Chain Extended Bismaleimides

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Abstract

4, 4'-Bismaleimidodiphenyl ether (BMIE) was synthesized by chemical imidization and chain extended with three different aromatic diamines (4,4'-diaminodiphenyl ether (E) , 4,4'-diaminodiphenyl methane (M) and 4,4'-diaminodiphenyl sulfone (S). The main objective of this work is to study the thermal curing kinetics and thermal degradation kinetics of the different chain extended BMIE resins using Differential Scanning Calorimeter (DSC), Thermo Gravimetric Analysis (TGA) and Differential Thermal Gravimetry (DTG). Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa and Friedman methods were adopted to compute apparent activation energy for the curing kinetics and degradation kinetics. Exothermic transition indicative of curing was observed in DSC traces in the temperature range of 50-450^{0}C. The onset curing temperature for the chain extended BMIE decreases nearly 60^{0}C compared to pure BMIE. The apparent activation energy (E_a) values for curing and thermal degradation of the chain extended BMIE decreases compared to pure BMIE. Heat of polymerization (ΔH) decreases significantly by chain extension with aromatic diamines. Higher end set value in the chain extended bismaleimides showed an improvement in thermal stability.

Key words: *Bismaleimides, Chain extension, DSC, Curing kinetics, TGA, Degradation kinetics*

1. Introduction

Bismaleimides have become a leading class of thermosetting polyimides. Their excellent processability and balance of thermal, mechanical and electrical properties have made them popular in advanced composites and electronics. The principal concern with bismaleimide resins has been their inherent brittleness owing to their high cross-link density. The most important property of bismaleimide is its ability to undergo a temperature-induced polymerization. The brittleness of the bismaleimides has been improved by various techniques

such as dispersion of nanoparticles into the bismaleimide resin systems, copolymerization with functionalized compounds such as epoxies, cyanates, allylphenols, Michael addition reaction of bismaleimides[1,2].

Varma *et al*. studied the thermal and mechanical properties of the chain extended bismaleimides using aliphatic diamines having 2,4 or 6 methylene groups (EDA,DAB,HMDA) and diethylene triamine (DETA).They reported that the chain extension of bismaleimides with aliphatic amines significantly reduces the curing temperatures increasing the methylene content of the aliphatic amines leads to slight reduction in onset temperature of curing ($\approx 6^0$C).Heat of polymerization (ΔH)decreases significantly by chain extension with diamines[3].

Reaction of the aromatic diamines with bismaleimides may yield products with better processing characteristics, However, only a small amount of such amines should be used in such reactions because the incorporation of aromatic amines in the polymer backbone may lead to deterioration in high temperature capabilities of these resins. It would be of interest to study the chain extension reaction of bismaleimides with aromatic diamines. In the present paper we report the effect of chain extension of BMIE on the three different model free kinetic methods (KAS, FWO and FRD) were used to calculate the apparent activation energies (E_a). The curing process and degradation process were investigated using DSC, TGA and DTA techniques and the results are presented and discussed.

2. Kinetic studies

The rate of solid-state reactions can be described using the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where dα/dt is the rate of the reaction, k(T) is the rate constant, and f(α) is the reaction model. According to Arrhenius's equation, the temperature-dependent rate constant, k(T) is defined using the following equation:

$$k(T) = A exp(-\frac{E_a}{RT}) \tag{2}$$

where A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, and T is the temperature.

The reaction extent (α) for the degradation reaction is calculated using the following equation:

$$\alpha = (W_0 - W_T)/(W_0 - We) \tag{3}$$

2.1.Kissinger-Akahira-Sunose (KAS) method

This method is based on the expression [4,5,6]

$$ln\,(\beta/T2) \;=\; ln(AR/Ea) - Ea\,/RT \tag{4}$$

Where, β= heating rate,T=temperature, A= pre-exponential factor, R= gas constant and Ea=apparent activation energy. The plot of $ln(\beta/T^2)$ *vs* 1/T gives straight line and the slope of this line equals -Ea/R by which the activation energy has been calculated.

2.2. Flynn-Wall-Ozawa (FWO) method [7]

Flynn-Wall-Ozawa method is widely used for dynamic kinetic analysis and does not require any assumptions to be made about the conversion dependence. This method involves the measurement of the temperature T, corresponding to a fixed value of degree of conversion α, from the experiments at different heating rates, β.

The FWO method uses Doyle's approximation and the equation is given as

$$\log \beta = 0.457(-Ea/RT) + [\log(A\,Ea/R) - \log f(\alpha) - 2.315] \tag{5}$$

The plot of log β *vs*1/T gives the slope which equals -0.457 Ea/R by which the activation energy has been calculated. If the determined Ea is the same for the various values of *α*, the existence of a single step reaction can be concluded with certainty.

2.3. Friedman (FRD) method

This is one of the differential methods to calculate the apparent activation energy and the equation is:

$$ln\,(d\alpha/\,dt)=ln\,z +n\,ln\,(1-\alpha)-(Ea/RT) \tag{6}$$

where α is the reaction extent and z is constant. From the slope (-Ea/R) of the linear plot between ln(dα/dt) versus 1/T, the activation energy Ea of the system can be calculated.

3 Experimental

3.1. Materials

Toluene, N,N'-dimethyl formamide (DMF), *p*-toluene sulfonic acid (*p*-TSA), maleic anhydride and acetone were obtained from s.d. fine chemicals Pvt. Ltd., Mumbai. 4,4'-Diaminodiphenyl ether, 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl sulfone were purchased from Hi-media Pvt. Ltd., Mumbai.

3.2. Preparation of bisamic acid

4, 4'- Diaminodiphenyl ether (12.62 g) and 160 mL of acetone were taken in a 250 mL round bottom flask. The contents of the flask were continuously stirred with the help of a mechanical stirrer. After 5 minutes of stirring, 12.36 g of powdered maleic anhydride was added in small portions and it was allowed to stir for a further period of half an hour. Yellow precipitate of bisamic acid was obtained. Finally the precipitate was filtered, washed with cold acetone and dried. Bisamic acid was synthesized in our laboratory as per the reported procedure(Scheme 3.1)
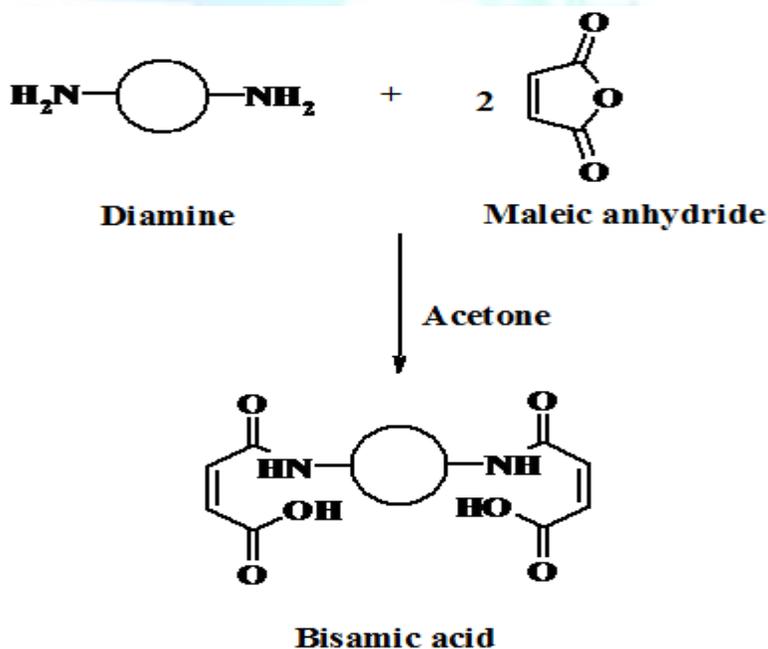
Scheme 3.1 Formation of bisamic acid

3.3. Preparation of 4,4'-bismaleimidodiphenyl ether(BMIE)

By using the appropriate bisamic acid (21.8 g) the BMIE was synthesized in toluene medium. Toluene (105 mL) was used to form a slurry of the bisamic acid and this slurry was constantly stirred using mechanical stirrer. After 10 minutes, 1.29 g of *p*-TSA was added to the mixture with continuous stirring. Then the reaction flask was heated to 120 °C by using an electrically heated oil bath. To the mixture, 9 mL of DMF was added in portions. The reaction was carried out with constant stirring for 8 to 10 hours until a clear solution was obtained. During the time of refluxing, 1.8 mL of water was separated. Maximum amount of toluene was removed by distillation and the concentrated reaction mixture was sufficiently cooled and poured into copious amount of crushed ice kept in a beaker. The precipitate was filtered and dried. Bismaleimide was synthesized as per the scheme 3.2.
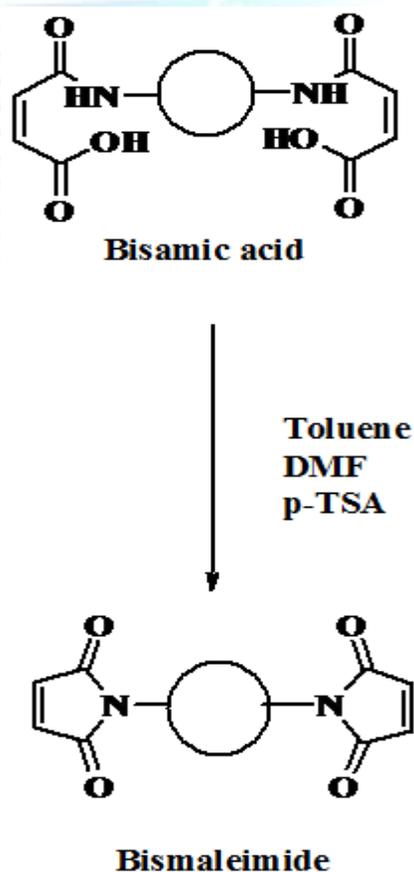
Scheme 3.2. Synthesis of bismaleimide

3.4. Synthesis of chain extended bismaleimides

The bismaleimide was dissolved in 50 mL of acetone kept in a 100 mL round bottom flask. The requisite quantity of the aromatic diamine (0.3mol) was added to the bismaleimide solution and the content was refluxed. After 5 hours, acetone was distilled and the shinning powdery product of chain extended bismaleimide was obtained. By using t h e bismaleimide (BMIE) and three different aromatic diamines (E, M and S), three different chain extended bismaleimides (BMIE-E, BMIE-M and BMIE-S) were synthesized.

4.Methods

Differential scanning calorimetry.

Differential scanning calorimetric analysis was carried out by using DSC Q20 of TA instruments (New Castle, Delaware, USA). Nearly 2.4 mg of the sample was used to do the experiment. The DSC curves were recorded by heating the material at different heating rates (β = 10, 20 and 30^{0}C/min) from 50^{0}C to 350^{0}C in a constant flow of nitrogen (50 mL /min). Thermogravimetric analysis.

The degradation behavior of the chain extended bismaleimides was examined using TG analyzer (model Q50, TA Instruments). The measurements were carried out using approximately 4–5 mg sample under nitrogen atmosphere and the flow of nitrogen to the balance area was 40 mL/ min, and the sample was swept with a nitrogen flow of 60 mL/ min and the materials were heated from 40^{0}C to 800^{0}C using different heating rates(10, 20 and 30^{0}C/min).

5.Results and Discussion

DSC Studies

The DSC traces for the curing of pure BMIE and BMIE-S at different heating rates 10, 20 and 30^0 C/min are shown in figure 5.1. The values obtained from the DSC curves such as onset (T_i), maximum (T_{max}) and endset (T_e) curing temperatures of BMIE, BMIE-E, BMIE-M and BMIE-S cured at 10, 20, and 30^{0}C are tabulated in Table5.1. The DSC curves for all the four materials at a heating rate 20^{0}C are shown in figure 5.2. The detailed observations from the DSC curves recorded at 20^{0}C/min are discussed.
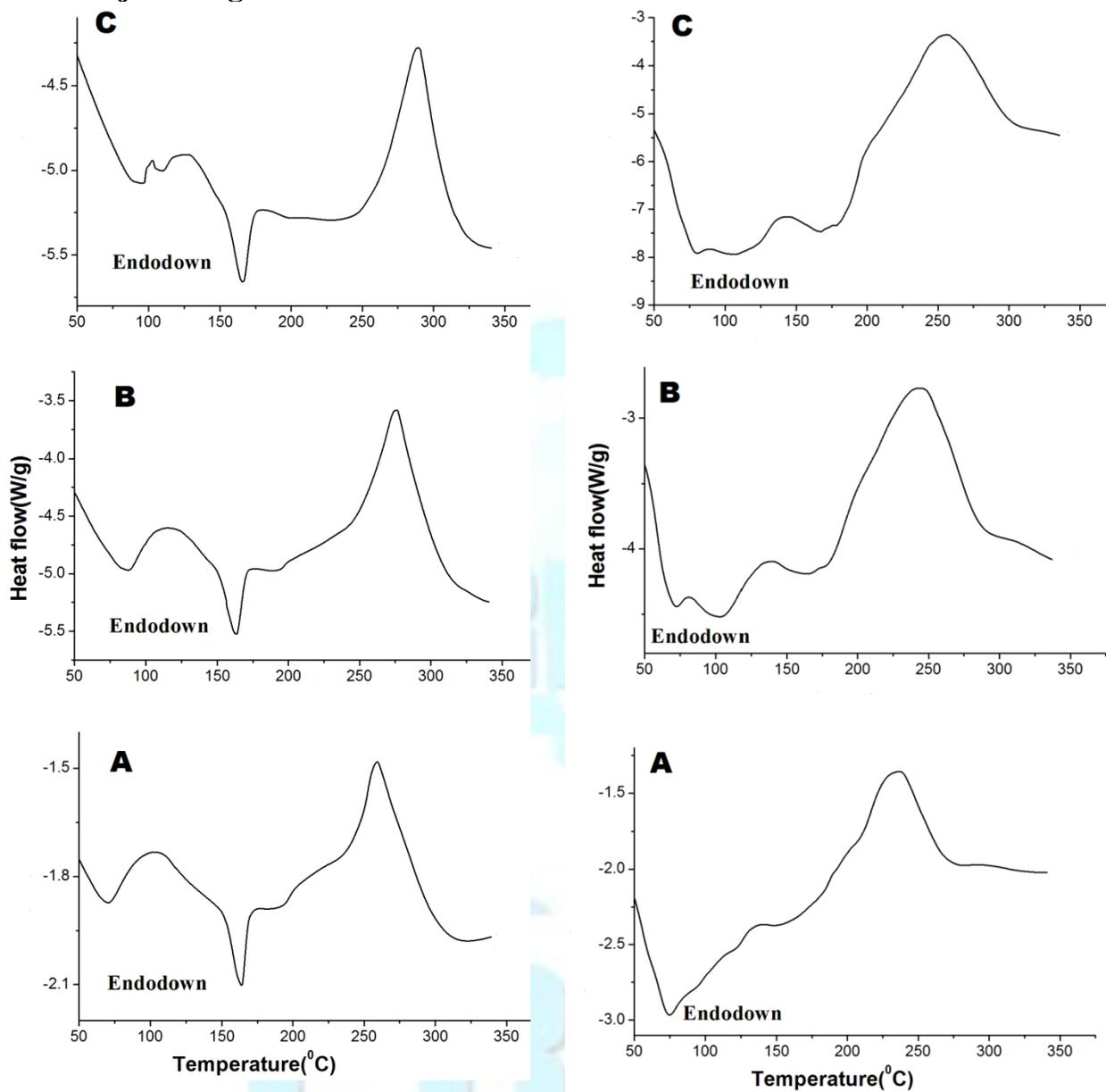
Figure 5.1.DSC curves for BMIE and BMIE-S at A=10 B=20 and C=30^0C/min.

Table 5.1. DSC parameters for BMIE and Chain extended BMIE's

Material	Heating rate	T_m (^0C)	T_s (^0C)	T_{max} (^0C)	T_e (^0C)	ΔH_C (J/g)
BMIE	10	163	180	258	340	126
	20	167	190	277	335	218
	30	108	205	289	340	79
BMIE-E	10	135	150	225	300	65
	20	105	160	244	298	52
	30	135	165	268	310	91
BMIE-M	10	120	134	247	288	51
	20	118	150	263	287	76
	30	122	157	264	290	80
BMIE-S	10	75	150	238	325	310
	20	72	163	249	327	282
	30	73	180	245	340	482

BMIE shows a sharp melting point at 167^0C and the material is found to be stable till 190^0C and this thermal polymerization is over at around 335^0C and the maximum is located at 277^0C. The enthalpy of curing for the polymerization of BMIE is 218J/g. The area under the exothermic represents 100% of cure. Similarly the compound such as BMIE-E, BMIE-M and BMIE-S shows sharp melting points at 105^0C, 118^0C and 72^0C respectively. It starts to cure at around 160^0C, 150^0C and 163^0C and the thermal polymerizations are over at around 298^0C, 287^0C and 327^0C. T_{max} at 244^0, 263^0 and 249^0C respectively. The enthalpy of curing for the polymerization of BMIE-E, BMIE-M and BMIE-S are 52, 76 and 282 J/g respectively. The variation of the ΔH_c values with change in heating rate may be attributed to the different in the nature and extent of the cure reaction followed by change in the structure of the cross-linked molecular network[8].
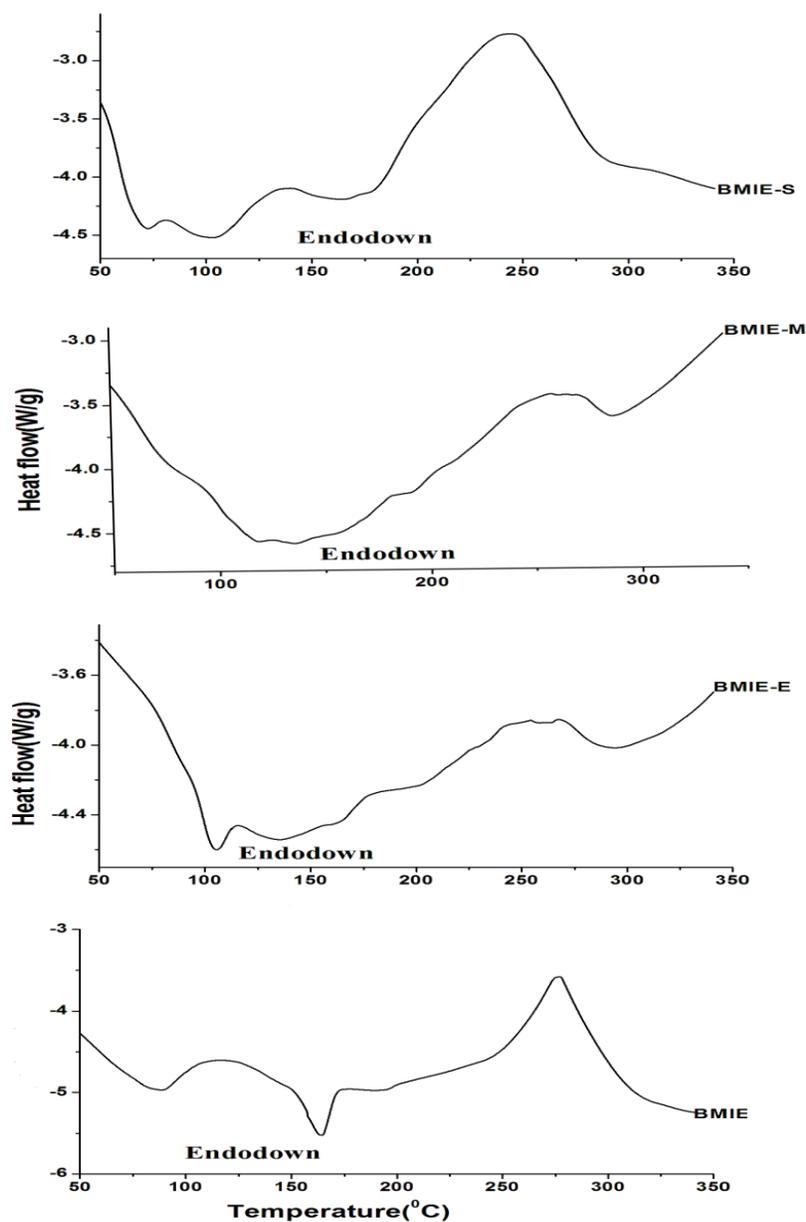
Figure 5.2. DSC curves for BMIE and Chain extended BMIE's

In all the cases there is a considerable decrease in the curing onset maximum and end set temperatures of BMIE-E, BMIE-M and BMIE-S when compared to pure BMIE. This is due to the chain extension of bismalemides.

CURE KINETICS

Experimental data obtained from the DSC curves for the BMIE and chain extended BMIE's at three different heating rates (10, 20, 30^{0}C/min) are used for the kinetic analysis of the curing behavior. The apparent E_a for the curing process has been calculated using three model free kinetics methods, namely KAS, FWO and FRD of which FRD method belongs to differential approximation method, whereas the other two methods are integral approximation methods. The apparent E_a is calculated for various reaction extents (α) ranging from 0.2 to 0.8. The following recommendation was developed by the kinetics committee of the international confederation for thermal analysis and calorimetric that the relative experimental errors in the kinetic data are larger at the lowest and highest conversions, it might be advisable to limit analysis to certain ranges[9,10].
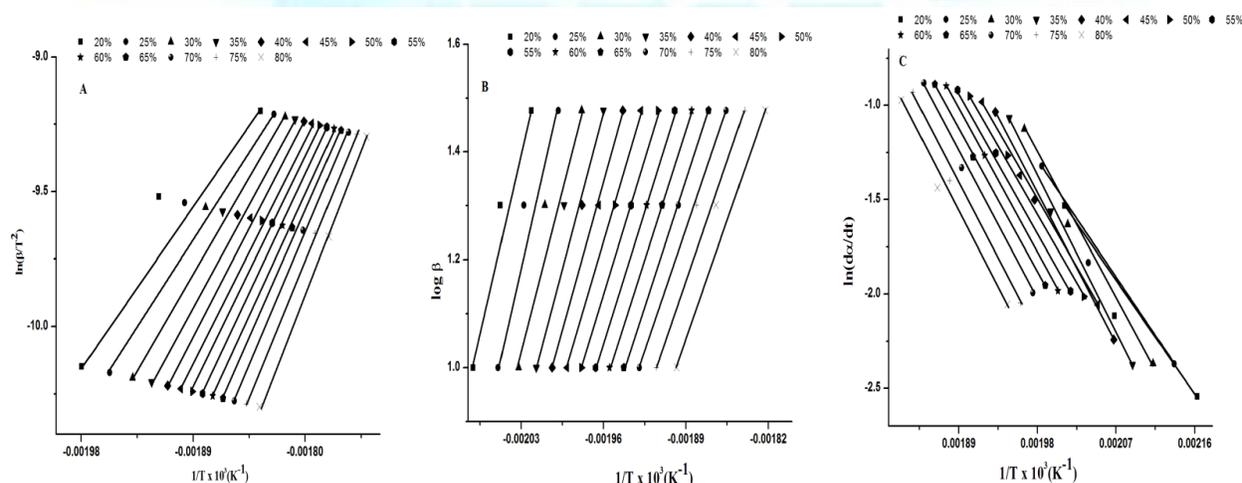

Figure5.3. (A) KAS plot for BMIE (B) FWO plot for BMIE-S (C) FRD plot for BMIE-E

KAS, FWO and FRD plots for the samples BMIE, BMIE-S and BMIE-E are represented in figure 5.3. The straight lines in the plots indicate the validity of the KAS, FWO and FRD analysis for this system investigated. In the FRD plots, the lines are nearly parallel above 30% conversion, which implies the possibility of single reaction mechanism. The apparent activation energy for the curing of the BMIE and chain extended BMIE's calculated using these three methods are tabulated in table5.2

Generally in the curing process (or) the curing reactions off thermoset resins, molecules undergo gelation ie., from liquid to rubber and finally vitrification like rubber to glass transitions. The cross linking process reduces the molecular mobility and results in a change from a kinetically controlled to a diffusion controlled reaction during the curing of thermosetting resins.[11,12] Hill and Coworkers studied the kinetics and curing mechanism of bismaleimide-diamine thermosets matrix systems. They reported that an excellent fit to the experimental data for the consumption of primary and secondary amines was obtained with the kinetic rate laws up to approximately 70% conversion at higher conversions, a negative deviation from the predicted rates was found. This was attributed to vitrification, which to an element of diffusion control in the reaction [13].

The plots between the different α values and the corresponding E_a values for the compounds BMIE and BMIE-M are presented in figure 5.4. Both the integral methods lead to nearly the same E_a value and the trend in variation of E_a with respect to α was also found to be similar. Although the E_a values calculated using the differential method are within the range, slight deviations are noted and is attributed to the initial approximations made.
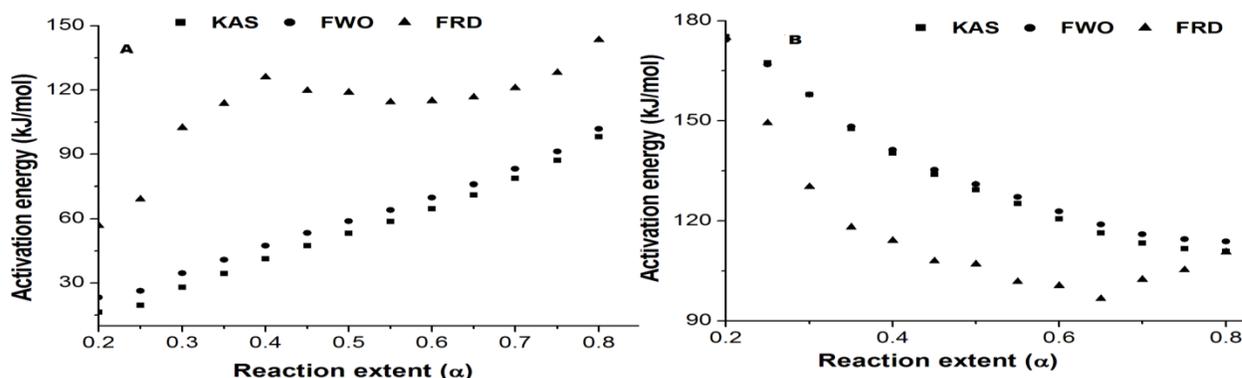
Figure5.4. KAS, FWO and FRD plots for BMIE-M and BMIE-S

The change in E_a with respect to the reaction extent for the methods, KAS and FWO are found to be very similar and the values are in close agreement, but the values differed substantially from the value of E_a obtained with the iso-conversional method suggested by FRD. The plots of activation energy versus reaction extent for the curing of the samples calculated

using KAS method is shown in figure5.5.The shape of the activation energy curve $E_a = f(\alpha)$, indicates directly whether the reaction is simple or complex. For a simple process, it is practically constant as defined by the nth order kinetics (NOK) model.

So in this investigation the apparent activation energies of pure BMIE and chain extended BMIE's were calculated for the reaction extent values of 0.2-0.8.The apparent activation energy values for BMIE were observed to increase (55-95 KJ/ mol) gradually with increasing extent of reaction (α) (0.2-0.8) using KAS method. Initially, the concentration of the monomer BMIE was high and hence, the polymerization reaction was easier and required low energy for the reaction. As the reaction proceeded, apart from increase in viscosity,the availability of monomer for the polymerization is decreased. This increase in viscosity and the dearth in the polymerizable groups made the cross linking reaction difficult.

Table 5.2 Activation energies for the curing BMIE and chain extended BMIE's

Sample	Ea values (KJ/mol)												
α	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75	0.8
BMIE	KAS	53.6	59.6	65.2	70.2	74.5	77.9	80.6	82.9	85.1	87.7	90.8	93.6	96.7
	FWO	59.2	64.9	70.4	75.2	79.3	82.6	85.2	87.4	89.5	92.0	94.9	97.7	100.6
	FRD	98.9	108	112	115	114	111	111	110	114	119	124	126	122
BMIE-E	KAS	52.4	52.0	53.4	56.0	58.55 59.9	60.9	61.6	70.9	63.2	64.1	65.1	66.20
	FWO	57.3	57.1	58.5	61.0	63.5	64.8	65.8	66.6	67.4	68.3	69.2	70.2	71.3
	FRD	53.7	56.0	69.1	76.3	73.1	66.9	67.9	68.8	70.5	69.8	73.2	74.3	73.1
BMIE-M	KAS	16.4	19.5	27.9	34.4	41.3	47.5	53.1	58.6	64.7	71.1	78.7	87.1	98.2
	FWO	23.3	26.4	34.6	40.8	47.4	53.4	58.8	64.1	69.8	75.9	83.2	91.3	101
	FRD	56.8	69.1	102	113	125	119	118	114	115	117	121	128	143
BMIE-S	KAS	175	167	157	148	140	134	129	125	120	116	113	111	110
	FWO	174	167	158	148	141	135	131	127	123	119	116	114	113
	FRD	175	149	130	118	114	108	107	102	101	97	102	105	111

At the temperature increased linearly in the non isothermal experiments, the chain mobility increased and the chemical reactions were reactivated. This results in increase in the

activation energy or the higher reaction extent levels. So at this stage, the system needs higher energy for polymerization and so the apparent activation energy gradually increased.

The rapid decrease in the activation energy at higher reaction extent levels could be explained by the change in the reaction mechanism from kinetically controlled to diffusion controlled and the monomer molecules became frozen in their position in the glassy state and this resulted in a virtual cessation of the reaction, the chemical reactions were considerably reduced. This meant that vitrification caused dramatic decreases in the molecular mobility, which led to a decrease in the effective activation energy with increasing extent of reaction. The chain extension using sulphone in the BMIE-S must have some influence on the curing process of BMIE[14,15].
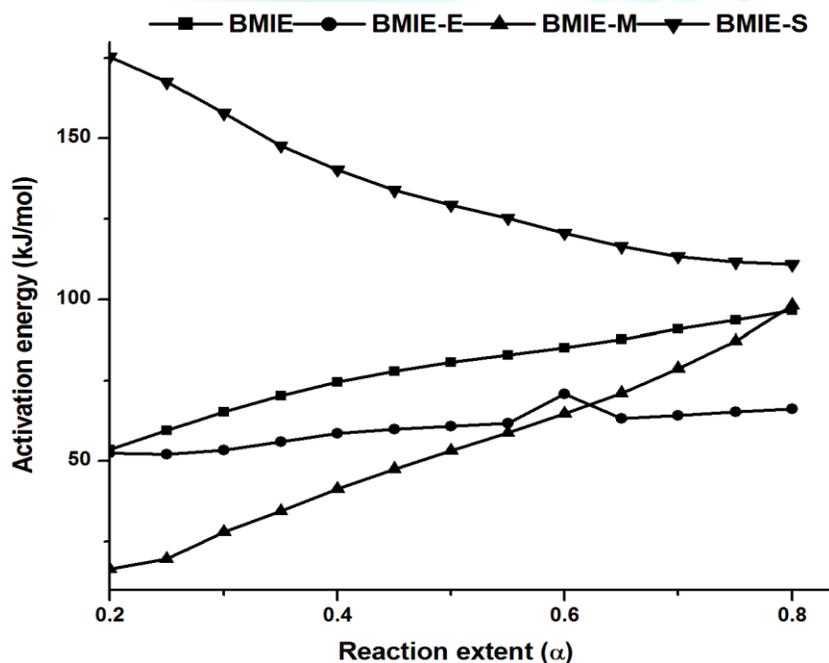
Figure 5.5. Activation energies calculated using KAS method for different conversions of BMIE and chain extended BMIE's

Similarly BMIE-M shows in the variation of activation energy like that of BMIE but the activation energy of BMIE-E is having a small change up to 0.8 reaction extent. The activation energy for the curing process of BMIE-S increases nearly by 120 KJ/mol than BMIE. Increase in the activation energy means that more energy is required for the reaction component to complete the reaction in addition to the exothermic reaction indicating an acceleration effect. This phenomenon is exhibited in the case of BMPM/diallyl bisphenol A resin system. In the case of BMPM/DABA, the allyl phenol compounds react with BMPM to give linear chain extension by an ene type reaction and this is followed by a Diels-Alder reaction at a higher temperature.

The reaction is complex with multiplet reactions and formation of succinimide groups by the conversion of maleimide moieties occurs. The activation energy steadily increases at approximately 6 KJ/mol per percentage conversion. It is noteworthy to mention at this juncture,the calculation of kinetic parameters from single thermogram must be totally avoided as per the recommendations made by The International Confederation of Thermal Analysis and Calorimetry projects (ICTAC) 2000 for valid reasons mentioned.

TGA and DTG studies

The TG and derivative TG curves for thermally cured BMIE and chain extended BMIE's are recorded at various heating rates (10,20 and 30^0C/min) under nitrogen atmosphere are shown in figure 5.6.All the thermograms are shifted to higher temperatures with increasing heating rates. The T_i ,T_{max} , T_e values for the degradation and char residue obtained at 800^0C for all the samples noted at multiple heating rates 10, 20 and 30^0C are tabulated in table 5.3.The detailed observations of the thermogravimetric data for the samples obtained at a heating rate of 20^0C/min are discussed below and shown in figure 5.7 .
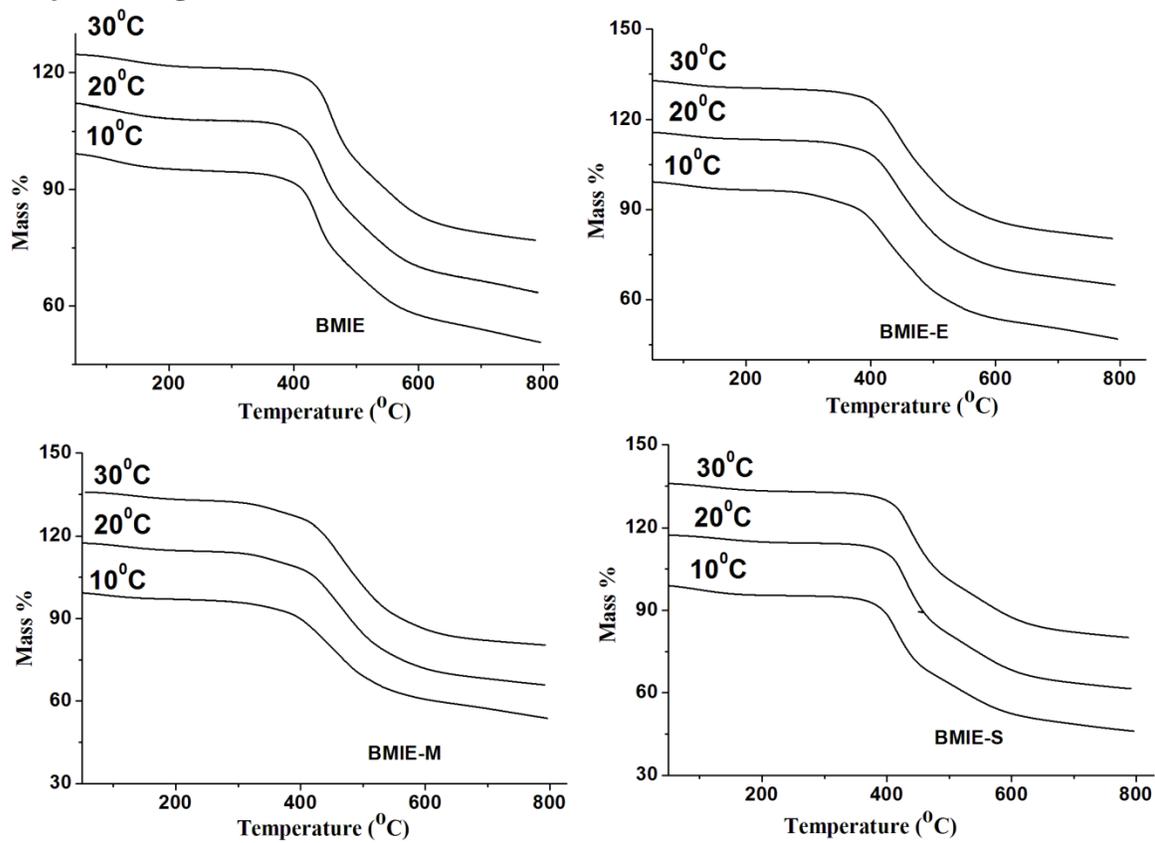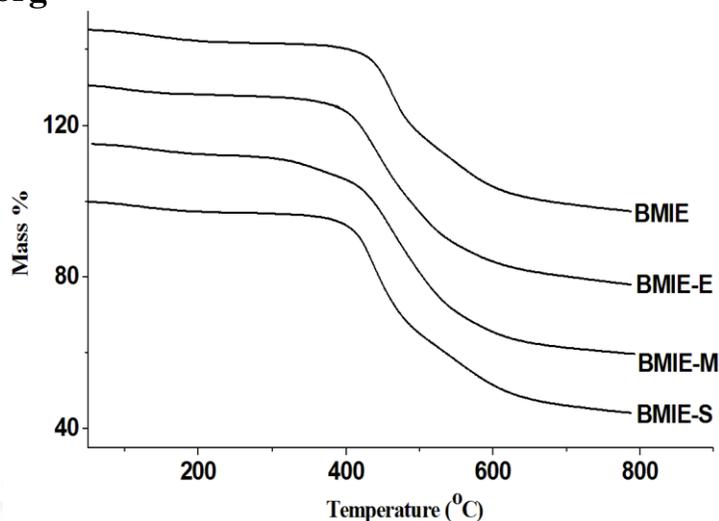
Figure 5.6.TG curves of BMIE and chain extended BMIE's.

The DTG curve of thermally cured BMIE and chain extended BMIE's are shown in figure 5.8. BMIE shows two degradations overlapping each other indicating that the second degradation of the BMIE starts before the completion of the first degradation. The initial weight loss starts at around 395^0C and the second weight loss starts at 520^0C.The amount of char left over at 800^0C is found to be 55%.The introduction of aromatic diamines in pure BMIE and the polymers derived from them by thermal curing BMIE-E, BMIE-M and BMIE-S shifts the initial degradation temperature to 325,340 and 365^0C respectively, a heating rate at 20^0C/min.

| Material	Heating rate (°C/min)	Onset Ts(°C)	Maximum Tmax(°C)	Endset Te(°C)	Char value at 800^0C(%)
BMIE	10	390	440	570	55
	20	395	445	580	54
	30	380	460	610	55
BMIE-E	10	290	410	575	46
	20	325	425	600	47
	30	340	425	615	47
BMIE-M	10	315	450	560	48
	20	340	460	605	48
	30	340	450	645	47
BMIE-S	10	350	410	610	44
	20	365	420	640	45
	30	370	420	650	45

Table 5.3 Data obtained from the thermogravimetric curves of thermally cured pure BMIE and chain extended BMIE'S

Figure 5.7 TG curves of BMIE and chain extended BMIE's at 20^0C/min

Among the different chain extended BMIE's, BMIE and BMIE-E shows very fast degradation as evidenced by the DTG curves. The authors investigated the thermal properties of thermally cured structurally different bismaleimides. All the investigated materials show two overlapping degradations. From this one can conclude that the bismaleimide matrix systems are having nearly similar degradation mechanisms.
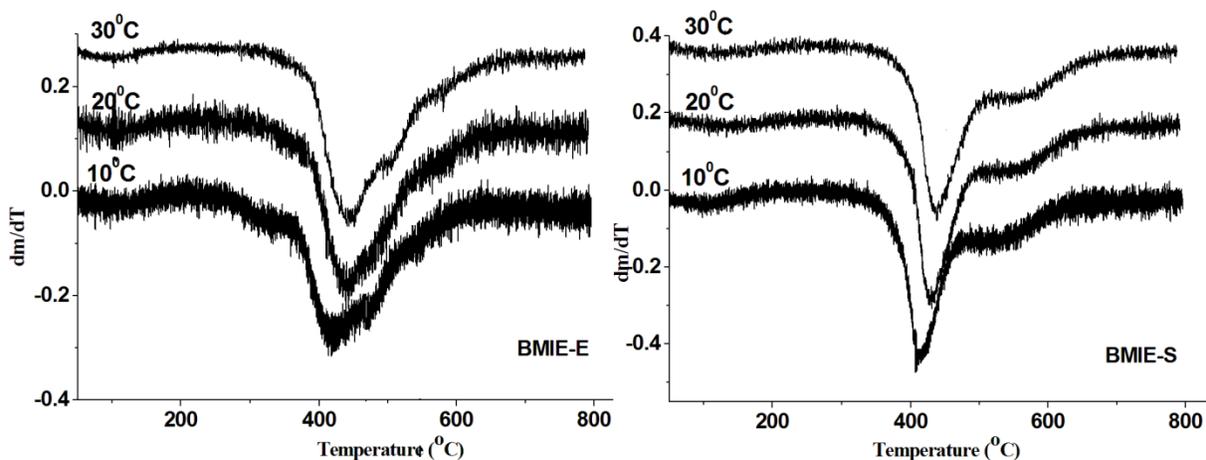

Figure5.8. DTG curves of BMIE and chain extended BMIE's

The first stage decomposition was accounted for a 20% weight loss up to 520^0C.The reason for the early weight loss compared to BMIE may be due to the loss of diamine *via* Michael addition.

Kinetic analysis

Experimental data obtained from TG curves for all the thermally cured materials at three different heating rates (10, 20, 30 ^{0}C /min) are used for the kinetic analysis of the degradation. Present study utilizes three model-free iso-conversional kinetic methods (KAS, FWO and FRD) for the calculation of apparent activation energies, for the degradation of thermally cured samples and the results are compared. Straight lines are obtained for the plot of ln (β/T2) versus 1/T, log β versus 1/T, and ln(dα/dt) versus 1/T for KAS,FWO and FRD, respectively, indicate the validity of the three methods for the present systems. In these plots, the lines are nearly parallel up to 65 % degradation, which implies the possibility of single reaction mechanism. But above 65 % degradation the lines are not parallel; indicating the occurrence of much complex degradation reactions. Similar trend is noticed for other cured materials investigated. The apparent activation energy values calculated for the degradation of cured samples by KAS and FWO methods are same, but the values obtained by the FRD method differ from other two methods. This is due to the way in which the activation energy was calculated that is KAS and FWO methods are integral methods and FRD is differential method.
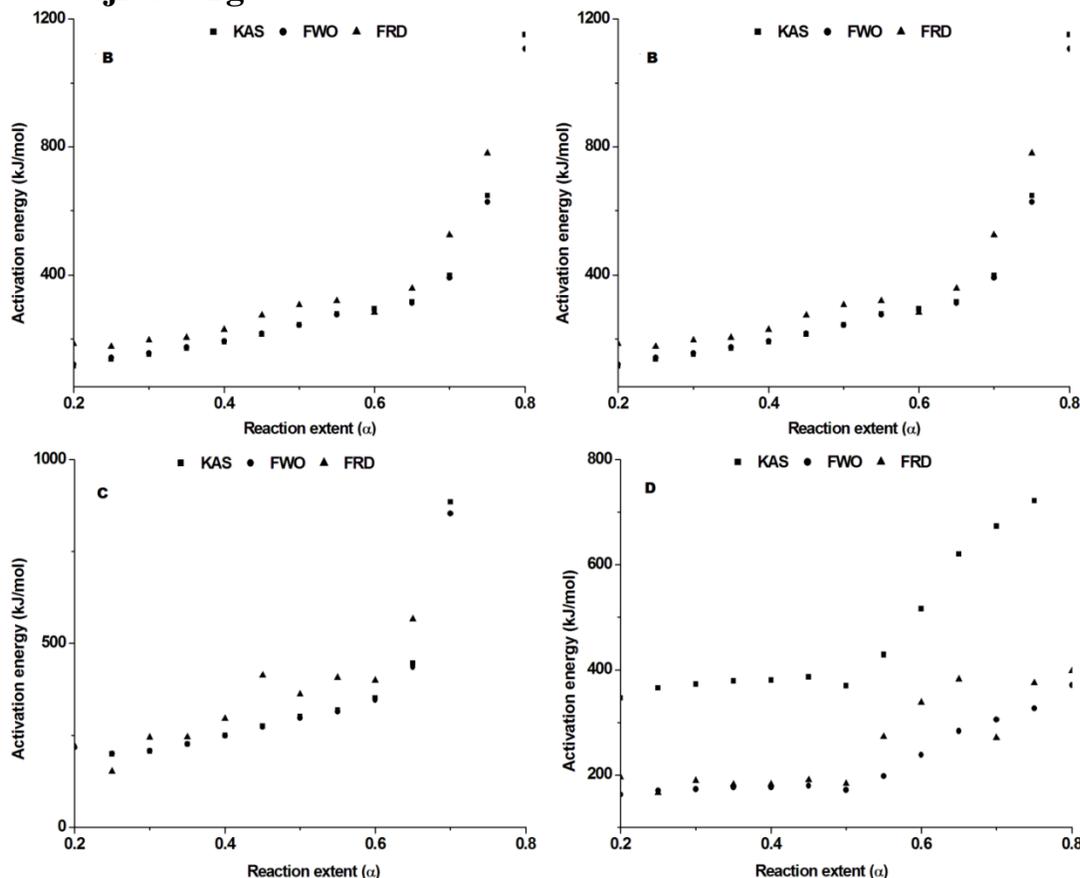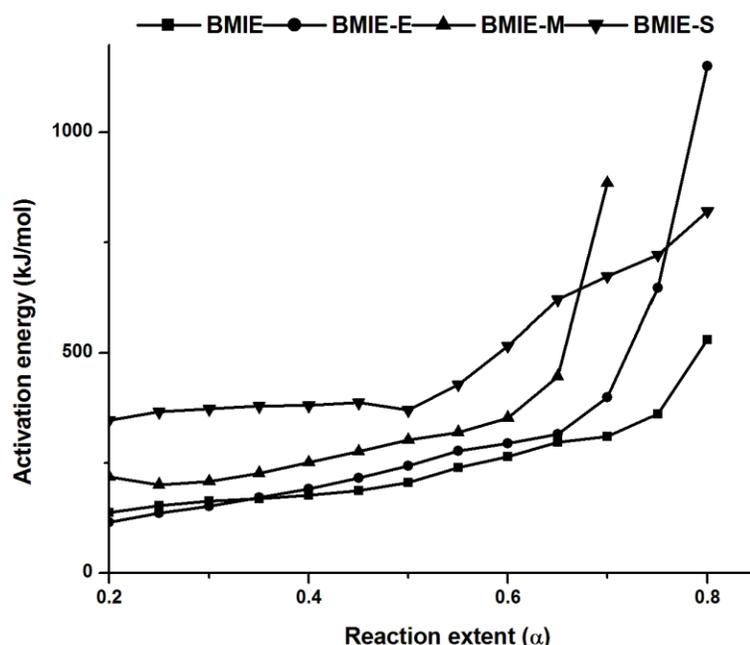
Figure 5.9 Plots between the activation energy and reaction extent for the degradation of thermally cured A=BMIE,B=BMIE-E,C=BMIE-M and D= BMIE-S

Surender *et al.* studied the kinetics of thermally curing and degradation of indane-based bismaleimide and cloisite 15 a clay nanocomposites using TGA by three isoconversional model free kinetic methods such as FWO, VYZ and FRD methods. The trends noted in the variation of apparent activation energy for the degradation of thermally cured sample obtained by the three kinetic methods are same and the values are in good agreement. The slight deviation noted in the apparent activation energy values between these methods is due to the different approximation used in the kinetic methods[16].

The plots of activation energy versus reaction extent for the degradation of cured samples are calculated using KAS method and are shown in Figure 5.9.In the thermal degradation of N-(4—hydroxy phenyl) maleimide (HPMI) and its funtionalized material PCNHPMI, the thermal apparent activation energy values calculated using VYZ method increased from 54 to 310 kJ/mol with

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increasing extent of reaction(α=0.2 -0.8).Because during the curing process of CNHPMI, apart from the trimerization of the cyanate groups, the bismaleimide double bond entering in the cyclization reaction with the cyanate groups is highly probable. Hence PCNHPMI needs higher energies for the thermal degradation.

Figure 5.10 Plots between the activation energy and reaction extent for the degradation of thermally cured BMIE, BMIE-E,BMIE-M and BMIE-S

Torrecillas et al. [17] studied the thermal pyrolysis products of polymerized bismaleimide, 4,4'- bismaleimido diphenyl methane at 500, 600 and 700^{0}C in air and 500 and 600 ^{0}C in nitrogen using GC–MS technique. They found that the main substances formed are aniline and phenylisocyanate, which occur in the first phases of degradation (500^{0}C), whether under air or nitrogen and also they suggested the degradation mechanism for the formation of isocyanate derivatives from crosslinked polybismaleimides which releases CO, CO_2, and H_2O molecules. The thermal properties of four different polymerization of monomeric reactants (PMR) polyimides were studied using TG/FTIR/MS by Xie et al. [18]. They reported that carbon dioxide is the major compound released from the polyimides and it will release in two stages. The release of CO_2 is detected before CO, which indicates that both CO and CO_2 are the direct products from the

decomposition of polyimides. The other major product obtained from the degradation of polyimides is phenyl isocyanates. The detection of benzonitrile by TG-MS strongly confirmed the cleavage of carbonyl group in the imide rings. Finally, they conclude that carbon monoxide is the direct degradation product from imide rings and carbon dioxide is produced through the further combination of CO with oxygen radicals during pyrolysis of hydrocarbon polymers. From the above results, one can conclude that during the thermal degradation of polybismaleimide, the major degradation product formed is amine and isocyanate of the corresponding polybismaleimide by the release of carbon monoxide and carbon dioxide. So, the increase in the activation energy is due to the formation of aniline and phenylisocyanate during the degradation of BMIM. Before the reaction extent 0.55 reasonable amounts of CO and CO_2 may be released from the degrading polymerized BMIM. Owing to the destruction of the imide rings and the presence of favorably structured degrading BMIM requires considerably less energy for degradation after $\alpha = 0.55$. After the reaction extent value of 0.65, the degraded BMIM may form coke; it may form a surface layer of protective char for the degrading BMIM and restricts further degradation. So,the system needs more amount of energy for degradation,hence the activation energy for the system increases.

The activation energy for the degradation of BMIE varies from 110 to 550 kJ/mol. Initially the activation energy value increases slowly from 110 to 250 kJ/mol up to the reaction extent level 0.65 and steep increase (250-550kJ/mol) is noted for higher ($\alpha > 0.65$) reaction extent levels. The activation energy for the degradation of the material BMIE-E varies from 125 to 1250 kJ/mol. A slight increase in activation energy noted for the reaction extent levels (0.2 – 0.65) similar to BMIE. After the reaction extent 0.65 a deep increase in the activation energy is due to the formation of aniline and phenyl isocyanate during the degradation.

The activation energy values for the degradation of BMIE-M is very similar to that of BMIE up to the reaction extent 0.65.But after the reaction extent 0.65 the activation energy for the total degradation process of BMIE-M increases by nearly 850kJ/mol. The observed increase in activation energy after $\alpha=0.65$ may be due to restriction of mobility of the segmental movement of degrading chains due to the enhanced chain extension of BMIE using aromatic methylene diamines. The activation energy variation noted for the degradation of the material BMIE-S is slightly different from the other two chain extended bismaleimides. It's activation

energy is 180kJ/mol more when compared to pure BMIE. There is a slight decrease in the activation energy for the reaction extent (0.45-0.55). After the reaction extent of 0.55 the activation energy values increases up to the reaction extent 0.8.From the activation energy trends of BMIE-E, BMIE-M and BMIM-S, authors conclude that the chain extension using E ,M and S plays a major role in the degradation mechanism of the pure BMIE.

Varma *et al.* were prepared 4,4'-bismaleimidophenyl methane (BM) and 3,3'-bismaleimidophenyl sulfone (BS) in solution using weight ratios 3:1 (MS31),2:1 (MS21),1:2(MS12) and 1:3 (MS13)(1986).They also prepared the chain extended bismaleimide resins by treating 3,3' bismaleimido phenyl sulfone (BS)/4,4'bismaleimidophenyl methane (BM) with 4,4'-diaminodiphenyl ether in molar ratios of 1:0.3 (BM-E and BS-E resins) . Thermogravimetric analysis of samples isothermally cured at 180^0C and 220^0C (1h each) was carried out in nitrogen atmosphere[19]. They reported that thermal stabilities improved of chain extended bismaleimides on blending.

Rajasekaran *et al.* studied the effect of polyether sulfone and N,N'-bismaleimide-4,4'-diphenylmethane on the epoxy resins. In order to improve thermo mechanical properties of cured epoxy resins, hydroxyl terminated polyethersulfone (PES) and N,N'-bismaleimido-4,4'diphenylmethane(BMI) were incorporated to diglycidyl ether of bisphenol A (DGEBA) type epoxy resin and cured with diaminodiphenylmethane (DDM).Polyethersulfone incorporation into epoxy resin improved thermal stability and enhanced the degradation temperature compared to the unmodified epoxy resin according to its percentage concentration. The presence of polyethersulfone skeleton in the epoxy system delays the degradation process and high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. The delay in degradation caused by the addition of polyethersulfone with a high *Tg* increased the viscosity of the system and in turn induced the formation of interpenetrating polymer network (IPN) within the system. The thermal degradation temperature of the BMI modified epoxy systems and BMI modified polyethersulfone epoxy systems were found to be increased with increasing bismaleimide concentration. It is evident that the degradation temperature was increased with increasing BMI concentrations as observed in the case of

polyethersulfone modified systems and this may be due to the rigidity and enhanced crosslink density imparted by bismaleimide.

6. Conclusion

The three different chain extended bismaleimides were prepared using three different aromatic diamines. DSC analysis was used to investigate the curing behavior of 4,4.-bismaleimidodiphenyl ether (BMIE) and chain extended BMIE. Chain extension considerably reduces the melting point and also the amount of heat released during the thermal curing. The apparent E_a values of the curing reactions were calculated using KAS, FWO and FRD kinetic methods. The KAS, FWO methods, gave nearly similar activation energies. The chain extended BMIE behaves differently during the thermal curing process as evidenced by the E_a values. Thermal stability of cured resins is influenced by the structure of the material. The apparent activation energy values for the thermal degradation of the chain extended bismaleimides are low compared to pure BMIE.Chain extended bismaleimides showed an improvement in thermal stability.

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