International Journal of Education and Science Research
Review
E-ISSN 2348-6457
Volume-3, Issue-1
February- 2016
www.ijesrr.org
Email- editor@ijesrr.org

Curing Kinetic Studies of N, N-Dimethyl Terephthalamide and Terephthalic Dihydrazide with Di-Glycidial Ether of Bis Phenol-A from PET Waste

Anjali Verma, R. K. Soni
Department of Chemistry
Ch. Charan Singh University
Meerut

Krishna Dutt
Department of Polymer Science
Bhaskaracharya College of Applied Sciences
University of Delhi, Delhi

ABSTRACT:

Aromatic amide hardening system for epoxy resin based on diglycidyl ether of Bisphenol-A was developed through aminolysis of PET waste with methyl amine and hydrazine monohydrate. The aminolyzed end products were used as hardener in epoxy resin (DGEBA) with triethylamine and sodium hydroxide which act as catalysts. The curing kinetics was studied with the help of DSC by iso- thermal method. The curing kinetics of N, N-Dimethyl terephthalamide and Terephthalic dihydrazide with epoxy resin shows lower energy of activation as 23.67 and -0.16 KJ/mole. The optimum curing of epoxy resin heated with N, N-Dimethyl terephthalamide hardener can be obtained in 15 minutes at 280 ^{0}C and the optimum curing of epoxy resin heated with Terephthalic dihydrazide hardener can be obtained in 16.64 minutes at 100 ^{0}C.

KEYWORDS: PET waste, recycling, aminolysis, infrared spectroscopy, NMR, curing, DGEBA

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, and paints as well as laminating resins for a variety of industrial 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. Several workers investigated the cure kinetics of DGEBA with different amine systems such as poly (oxypropylene) triamine [9], poly (oxypropylene) diamines [10], 4, 4'- diaminodiphenylsulphone [11], 4, 4' diaminediphenylmethane [12] etc by means of DSC. The objective of the current research is to develop an aromatic amide hardening system for epoxy resin, through aminolysis of PET waste with methyl amine and hydrazine monohydrate [13-15] at ambient conditions of temperature and atmospheric pressure. The end product obtained by the aminolysis of PET waste was characterized as N, N-Dimethyl terephthalamide and terepthalic dihydrazide with the help of spectroscopic techniques, Differential Thermal Analysis. Several samples were prepared using epoxy resin with N, N-Dimethyl terephthalamide and terepthalic dihydrazide. The isothermal cure kinetics of diglycidyl ether of Bisphenol-A using N, N-Dimethyl terephthalamide and terepthalic dihydrazide use as hardener has been investigated by means of DSC both in absence and presence of catalysts. Dyanamic characterization of the samples were also performed at a constant heating rate within the temperature range of 40 ^{0}C – 400 ^{0}C.

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 and chopped into small flakes and cleaned thoroughly by washing firstly with soapy water and then with distilled water. The cleaned PET waste flakes were dried at 80 ^{0}C for 5-hours.vThe aqueous methyl amine (40%) for the aminolysis of PET waste procured from M/s Quligens and used as such. Hydrazine monohydrate (90-100%) was procured from M/s Quligens fine chemicals and used as received without further purification and was of LR grade. 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.

2.2. AMINOLYSIS OF PET- WASTE WITH METHYLAMINE:

The PET waste flakes were treated with aqueous methylamine (40% weight/weight) in a properly sealed reaction vessel. The reaction proceeds at room temperature with continuous stirring. The white precipitate starts appearing within few hours from the start of the reaction in the vessel and after 45 days no PET flakes left unreacted.

2.3. AMINOLYSIS OF PET WASTE WITH HYDRAZINE HYDRATE:

The aminolysis of PET waste flakes was performed with hydrazine monohydrate (99-100 %). PET waste flakes (50 g) were reacted with hydrazine hydrate (100 mL). The reactions were performed in a properly sealed reaction vessel with continuous constant stirring at ambient temperature and pressure. The light yellow precipitates start appearing in the reaction vessel, within few minutes from the start of the reaction and the reaction was completed within 24 hours. The aminolysed products from degradation experiment were separated after 24 hours and washed with distilled water severely and the product so obtained was dried under vacuum.

2.3. CURING KINETICS OF EPOXY RESIN WITH N, N DIMETHYLTEREPTHALAMIDE, AND TEREPHTHALIC DIHYDRAZIDE:

The curing of epoxy resin with aromatic amides hardening system generated from PET waste were 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. The curing kinetics of epoxy resin with N,N dimethylterepthalamide, and Terephthalic dihydrazide produced by aminolysis of PET waste was studied by mixing 7.2 g of epoxy resin (DGEBA) with N,N dimethylterepthalamide, and 3.88g Terephthalic dihydrazide (as hardeners) at ambient temperature. The thoroughly mixed solution of epoxy and hardener was used to carry out the curing kinetics. Dynamic DSC experiments were performed to determine the curing temperatures for each sample keeping constant heating rate of 10 ^{0}C within the temperature range of 40 – 400 ^{0}C. The sample mass used was kept in the 7 to 35 mg range. 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).

.3 RESULTS AND DISCUSSION:

3.1. SYNTHESIS OF N, N, DIMETHYLTEREPTHALMIDE:

The degradation of PET waste flakes was studied with methylamine. The white precipitates were obtained, which were separated by simple filtration and dried under vacuum. The most significant ratio for aminolysis of PET waste with aqueous methylamine was found to be 1 : 10 (g/mL). Thus, (10 g) of PET waste flakes were treated with (100 mL) of aqueous methylamine and the degradation products so obtained were separated.

3.2. SYNTHESIS OF TEREPTHALIC DIHYDRAZIDE (TPD):

It was seen that PET flakes have been completely depolymerized and only a few small pieces left unreacted in this case. The reaction was completed in 24 hours. A fresh reaction was started by mixing PET waste (50 g) with hydrazine monohydrate (100 mL). The reaction was stopped after 24 hours by pouring reaction mixture in the water. The product was filtered and dissolved in DMSO, refiltered to separate the unreacted PET waste. The product was recovered then dried. The light yellow precipitate was separated and dried at 70 ^{0}C under vacuum for 4 hours till constant weight is obtained.

3.3. DYNAMIC DSC CHARACTERIZATION:

DSC thermo grams of the investigated systems ($S_{0a,\ and}$ $S_{0b,}$) at heating rate of 10 ^{0}C within the temperature range of 40 ^{0}C – 400 ^{0}C are shown in fig 8 and fig 9 respectively. All the exothermic peaks are symmetrical and give curing temperature for each reaction mixture. For S_{0a} formulation, which is a control sample the reaction mixture was cured between 282.74 - 332.03 ^{0}C with a peak temperature 303.49 ^{0}C, while for the formulation S_{0b} which is also control system and is cured between 247.26 - 258.53 ^{0}C.

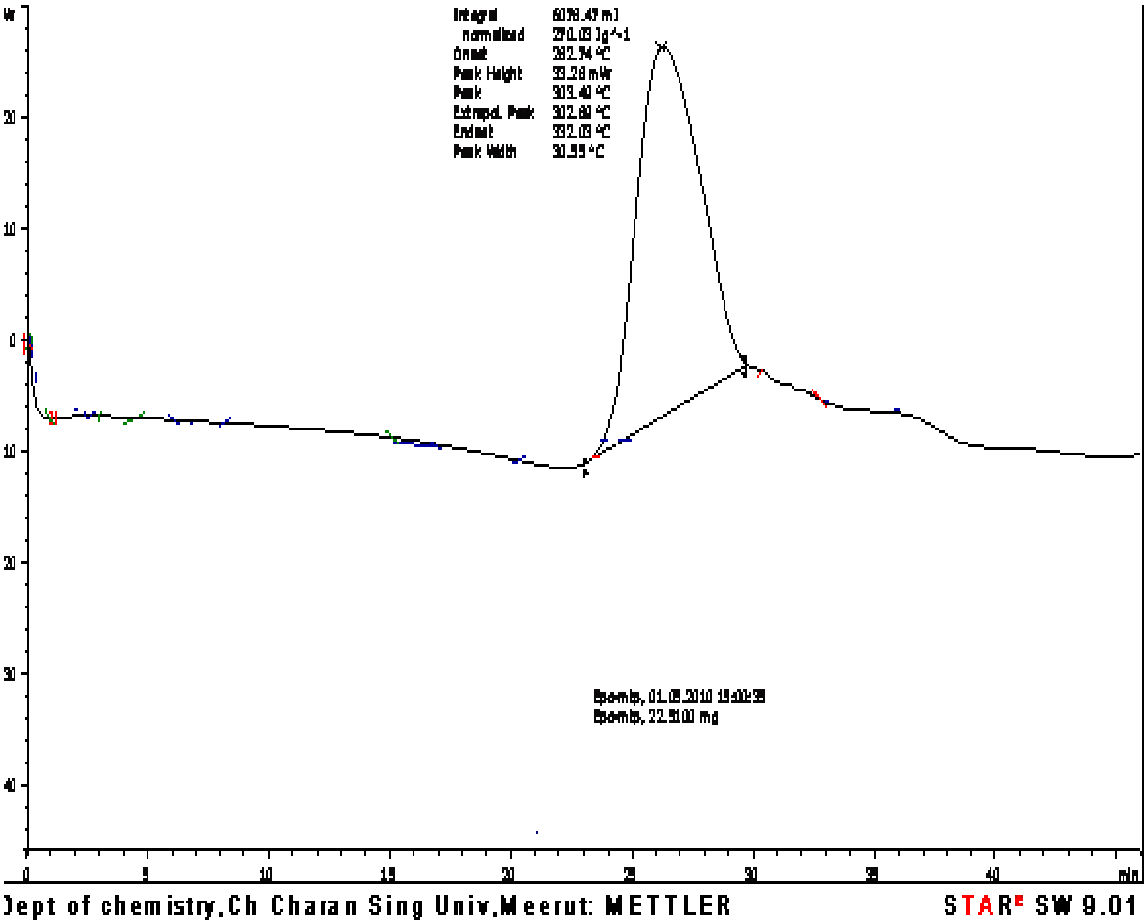


Fig 1 Dyanamic DSC Thermograms of N, N-Dimethyl terephthalamide with epoxy.

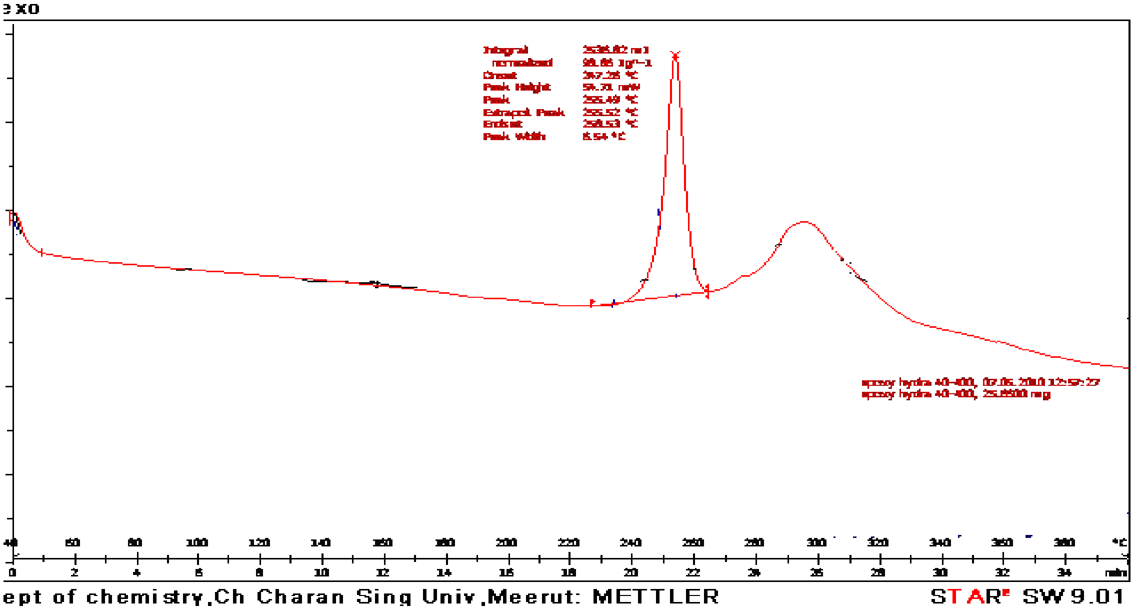


Fig 2 Dyanamic DSC Thermograms of Terepthalic dihydrazide with with epoxy

The curing kinetics of this sample was studied by DSC isothermal method keeping three constant temperatures at 260, 270 and 280 ^{0}C.

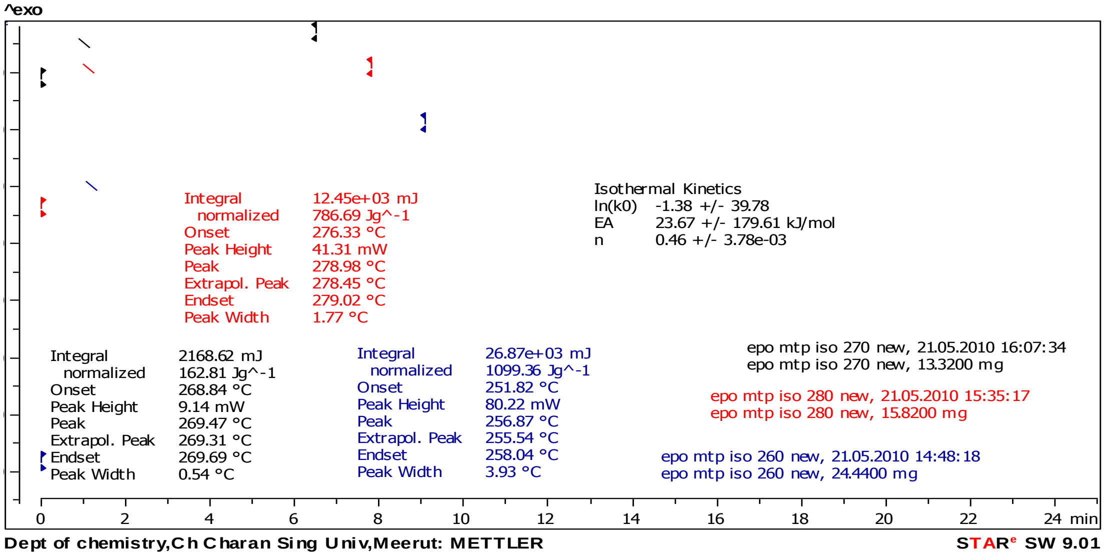


Fig 3. DSC Thermogram of the isothermal curve of N, N-Dimethyl terephthalamide with epoxy at 260, 270 and 280 ^{0}C

Small samples of 13.3, 15.8, 24.4 mg were weighed with the help of electronic balance. And these aluminum crucibles containing sample mixture were then sealed with the help of a hard press. The DSC thermograms recorded at three different temperatures were analyzed with the help of DSC kinetics software (STARe). The curve shows that increasing the temperature with increases the rate of reaction. These thermogram were analyzed with the help of STARe software and the analytic results shows that the energy of activation was found to be quite high of the range of 23.67 KJ/mole at 303.49 ^{0}C and the order of the reaction was observed near one i.e. 0.46.

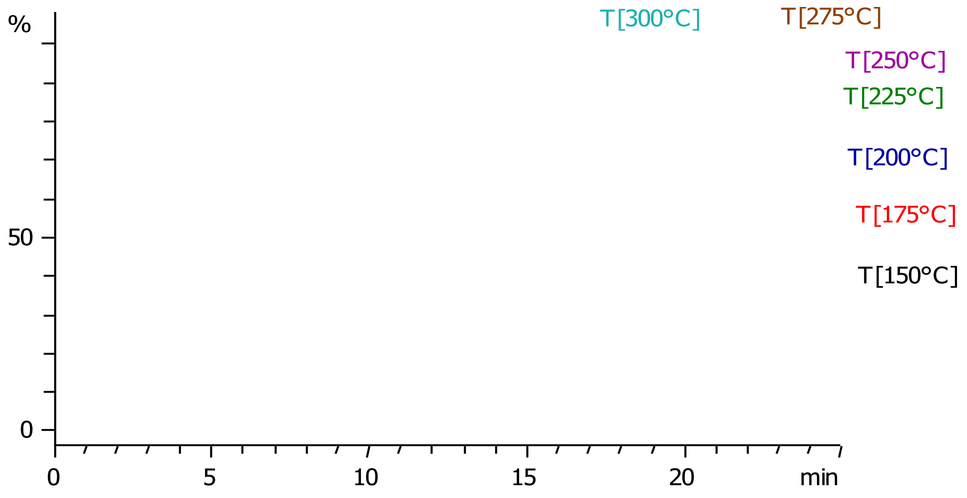


Fig. 4. Conversion kinetics of N, N-Dimethyl terephthalamide with epoxy

The Fig.4 shows as conversion plot between percentage of conversion verses time temperature constant at 150, 175, 200, 225, 250, 275 and 300 ^{0}C. It can be recorded that at 150 ^{0}C in 25 % is cure takes place with 25 minutes. While more than 90 % conversion can be obtained in 17.5 minutes at a cure in temperature of 300 ^{0}C.

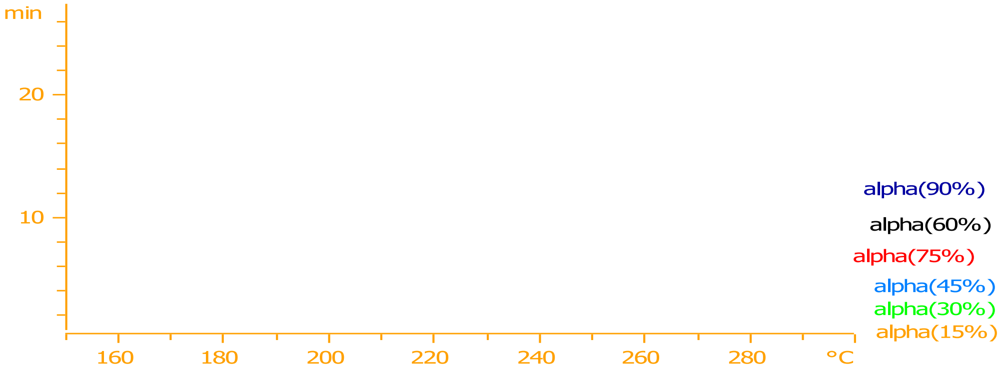


Fig. 5. Iso-conversion kinetics of N, N-Dimethyl terephthalamide with epoxy

Fig. 5 shows iso-conversion plot between curing time verses temperature. The slope line shows 15, 30, 45, 60, 75, and 90 % conversion at different temperature such as 150–300 ^{0}C. In this case the 90 % iso-conversion takes place at 280.09 ^{0}C and 250.8 ^{0}C in 15 minutes and 20 minutes respectively.

3.7. CURING KINETIC STUDIES OF TEREPTHALIC DIHYDRAZIDE WITH WITH EPOXY:

The curing kinetics of this sample was studied by isothermal method keeping temperatures constant at 230, 240 and 250 ^{0}C. Small samples of 21.0, 13.7, 27.9 mg were weighed with the help of electronic balance and these aluminum crucibles containing sample mixture were then sealed with the help of a hard press. The DSC thermograms recorded at three different temperatures were analyzed with the help of DSC kinetics software (STARe). The curve shows that increasing the temperature with increases the rate of reaction.

These thermogram were analyzed with the help of STARe software and the analytic results shows that the energy of activation was found to be quite high of the range of -0.16 KJ/mole at 253.49 ^{0}C and the order of the reaction was observed near one i.e. 0.76.

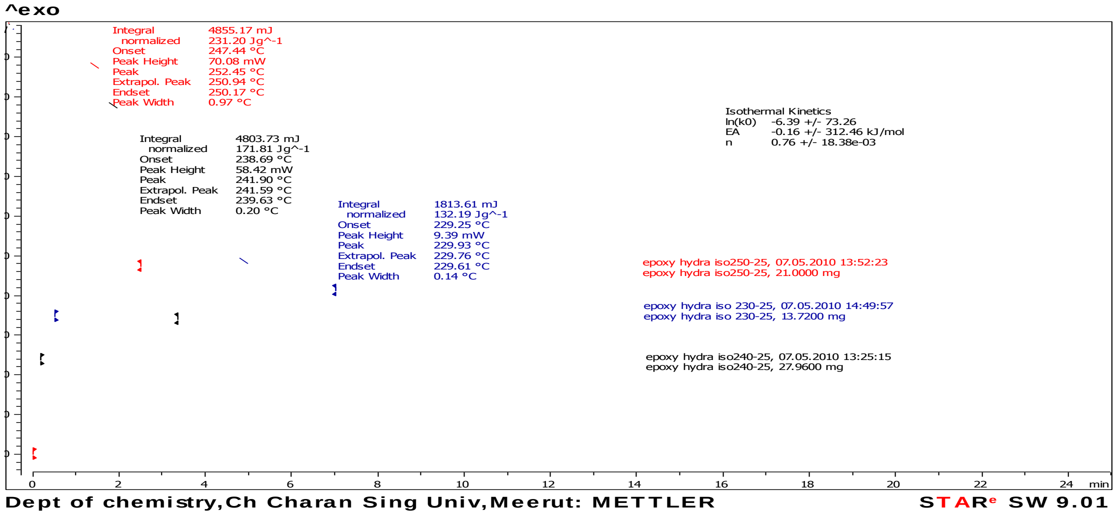
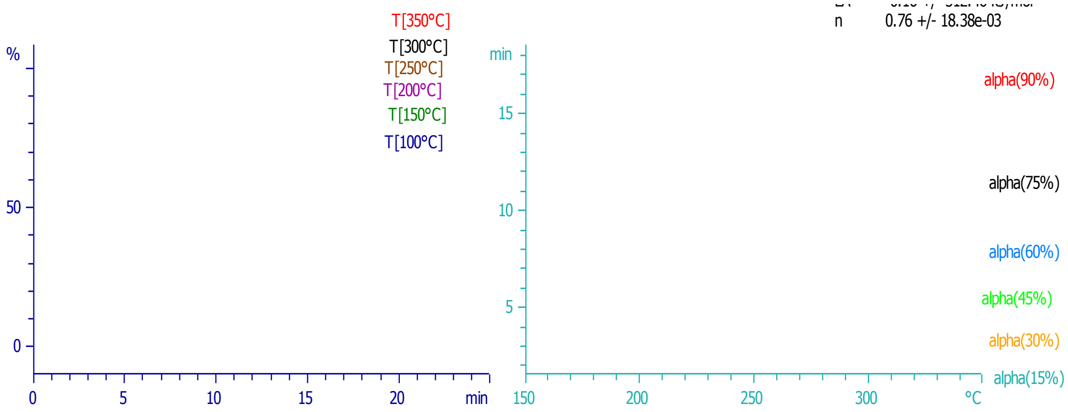


Fig-6. DSC Thermogram of the isothermal curve of Terepthalic dihydrazide with with epoxy at 230, 240 and 250 ^{0}C



(a) (b)

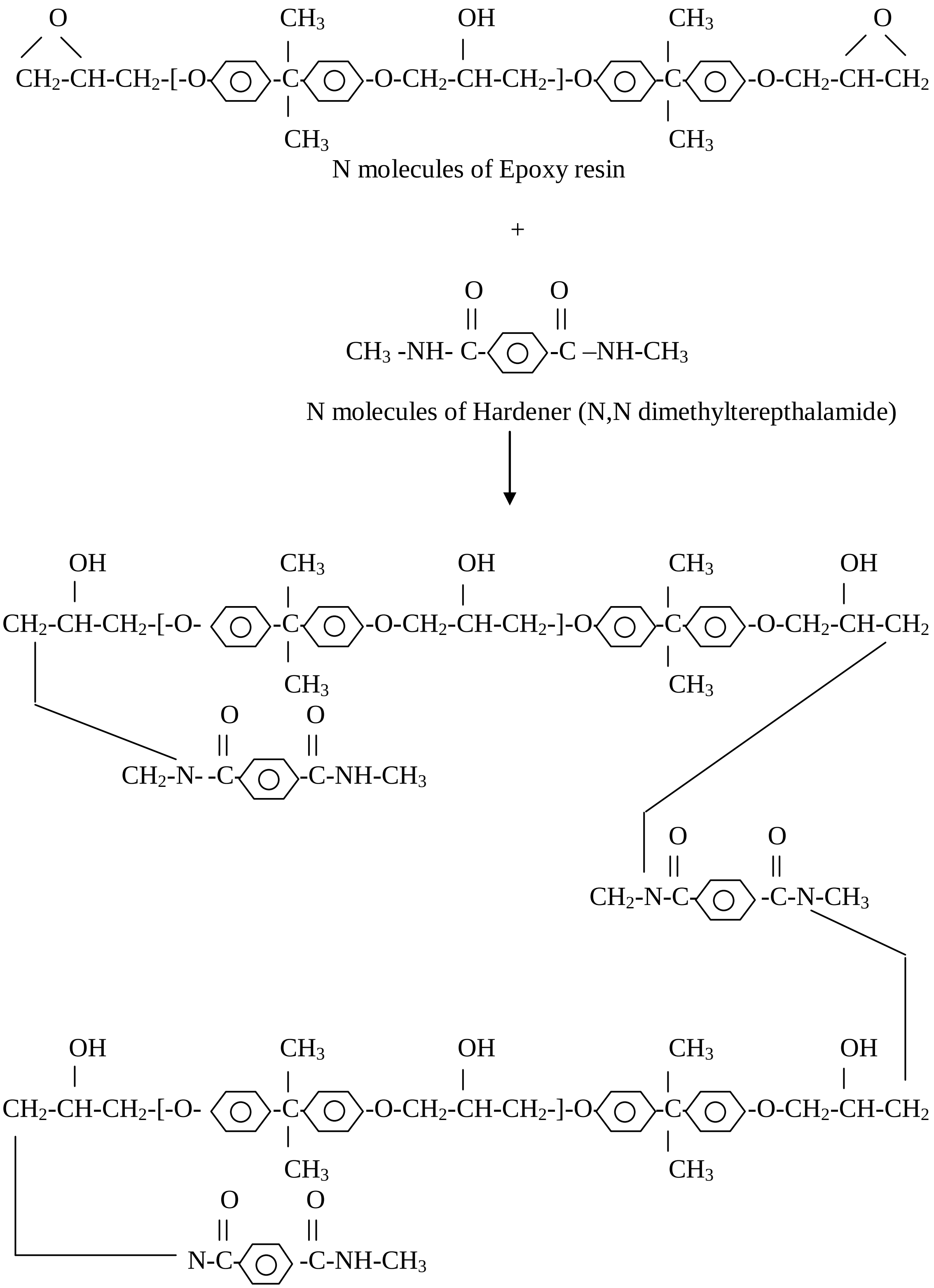
Fig. 7 Conversion and iso-conversion kinetics of Terepthalic dihydrazide with with epoxy

The Fig. 7.a. shows as conversion plot between percentage of conversion verses time temperature constant at 100, 150, 200, 250, 300 and 350 ^{0}C. It can be recorded that at 150 ^{0}C in 30 % is cure takes place with 3.25 minutes. While more than 90 % conversion can be obtained in 16.99 minutes at a cure in temperature of 350 ^{0}CThe Fig. 14.b. the slope line shows 15, 30, 45, 60, 75, and 90 % conversion at different temperature such as 150–350 ^{0}C. In this case the 90 % iso-conversion takes place at 100 ^{0}C and 350 ^{0}C in 16.64 minutes and 16.99 minutes respectively.

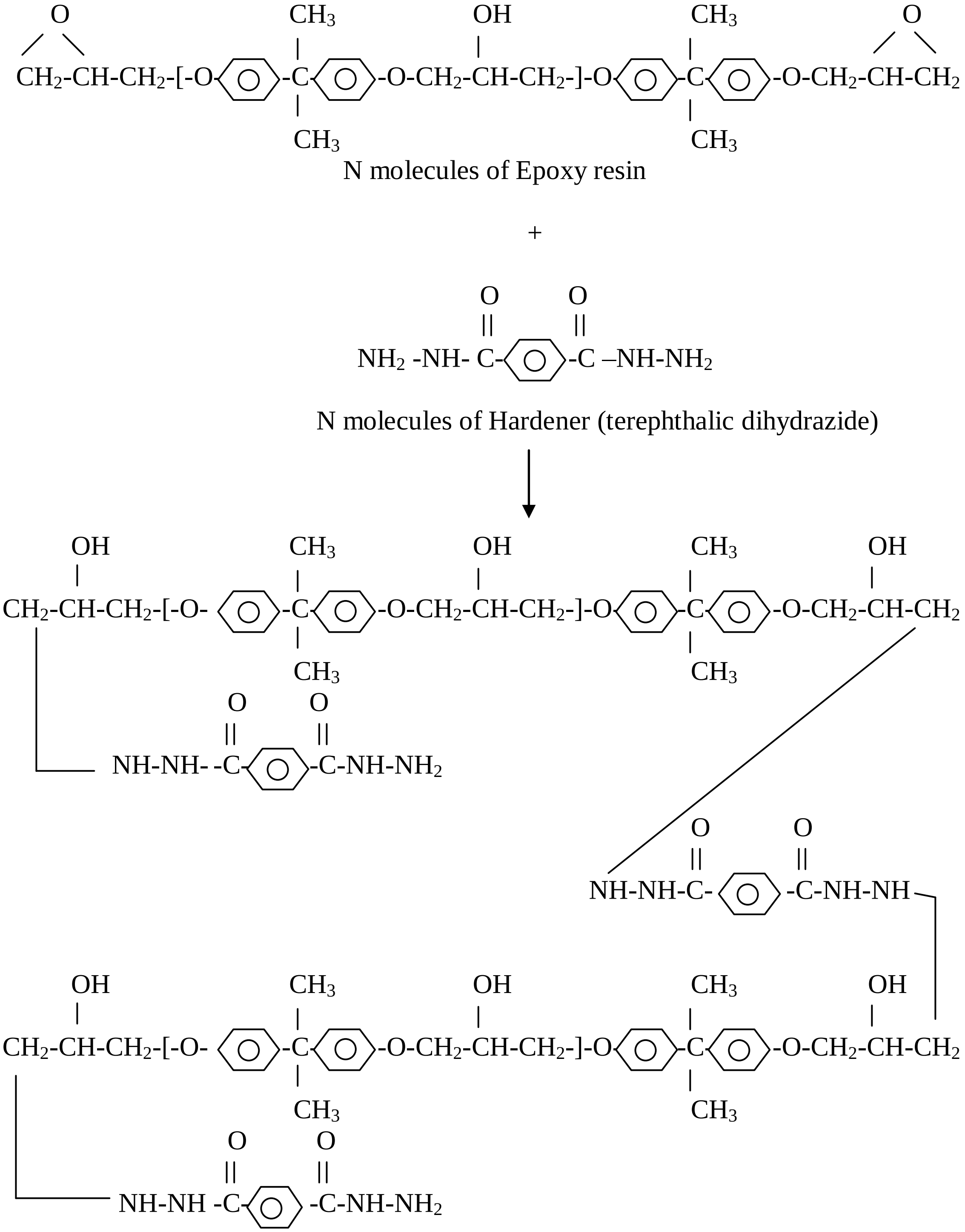
3.8. REACTION MECHANISM OF CURING:

The curing of the epoxy resin with aromatic amide 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 following reaction:

REACTION MECHANISM OF N, N-DIMETHYL TEREPHTHALAMIDE:-



REACTION MECHANISM OF TEREPTHALIC DIHYDRAZIDE:-



4 CONCLUSIONS:

The objective of the present work was develop an efficient methodology for aromatic amides hardening system for epoxy resin, which works at ambient conditions of temperature and pressure and consumes lesser time. The curing kinetics of aromatic amides used as hardener in di-glycidyl ether of bis-phenol was determined with the help of DSC by isothermal method. Thus, by using this reaction present recycling system could be transformed into a more eco friendly recycling technology.

REFERENCES:

1. Liello V.D, Martuscelli E, Musto P, Ragosta G, Scarinzi G, Thermochim. Acta, 344 (2000) 137.
2. Bonnet B. Lestriez, J. P. Pascault and H. Sautreau, J. Polym. Sci., Part B : 39 (2001) 363.
3. J. P. Pascault, H. Sautereau, J. Verdu and R. J. J. Williams, Thermosetting Polymers, Marcel Dekker Inc. New York 2002, p. 389.
4. Francis, G. V. Poel, F. Posada, G. Groeninckx, V. Lakshmana, R. Ramaswamy and S. Thomas, Polymer, 44 (2003) 3687.
5. J. M. Barton, in: Advances in Polymer Science, Vol. 72, Springer-Verlag, Berlin 1985, p. 112.
6. J. S. Shim, W. Lee and J. Jang, Polym. Bull., 25 (1991) 661.
7. H. Zhao, J. Gao, Y. Li and S. Shen, J. Therm. Anal. Cal., 74 (2003) 227.
8. R. M. Vinnik and V. A. Roznyatovsky, J. Therm. Anal. Cal., 76 (2004) 285.
9. S. Montserrat and I. Cima, Thermochim. Acta, 330 (1999) 189.
10. J. Macan, I. Brnardic, M. Ivankovic and H. J. Mencer, J. Therm. Anal. Cal., 81 (2005) 369.
11. Lapprand, C. Arribas, C. Salom, R. M. Masegosa and M. G. Prolongo, J. Mater. Process. Technol., 143 (2003) 827.
12. M. Sanchez-Cabezudo, M. G. Prolongo, C. Salom and R. M. Masegosa, J. Therm. Anal. Cal., 86 (2006) 699.
13. R. K. Soni and S. Singh, J. Appl. Polym. Sci. 96 (2005) 1515. Jain and R. K. Soni, J. Polym. Res. 14 (2007) 475.
14. Soni, R. K ; Soni, Dutt, K et. al. J. Appl. Polym. Sci. 113 (2009) 1090.
15. Soni, R.K; Singh, S; Dutt, K. J Appl. Polym. Sci. 115 (2009) 3074.