	160, 180, 200	11.50, 14.10, 17.70	- 0.29	0.51
4	S ₃	60, 70, 80	16.80, 13.18, 17.30	3.49	0.42
5	S ₄	120,130,140	18.60, 17.60, 15.50	5.22	0.42

**Figure 2:** DSC Thermogram of the isothermal curves of S₀ formulation at 290, 300 and 310 °C.**Figure 3:** Shows the conversion of S₀ formulation percentage conversion verses time at 300, 250, 200, 150, 100 & 50 °C.

100, 150, 200, 250 and 300 °C. It was observed that at 250 °C, nearly 70 % conversion takes place within 25

minutes. While more than 90 % conversion can be obtained in 12.67 minutes at a temperature of 300 °C.

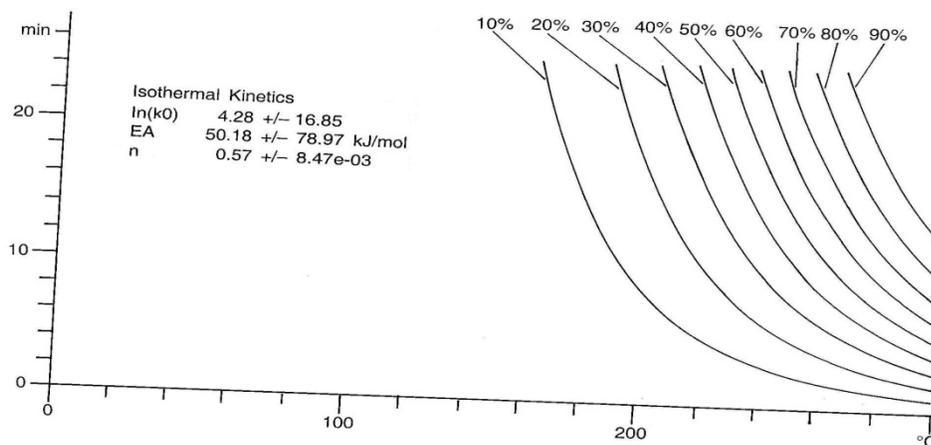


Figure 4: Shows the iso conversion of S_0 formulation time versus temperature.

Figure 4 shows iso-conversion plot between curing time vs temperature. The slope line shows 10, 20, 30, 40, 50, 60, 70, 80 & 90 % conversion at different temperature such as 0–300 °C. In this case the 90 % iso-conversion takes place at 290.4 °C and 280 °C in 14 minutes and 20 minutes respectively.

3.2.2. Curing Kinetics of Terephthalamide with Epoxy Resin in S_1 Sample

Figure 5 shows DSC thermogram of the sample S_1 showing iso-thermal curves at three different temperatures i.e. 125, 140 and 150 °C. The curves show that on increasing the temperature the rate of reaction increases. These thermograms were analyzed with the help of STARe software and the analytic results show that the energy of activation was found to be quite low of the range of 2.56 KJ/mol and the order of the reaction was observed near one i.e.0.45. The Figure 6 shows conversion plot between percentage of

conversion vs time at constant temperature of 0, 50, 100, 150, 200, 250 and 300 °C. It was found that at 250 °C, 70 % of conversion takes place in just 9 minutes. While more than 90 % conversion can be obtained in 12 minutes at a cure temperature of 300 °C. Figure 7 shows iso-conversion plot between curing time and temperature. It is seen that 90 % iso-conversion takes place at 290.4 °C and at 267.7 °C in 10 minutes and 16 minutes respectively.

3.2.3. Curing Kinetics of Terephthalamide with Epoxy Resin in S_2 Sample

Figure 8 shows a DSC thermogram of the sample which was prepared by mixing 4.5 g terephthalamide and recorded three different iso-thermal curves at 160, 180 and 200 °C temperatures. These thermograms were analyzed with the help of STARe software and the analytic results shows that the energy of activation was found to be quite low of the range -0.29 KJ/mol

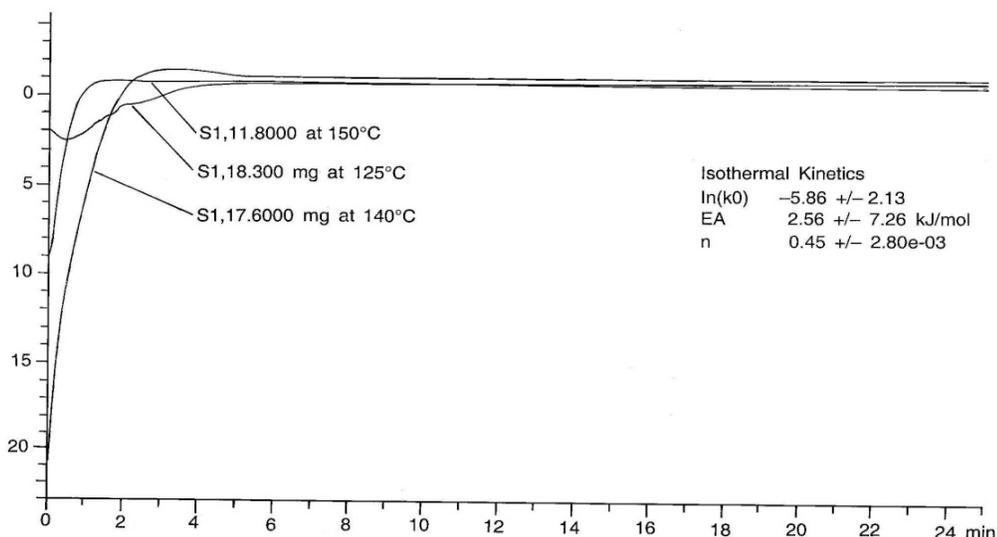


Figure 5: Shows the isothermal curves of S_1 formulation at 125, 140 & 150 °C.

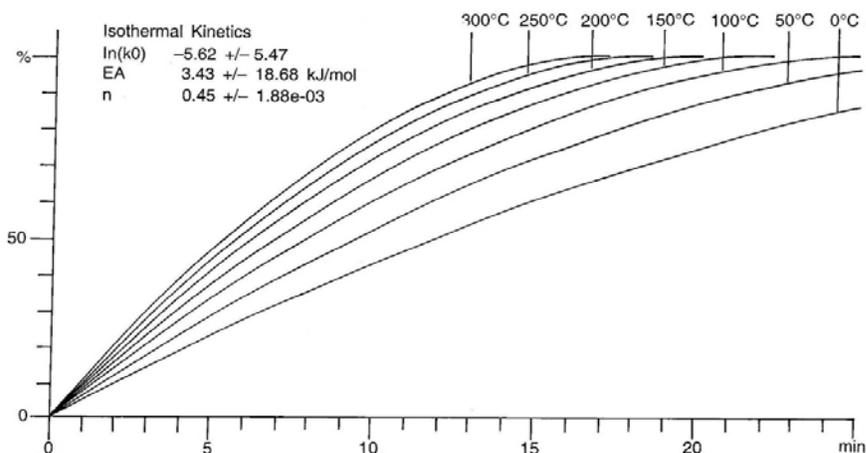


Figure 6: Shows the conversion of S_1 formulation percentage conversion versus time at 300, 250, 200, 150, 100, 50, 0 °C.

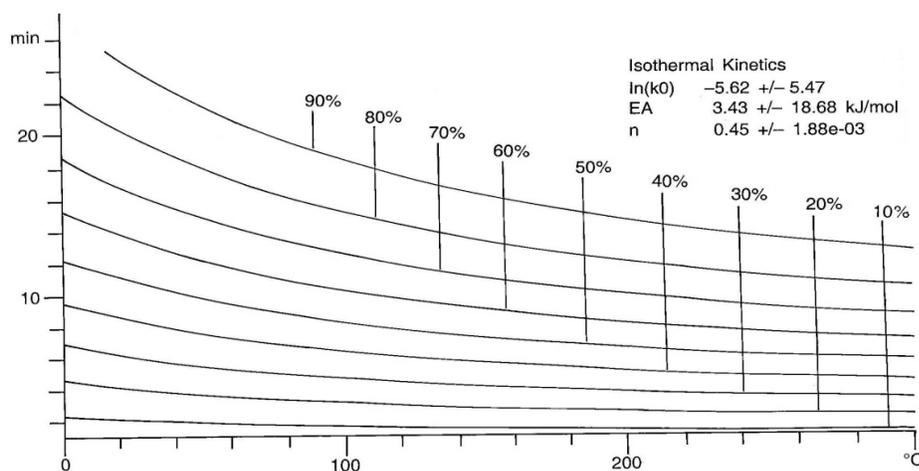


Figure 7: Shows the iso conversion of S_1 formulation time versus temperature.

and the order of the reaction was observed near one i.e. 0.51. The Figure 9 shows as conversion plot between percentage of conversion versus time at constant temperature 0, 50, 100, 150, 200, 250 and 300 °C. It can be recorded that 80 % of conversion takes place at 250 °C in 25 minutes. Whereas, 90 % of conversion can be obtained in 22.67 minutes at the cure temperature 300 °C. Here the effect of temperature is not significant. Figure 10 shows iso-conversion plot between curing time versus temperature. The slope line shows 10, 20, 30, 40, 50, 60, 70, 80 & 90 % conversion at different temperatures from 0 – 300 °C. In this case, 90 % iso-conversion takes place at 0 °C in 19.5 minutes. This figure shows that on increasing the temperature, the curing time is also increased.

3.2.4. Curing Kinetics of Terephthalamide with Epoxy Resin in S_3 Sample

Figure 11 shows DSC thermogram of the sample which was prepared by mixing 4.5 gm terephthalamide

and recorded at three different iso-thermal curves at 60, 70 and 80 °C. The curve shows that increasing the temperature increases the rate of reaction. This thermogram were analyzed with the help of STARe software and the analytic results shows that the energy of activation was found to be quite low of the range of 3.49 KJ/mole at 76 °C and the order of the reaction was observed near one i.e 0.42.

The Figure 12 shows as conversion plot between percentage of conversion versus time at constant temperature 0, 50, 100, 150, 200, 250 and 300 °C. It can be recorded that 90 % conversion occurs at 250 °C in 11 minutes. While more than 90 % of conversion can be obtained in 10.33 minutes at a curing temperature of 300 °C. Figure 13 shows iso-conversion plot between curing time versus temperature. The slope line shows 10, 20, 30, 40, 50, 60, 70, 80, 90% conversion at different temperature such as 0 – 300 °C. It is observed that 90 % iso-conversion takes place at 0.4 °C and 100 °C in 19 and 13 minutes respectively.

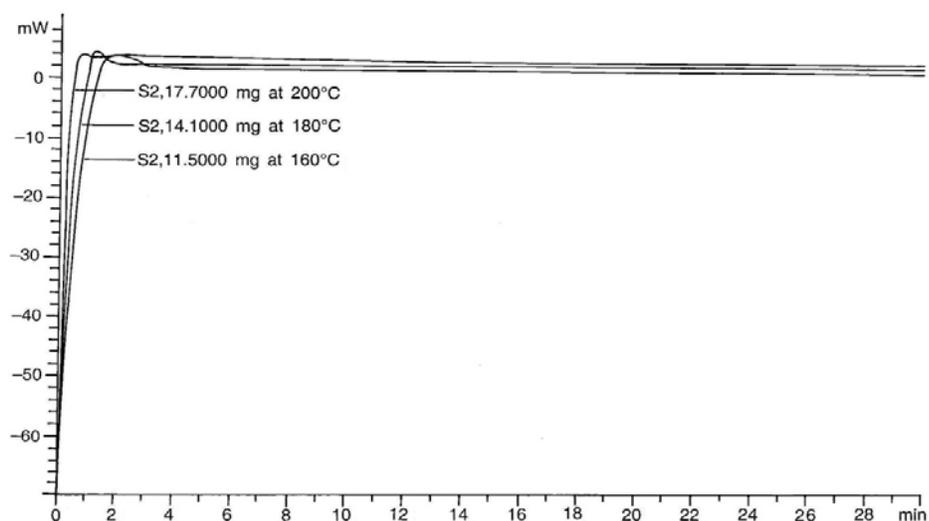


Figure 8: Shows the isothermal curves of S₂ formulation at 160, 180, 200 °C.

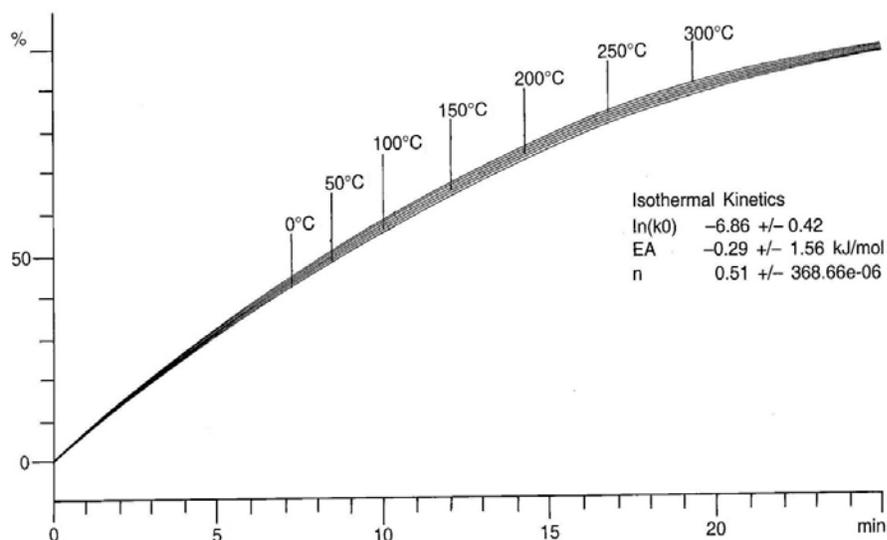


Figure 9: Shows the conversion of S₂ formulation percentage conversion verses time at 300, 250, 200, 150, 100, 50, 0 °C.

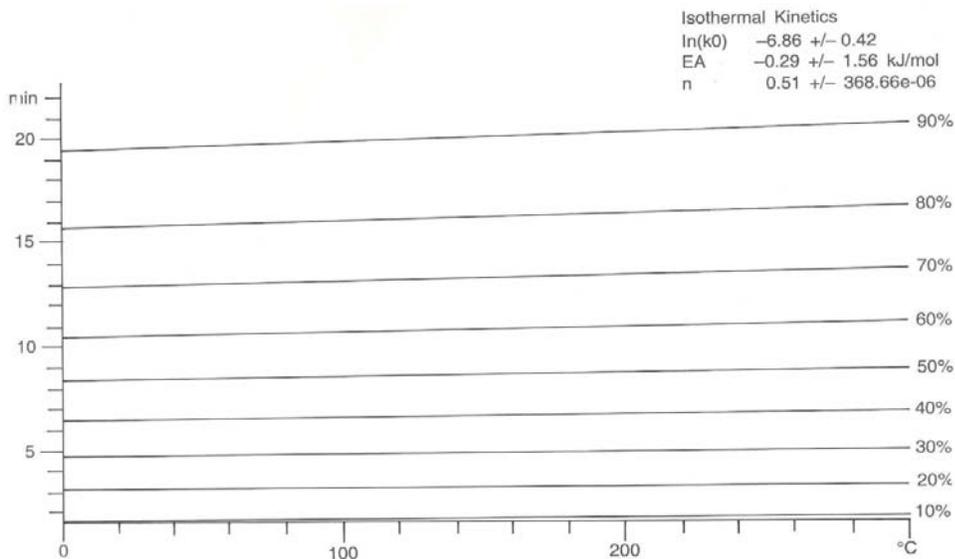


Figure 10: Shows the iso conversion of S₂ formulation time verses temperature.

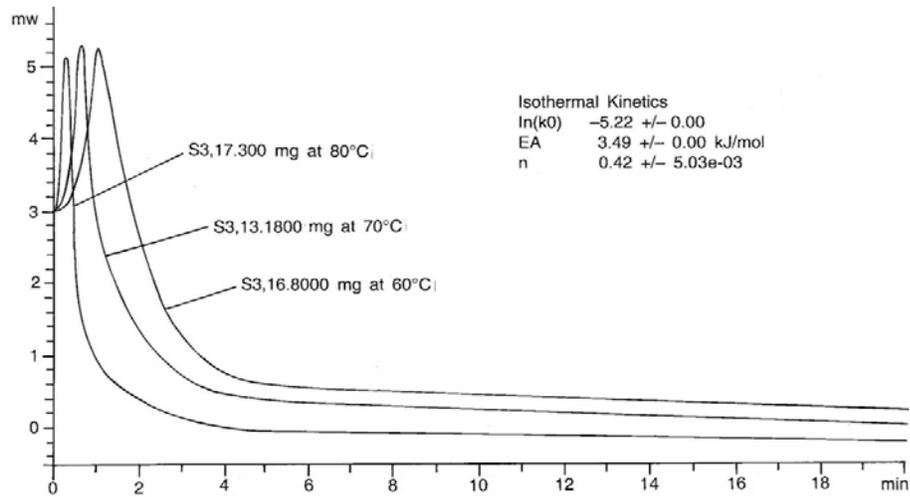


Figure 11: Shows isothermal curves of S₃ formulation at 60, 70 & 80 °C.

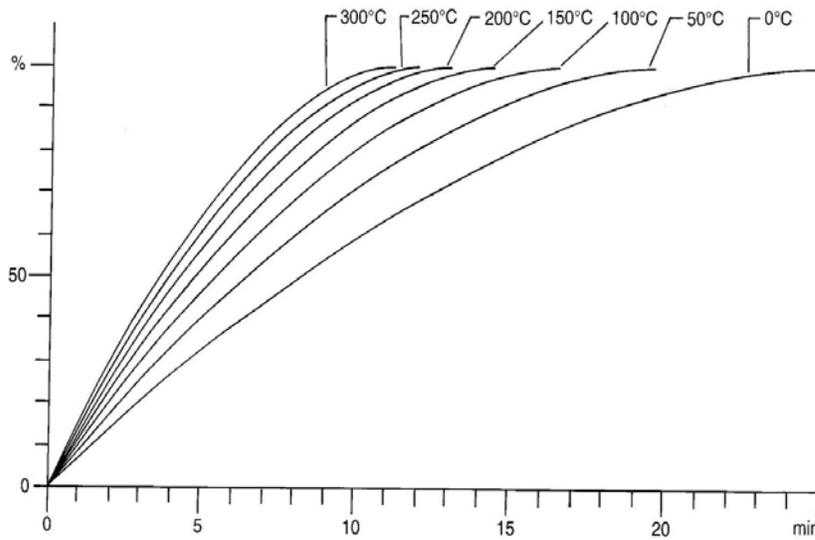


Figure 12: Shows the conversion of the S₃ formulation percentage conversion versus time at 300, 250, 200, 150, 100, 50 & 0 °C.

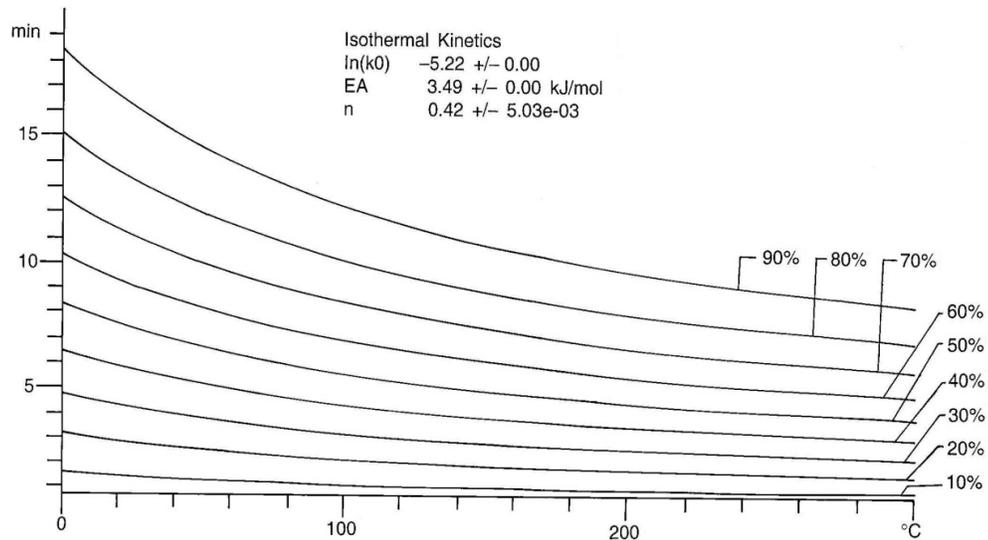


Figure 13: Shows the iso conversion curves of S₃ formulation time versus temperature.

3.2.5. Curing Kinetics of Terephthalamide with Epoxy Resin in S₄ Sample

Figure 14 again shows that increase in temperature increases the rate of reaction. These thermograms were analyzed with the help of STARe software and the analytic results shows that the energy of activation as 5.22 KJ/mole at 60 °C and the order of the reaction was observed near one i.e. 0.42. Figure 15 shows a conversion plot between percentage of conversion verses time at constant temperatures 50, 100, 150, 200, 250 and 300 °C. It can be recorded that at 250 °C, the conversion is 80 %. Whereas more than 90 % of conversion can be obtained in 12.67 minutes at a cure temperature of 300 °C. Figure 16 shows iso-conversion plot between curing time verses temperature. The slope line shows 10, 20, 30, 40, 50, 60, 70, 80, 90 % conversion at different temperature between 0 – 300

°C. In this case, 90 % iso-conversion was achieved at 290.4 °C in 10 minutes and at 267.7 °C in 20 minutes.

3.6. Reaction Mechanism of Curing Kinetics

The curing of the epoxy resin with amines is well established and has been shown to follow autocatalytic cure by several authors. The synthesized amide has free amine groups at the end of the molecule which can react with epoxy group of the epoxy resin as per the Reaction Scheme 1.

4. CONCLUSIONS

Curing kinetics of DGEBA- terephthalamide system was studied by means of DSC by isothermal method. Catalytic influence on the reaction rates has been described. An efficient methodology for aromatic amide hardening system for epoxy resin, which works at

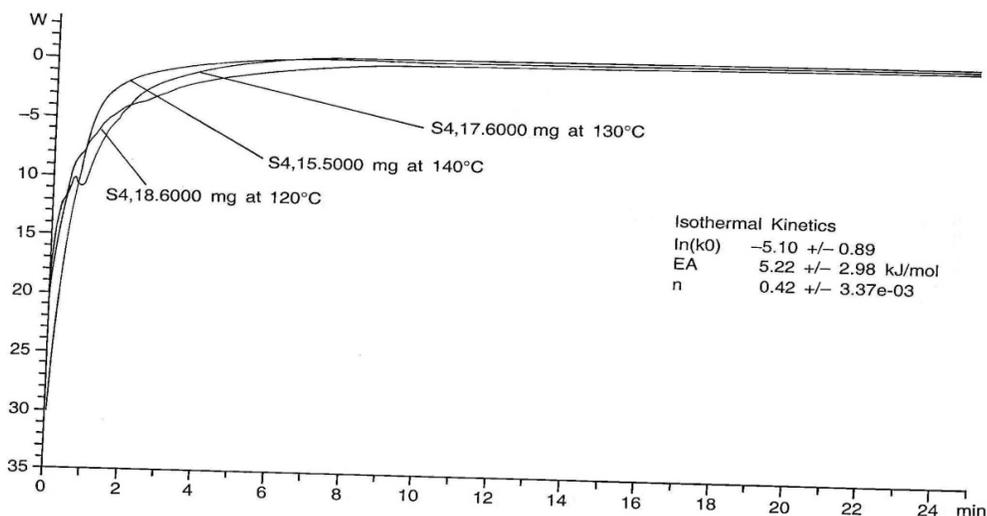


Figure 14: Shows the isothermal curves of S₄ formulation at 120, 130, 140 °C.

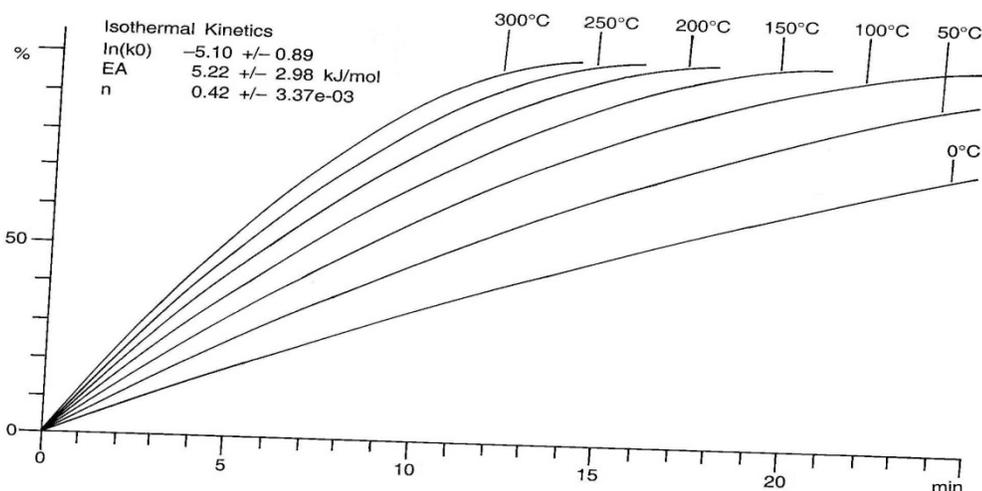


Figure 15: Shows the conversion of S₄ formulation percentage conversion verses at 300, 250, 200, 150, 100, 50, & 0 °C.

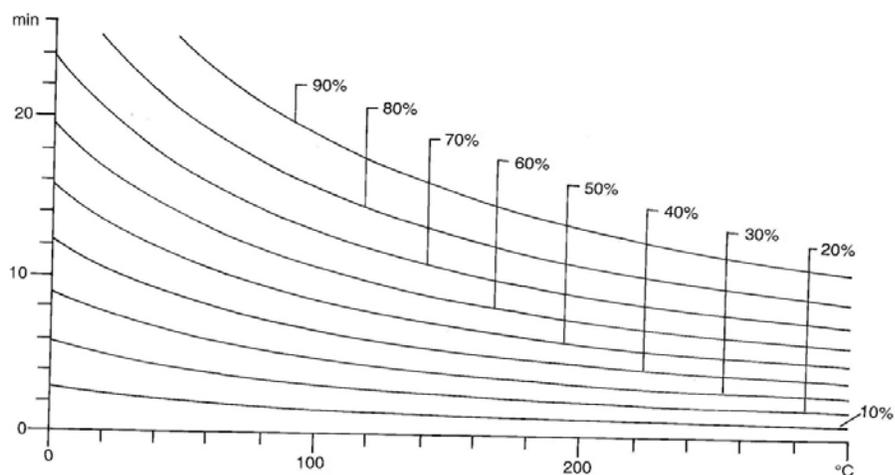
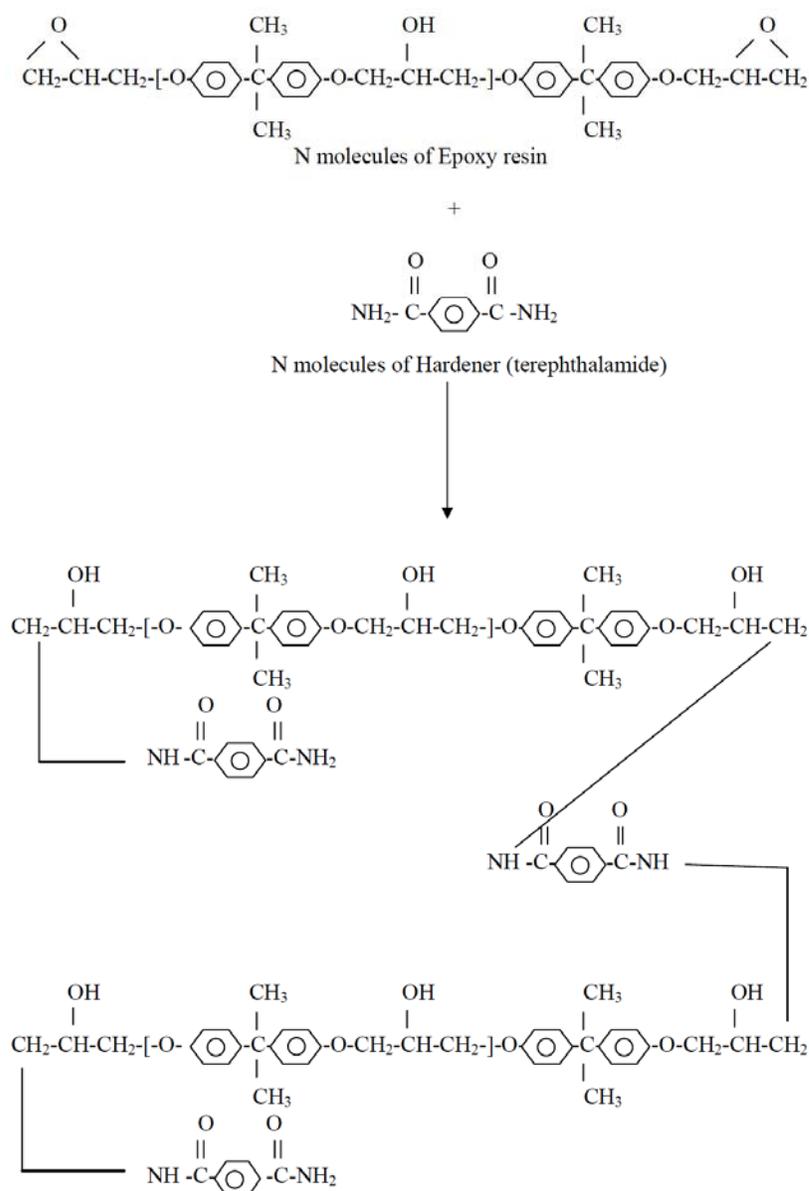


Figure 16: Shows the iso conversion of S₄ formulation time verses temperature.



Reaction Scheme 1: Mechanism for DGEBA-Terephthalamide hardening system.

ambient conditions of temperature and pressure have been developed. Terephthalamide used in the present study has been generated from PET waste, which offers another application of products obtained from PET waste recycling. In the present DGEBA-terephthalamide system, the energy of activation was markedly lowered from 50.18 KJ/mol to -0.29 KJ/mol for formulation S₂ in the presence of catalysts.

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