Thermal Studies on Chain Extended Bismaleimides

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Abstract

4, 4'-Bismaleimidodiphenyl sulphone (BMIS) 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 BMIS resins using Differential Scanning Calorimeter (DSC), Thermo Gravimetric Analysis (TGA) and Differential Thermo 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 BMIS decreases nearly 50^{0}C compared to pure BMIS. The apparent activation energy (E_a) values for curing of the chain extended BMIS decreases compared to BMIS. The apparent activation energy values for the thermal degradation of the chain extended bismaleimides are low after the reaction extent 0.5 compared to pure BMIS. Char yield was not significantly affected when pure bismaleimides were extended by aromatic diamines.

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

1. Introduction

High performance materials have been developed in the last decades to meet the requirements for advanced technology developments. Polyimide possesses the cyclic imide groups and aromatic groups in the main chain are recognized as very high performance polymers due to their excellent heat resistance and toughness. Polyimide's are stable over a wide range of temperatures from very low temperatures to temperatures above 300^{0}C, so they are suitable serene space environments [1]. Polyimide's were originally developed for the aerospace industry are now also used in airplanes and in machinery for various other industries , and are indispensable in the electronics industry as heat resistant insulators suitable for soldering processes[2].

Polybismaleimides is one of the important high performance thermosets and it possesses good thermal stability, high mechanical properties at high temperature, high tensile strength, corrosion and excellent chemical resistance and hot-wet performance. However, the pure bismaleimde resins suffer from brittleness due to their high crosslinking density and major problem for material durability. Due to hydrophilic nature, the bismaleimide composites cannot perform at temperature higher than 200^{0}C and cause the delamination of the composites. 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[3-5].

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 (≈6^{0}C).Heat of polymerization (ΔH)decreases significantly by chain extension with diamines[5].

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 BMIS on the three different model free kinetic methods (KAS, FWO and FRD) are used to calculate the apparent activation energies(Ea). 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:

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

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:

$$k(T) = A exp(-\frac{Ea}{RT}) \qquad (2)$$

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:

$$\alpha = (W_0 - W_T)/(W_0 - We) \qquad (3)$$

2.1.Kissinger-Akahira-Sunose (KAS) method

This method is based on the expression [6,8,9]

$$ln\,(\beta/T2) = ln(AR/Ea) - Ea\,/RT \qquad (4)$$

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

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

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:

$$\ln(d\alpha/dt) = \ln z + n\ln(1-\alpha) - (Ea/RT) \qquad (6)$$

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.

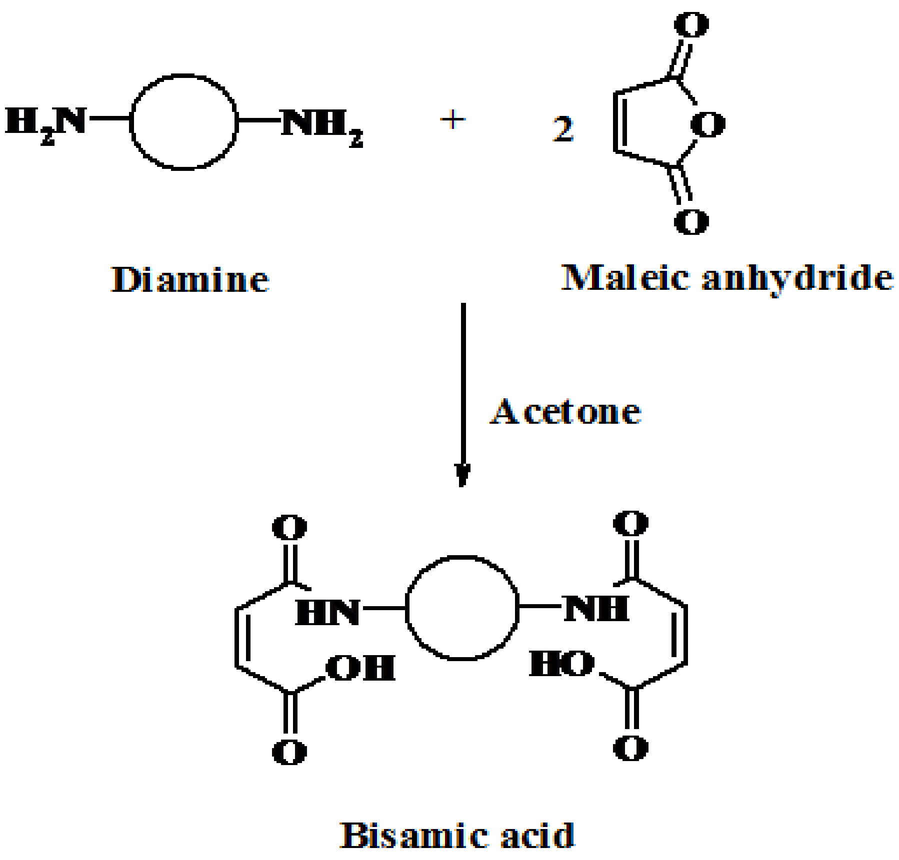
3. Experimental

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 sulphone (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)



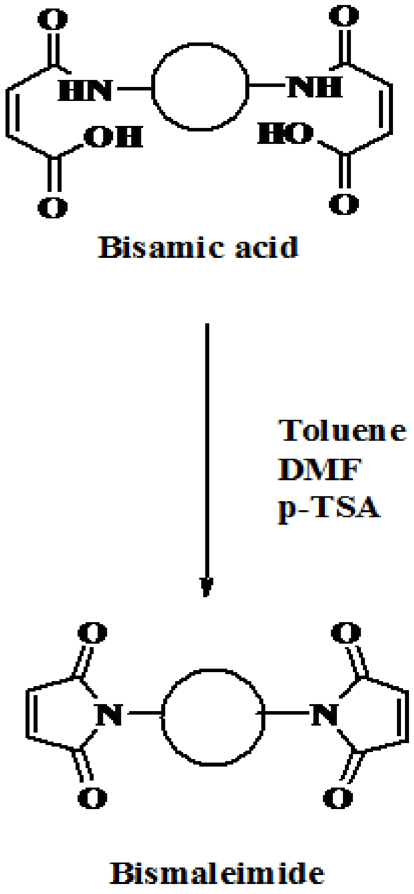
Scheme 3.1 Formation of bisamic acid

3.3.Preparation of 4,4'-bismaleimidodiphenyl sulphone(BMIS)

By using the appropriate bisamic acid (21.8 g) the BMIS 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 scheme3.2 .

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 the bismaleimide (BMIS) and three different aromatic diamines (E, M and S), three different chain extended bismaleimides (BMIS-E, BMIS-M and BMIS-S) were synthesized.



Scheme 3.2. Synthesis of bismaleimide

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 and30^{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 and30^{0}C/min).

5. Results and Discussion

DSC Studies

The DSC curves of pure BMIS and chain extended BMIS using three different diamines were recorded at multiple heating rates (β=10, 20, and 30^{0}C min^{-1}).The DSC curves for BMIS and BMIS-S recorded at multiple heating rates are shown in Figure5.1. The pure BMIS and chain extended BMIS DSC curves recorded at 20^{0}C min^{-1} heating rate are shown in Figure 5.2. The values obtained from the DSC curves such as melting point (Tm), enthalpy of fusion (ΔH_f), and curing temperatures at multiple heating rates for BMIS and chain extended BMIS are tabulated in Table5.1.

The detailed observations from the DSC curves recorded at β= 20^{0}C min^{-1} are discussed. The BMIS shows a sharp melting point at 103^0 C, T_s around 187^{0}C, T_{max} at 243^{0}C and T_e around 273^{0}C.The value of enthalpy of curing is 140 J/g. The chain extensions of BMIS using aromatic diamines are slightly affect the melting endotherm. The compounds BMIS-E, BMIS-M, BMIS-S show T_s around 115 ^{0}C, 116^{0}C and 165^{0}C, T_{max} at 200^{0}C, 186^{0}C and 210^{0}C and T_e around 293^{0}C, 285^{0}C and 290^{0}C respectively. The variation of the enthalpy of curing with change in heating rate may be attributed to the difference in the nature and extent of the cure reaction, followed by change in the structure of the cross-linked molecule network [10].

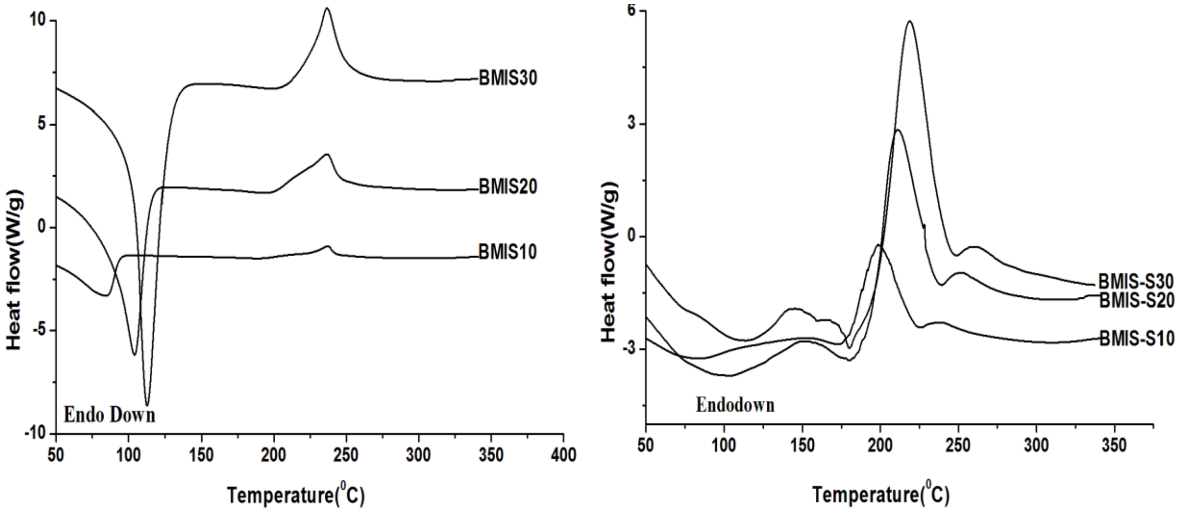


Fig. 5.1.DSC curves for BMIS and BMIS-S at 10, 20, and 30^{0}C min^{-1}

Table 5. 1. DSC parameters for BMIS and chain extended BMIS

Material	**Heating rate (°C/min)**	**Tm (°C)**	**Ts (°C)**	**Tmax (°C)**	**Te (°C)**	**ΔH$_C$ (J/g)**
BMIS	10 20 30	85 103 112	184 187 200	235 243 240	270 273 285	71 140 162
BMIS-E	10 20 30	100 90 90	110 115 119	150 200 210	300 293 300	125 306 190
BMIS-M	10 20 30	109 115 120	116 116 125	195 186 210	280 285 300	99 306 56
BMIS-S	10 20 30	85 105 120	160 165 167	198 210 218	280 290 289	431 486 434

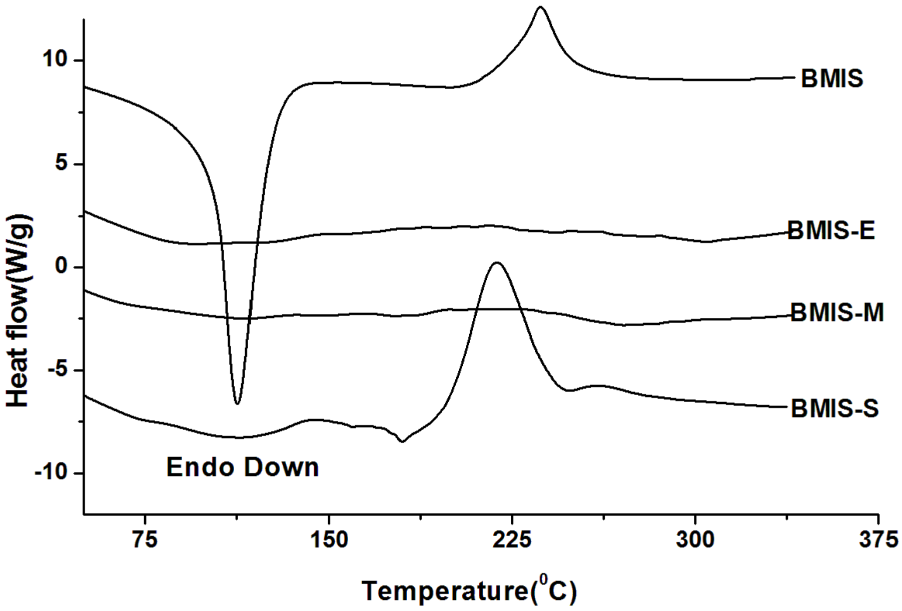


Fig. 5.2.DSC curves for BMIS and chain extended BMIS at 20^0 C min^{-1}

Table5. 2. Activation energies for the curing BMIS and chain extended BMIS

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
BMIS	KAS	213	233	252	278	304	333	366	405	425	439	417	378	336
	FWO	210	230	248	272	298	325	356	393	412	425	404	368	327
	FRD	302	348	388	434	478	519	521	513	440	349	257	191	201
BMIS-E	KAS	72	76	80	82	83	83	83	81	80	78	65	35	7
	FWO	62	65	68	70	72	71	71	69	69	66	54	25	15
	FRD	49	57	54	53	58	54	49	46	40	24	13	10	30
BMIS-M	KAS	132	158	101	87	86	88	89	88	86	82	76	68	58
	FWO	132	157	103	90	89	91	92	91	89	85	80	72	63
	FRD	251	81	34	69	88	92	87	81	74	64	54	38	17
BMIS-S	KAS	97	99	99	100	101	101	102	102	103	104	105	107	105
	FWO	100	101	102	102	103	104	104	105	106	106	108	109	108
	FRD	107	107	110	109	112	111	111	113	105	118	123	120	137

Cure Kinetics

The apparent activation energy (E_a) for the curing process of BMIS and chain extended BMIS has been calculated using three model free iso-conversional kinetics methods, namely, KAS, FWO and FRD.KAS and FWO methods are integral methods where as FRD method belongs to differential method. The apparent Ea is calculated for various reaction extents (α) ranging from 0.2 to 0.8. This range of α value is chosen as per the recommendations given by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry [11,12] because the relative experimental errors in the kinetic data are larger at the lowest and highest conversions.

FWO, KAS and FRD plots for the samples BMIS, BMIS-M and BMIS-S are represented in Figure5.3. The straight lines in the plots indicate the validity of the FWO, KAS and FRD analysis for the present system investigated. The FRD method for the sample BMIS-S the lines are parallel upto 75% conversion, which implies the possibility of single reaction mechanism. Due to the occurrence of complex reactions above 75% the line are not parallel [13,14].

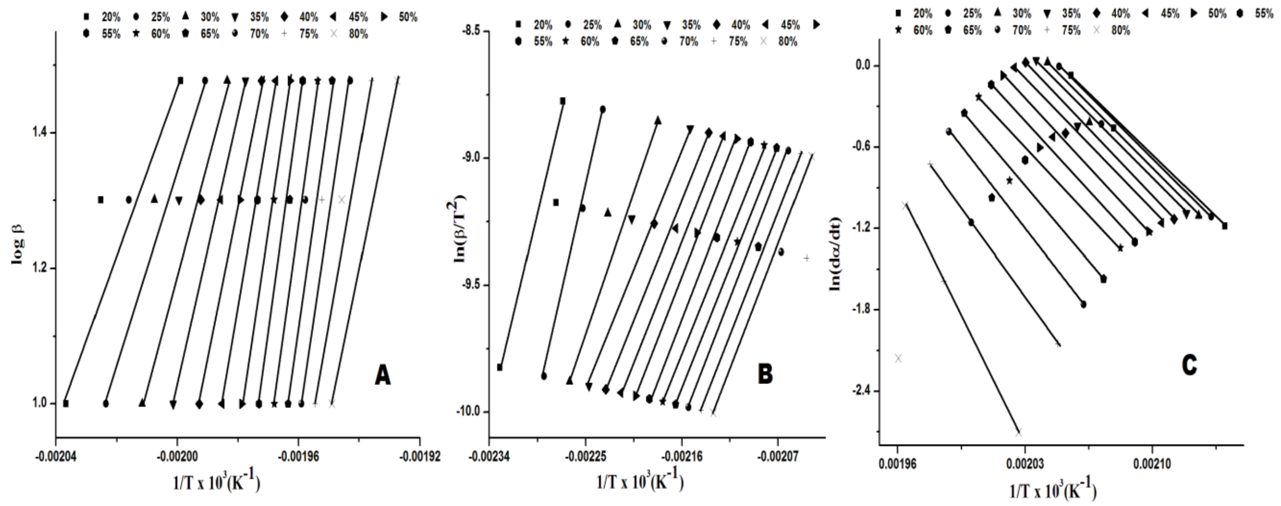


Fig. 5.3.(A)FWO plot for BMIS,(B) KAS plot for BMIS-M,(C) FRD plot for BMIS-S

The apparent E_a for the curing of BMIS and chain extended BMIS were calculated using KAS, FWO and FRD methods are given in Table 2.When compared to FRD method, the calculated apparent E_a values for KAS and FWO methods are nearly same. The deviations in the values calculated by FRD method is explicit (Figure5.4).This is due to the way in which the activation energy was calculated i.e..KAS and FWO method are integral methods and FRD is a differential method. Rajamani *et al.*[15] investigated the activation energy for the cured pure BMIM and BMIM/silica composites. In their study, the activation energy values obtained by the application of KAS and FWO methods are very similar, while Friedman method yielded to higher activation energy .This is due to the fact that both KAS and FWO methods are derived by the use of Doyle's approximation, while Friedman method is not based on any approximation. Therefore the accuracy of the apparent activation energy values obtained from Friedman method is greater and being more sensitive to change in mechanism.

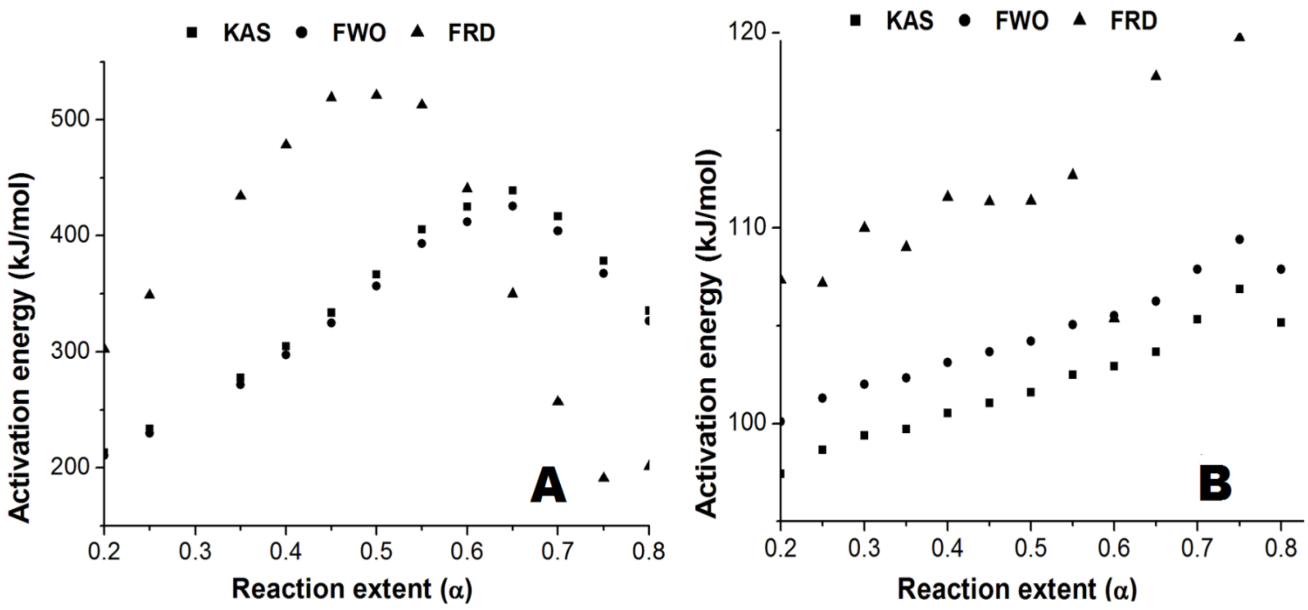


Fig. 5.4.KAS, FWO and FRD plots of A= BMIS and B= BMIS-S

The kinetics of polymerization of pure BMIS and its chain extension are studied using three different isoconversional methods such as KAS, FWO and FRD. The plots between apparent E_a for curing and the reaction extent (α) values for all the materials by KAS method are shown in Figure5.5.The apparent activation energy values calculated by these three methods agreed very well and the trends noted in the variation of apparent E_a for the curing of the different materials investigated were same. Generally, in the curing process of thermoset resins, molecules undergo gelation (from liquid to rubber) and finally, vitrification (from 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 [16,17]. After, a reaction extent value of 0.8, vitrification is caused in thermoset matrix systems and this, shifts the reaction from kinetic to a diffusion controlled.

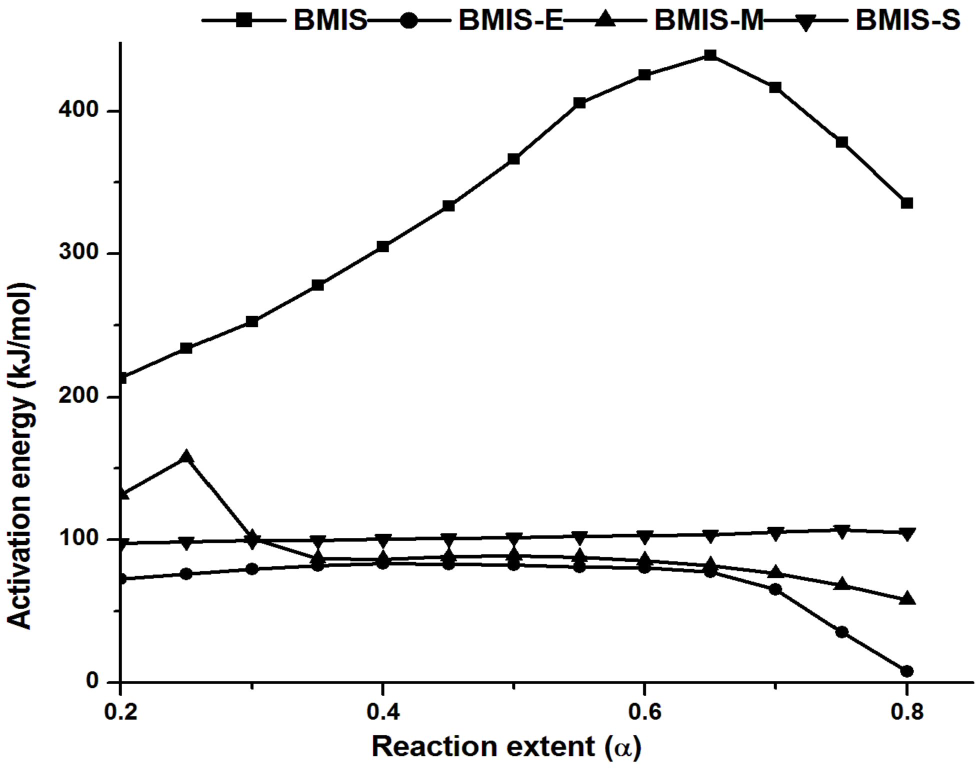


Fig. 5.5.Apparent E_a calculated using KAS method for BMIS and chain extended BMIS

Hill and coworkers [18] studied the kinetics and curing mechanism of bismaleimide–diamine thermoset 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 led to an element of diffusion control in the reaction. So, in this investigation, the apparent activation energies of pure BMIS and chain extended BMIS were calculated for the reaction extent values of 0.2–0.8.The apparent E_a values for BMIS was observed to increase (210–430kJ mol^{-1}) gradually with increasing extent of reaction(α) (0.2 to 0.6) using KAS method.

Initially, the concentration of the monomer (BMIS) 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 the monomer for the polymerization is decreased. This increase in viscosity and the dearth in the polymerizable groups made the cross linking reaction difficult. As the temperature increased linearly in the non-isothermal experiments, the chain mobility increased and the chemical reactions were reactivated. This results an increase in the activation energy for the higher reaction extent levels [19]. So at this stage, the system needs higher energy for polymerization and so the apparent ativation energy gradually increased. The rapid decrease in the activation energy at higher reaction extent (α>0.7) 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 positions 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 a dramatic decrease in the molecular mobility, which led to a decrease in the effective activation energy with increasing extent of reaction [20].The apparent E_a for BMIS-E, BMIS-M and BMIS-S lower than pure BMIS. The apparent E_a values are increases first and then decreases slowly from 120 to 70 KJ mol^{-1} for BMIS-E and from 80 to 70 KJ mol^{-1} for BMIS-M upto 0.65 reaction extent. But in the case of BMIS-S system the apparent E_a value is slightly increase from 100-109 KJ mol^{-1}.This is different from the pure BMIS, in which the trend noted in the apparent E_a for curing is different for different chain extension.

TGA and DTG studies

The TG and derivative TG curves for thermally cured BMIS and chain extended BMIS'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 table5.3.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 figure5.7.

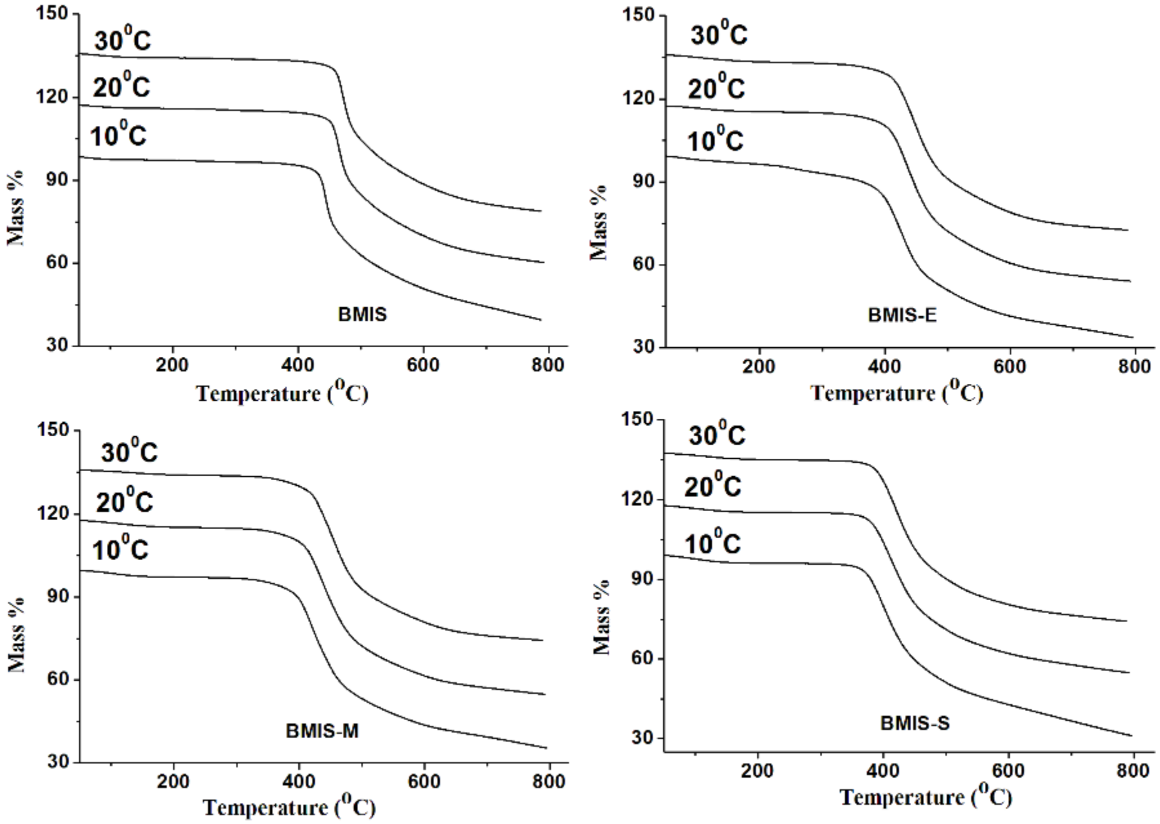


Fig. 5.6.TG curves of BMIS and chain extended BMIS's.

The DTG curve of thermally cured BMIS and chain extended BMIS's are shown in figure 5.8. The cured BMIS starts to thermally degrade (T_s) at 405^0C.The degradation reaches a maximum (T_{max}) at 460^0C and the decomposition ends (T_e) at 625^0C. For BMIS-E, BMIS-M and BMIS-S the decomposition starts at 350^0C, 320^0C and 345^0C respectively. For this chain extended bismaleimides the maximum decomposition occurs at 435^0C, 420^0C and 410^0C respectively and their decomposition ends at 610^0C, 620^0C and 520^0C respectively.

Material	**Heating rate (°C/min)**	**Onset Ts(°C)**
BMIS	10	405
	20	405
	30	420
BMIS-E	10	345
	20	350
	30	350
BMIS-M	10	310
	20	320
	30	320
BMIS-S	10	340
	20	345
	30	345

From the TG curves it is clear that the aromatic diamines has shown pronounced changes in the decomposition temperatures of pure BMIS which is effective in changing the thermal degradation behavior of bismaleimides.

Table 5.3. Data obtained from the thermogravimetric curves of thermally cured pure BMIS and chain extended BMIS's

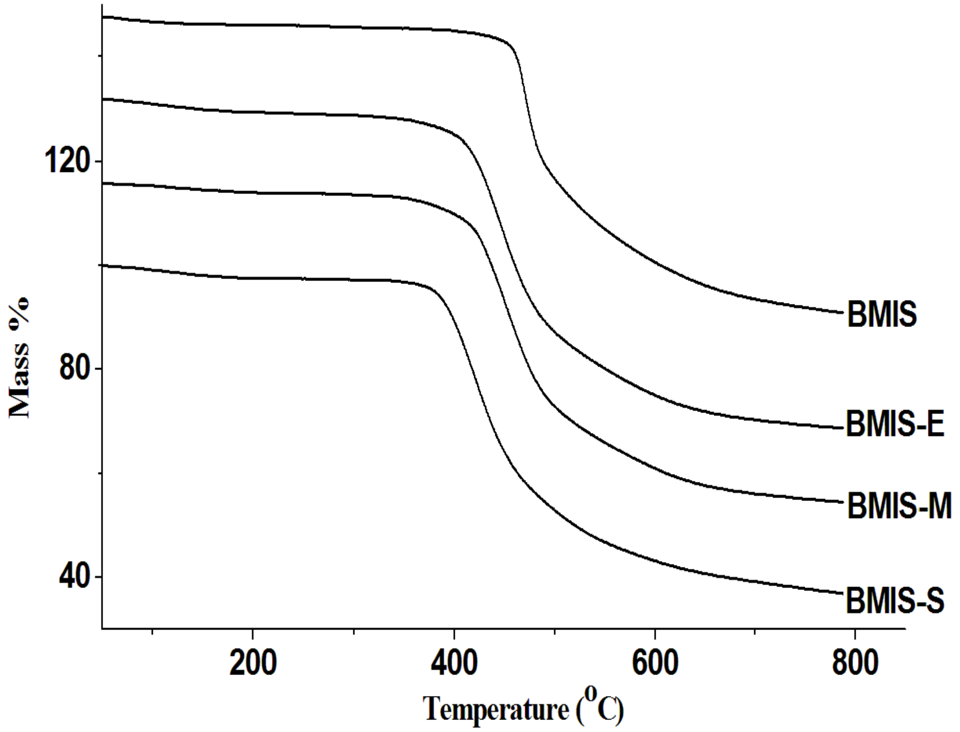


Fig. 5.7. TG curves of BMIS and chain extended BMIS's at 20^{0}C/min

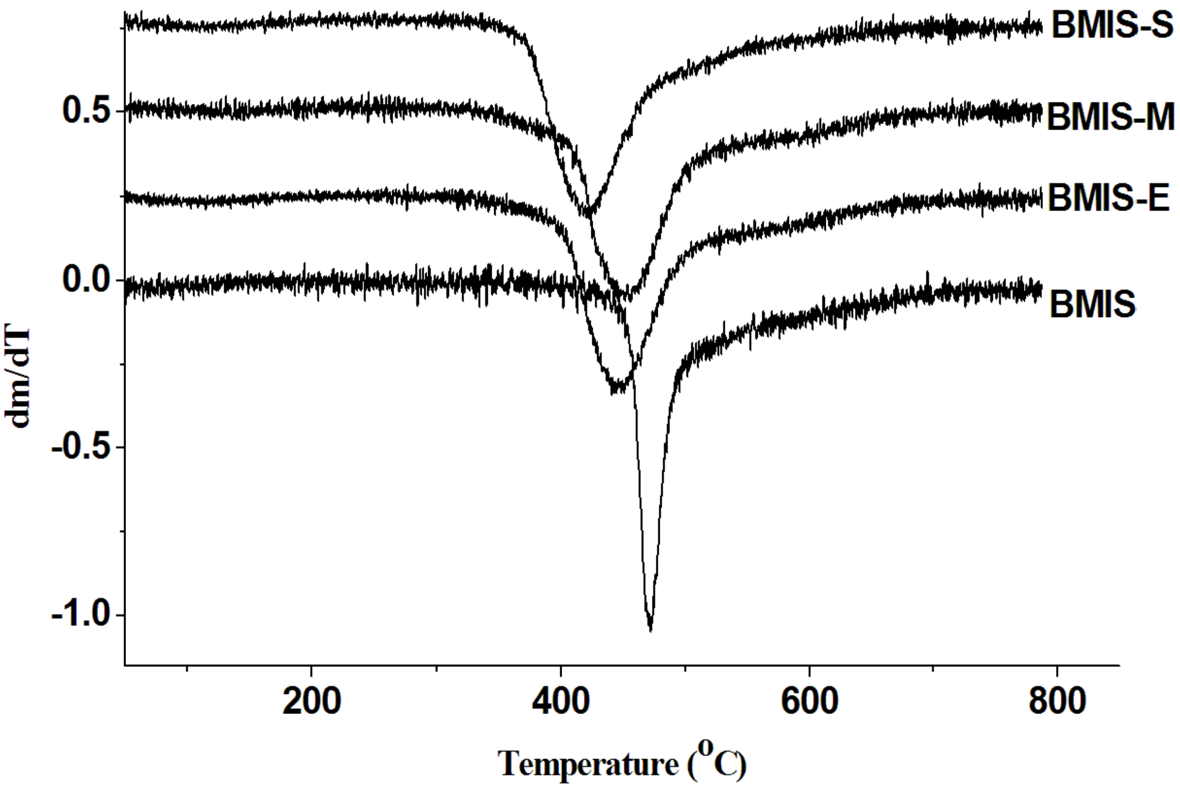


Fig. 5.8. DTG curves of BMIS and chain extended BMIS's at 20^{0}C

The first stage decomposition was accounted for a 20% weight loss upto 520^{0}C.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 are shown in figure5.9 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.

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
BMIS	KAS	159	159	167	163	171	196	238	285	357	516	946	306	576
	FWO	163	163	170	166	174	198	238	283	351	503	911	278	534
	FRD	165	166	170	214	226	250	458	290	418	506	1546	755	317
BMIS-E	KAS	110	134	147	156	163	170	175	182	191	218	301	460	851
	FWO	115	138	151	160	166	173	178	184	193	219	298	450	821
	FRD	228	178	182	206	194	193	202	200	260	292	454	481	1161
BMIS-M	KAS	169	172	173	176	183	194	210	226	250	307	422	287	263
	FWO	171	174	175	178	185	196	211	227	249	304	413	285	237
	FRD	183	164	196	199	191	260	299	269	375	447	509	366	429
BMIS-S	KAS	259	267	280	304	340	397	490	725	222	485	321	207	131
	FWO	257	265	277	300	334	388	476	700	200	449	293	184	111
	FRD	280	268	312	368	433	503	621	955	195	589	378	386	207

Table5. 4. Activation energies for the thermal degradation of BMIS and chain extended BMIS's

Jankovic et al. [21] studied the kinetics of nonisothermal dehydration of equilibrium swollen poly (acrylic acid) hydrogel using TG by five different isoconversional [FRD, FWO, KAS, Tang (T) and Vyazovkin (VYZ)] methods. The change in activation energy with respect to reaction extent for the methods, FWO, KAS, T, and VYZ lead to close values of Ea, but which differ substantially from the values of Ea obtained using iso-conversional method suggested by Friedman. They suggested that these differences could be due to the approximation of the relations that ground FWO, KAS, T, and VYZ methods and the differences between the apparent activation energies calculated using FRD method and values of Ea calculated using the other isoconversional methods are due to the way in which the relations that form the basis of the ''integral''methods are derived.

The plots of activation energy versus reaction extent for the degradation of cured samples are calculated using KAS method and are shown in figure 10. In the thermal degradation of aliphatic polyester, poly(ethylene adipate) prepared by two reaction methods, the activation energy values calculated using KAS and FWO methods are comparatively similar and the Ea can be considered as having almost constant average value up to 90 % conversion [22]. The activation energy for the degradation of thermally cured pure BMIS shows a slight increase up to the reaction extent values 0.6, and then a steep increase is noted up to the reaction extent value 0.7 and the activation energy decreases up to the reaction extent level 0.8. The apparent activation energy for the degradation of BMIS varies from -100 to 900 kJ/mol.

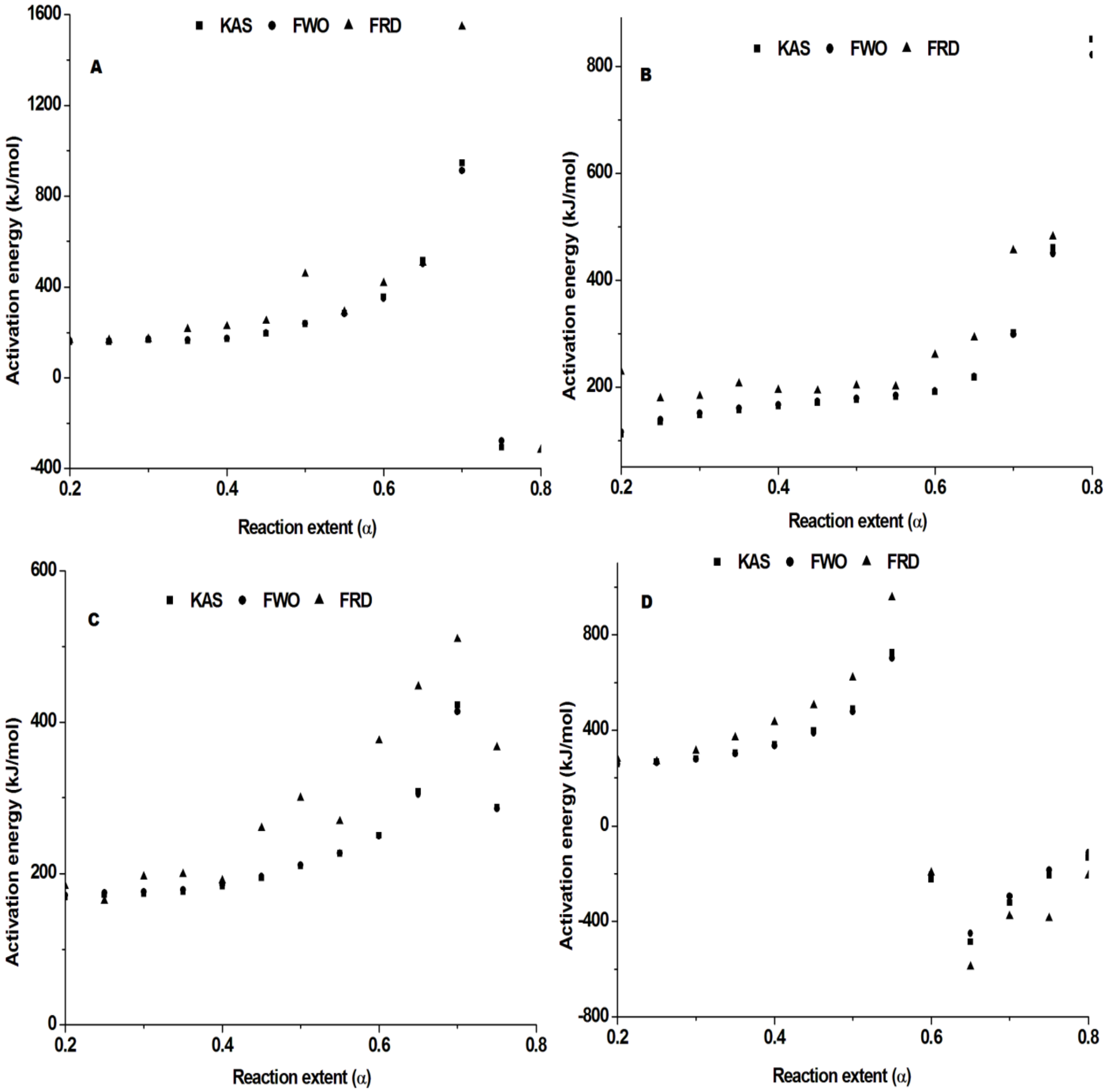


Fig. 5.9. Plots between the activation energy and reaction extent for the degradation of thermally cured A=BMIS,B=BMIS-E,C=BMIS-M and D= BMIS-S

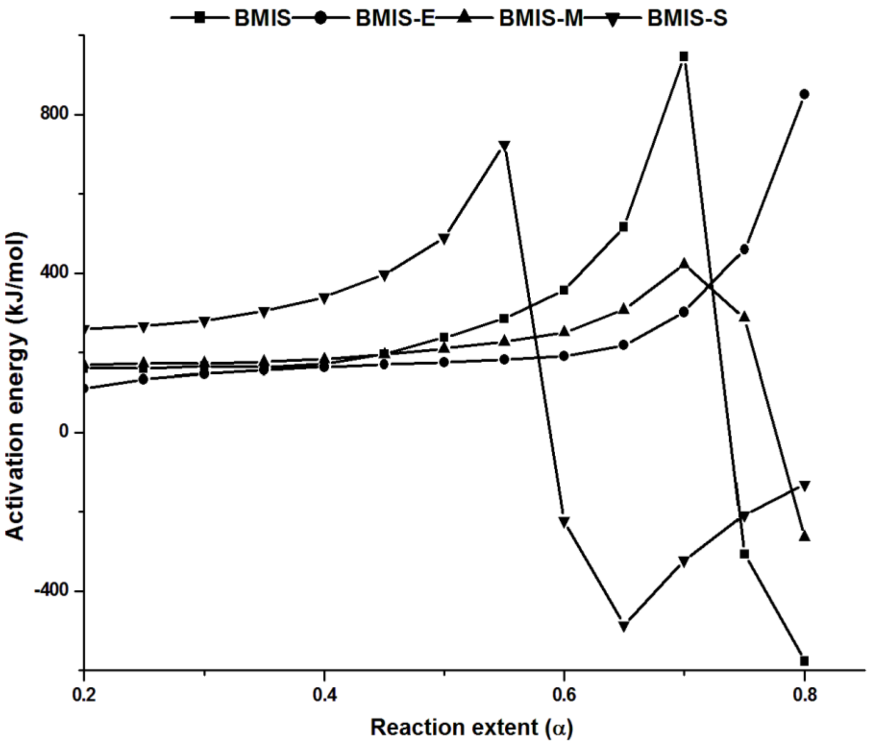


Fig. 5. 10.Plots between the activation energy and reaction extent for the degradation of thermally cured BMIS, BMIS-E,BMIS-M and BMIS-S

Torrecillas et al. [23] 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. [24]. 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 α = 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 variation of activation energy is noticed for the thermal degradation of the material BMIS-E shows slight increase in the activation energy upto the reaction extent 0.65.After the reaction extent 0.65 there is sudden increase in the energy of activation up to 0.8 is due to the formation of aniline and phenyl isocyanate during the degradation of BMIS-E. The apparaent activation energy for the degradation of BMIS-E varies from 100 to 900 kJ/mol.The activation energy values for the degradation of BMIS-M is very similar to that of BMIM. But the activation energy difference for the total degradation process of BMIS-M decreases by nearly 500kJ/mol. The observed increase in activation energy after α=0.55 may be due to restriction of mobility of the segmental movement of degrading chains due to the enhanced chain extension of BMIS using aromatic methylene diamines. The activation energy variation noted for the degradation of the material BMIM-S is different from the other three materials. It shows a deep increase in the activation energy upto the reaction extent 0.55.After that there is a sudden decrease in the activation energy till 0.65 then it is slowly increased upto the reaction extent 0.8.From the activation energy trends of BMIS-E BMIS-M and BMIS-S, authors conclude that the chain extension using E , M and S plays a major role in the degradation mechanism of the pure BMIS.

Varma *et al.* 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^{0}C and 220^{0}C (1h each) was carried out in nitrogen atmosphere. They reported that thermal stabilities improved of chain extended bismaleimides on blending[25].

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[26]. 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 from 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 sulphone (BMIS) and chain extended BMIS’s. Chain extension considerably reduces the melting point and also the amount of heat released during the thermal curing. The absence of a melting peak in the chain extended BMIS can thus be accounted by the initiation of curing reactions at temperatures lower than the melting point of pure BMIS. The apparent Ea 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 BMIS(BMIS-S) behaves differently during the thermal curing process as evidenced by the Ea 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 after the reaction extent 0.5 compared to pure BMIS. Char yield was not significantly affected when pure bismaleimides were extended by aromatic diamines.

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References

1. Y.L. Liu and Y.J. Chen, *Polymer*, 45, 1797 (2004).
2. T.K. Lin, S.J. Wu, J.G. Lai, and S.S. Shyu, *Compos. Sci.Technol.*, 60, 1873 (2000).
3. R. Girase, R. Jaiswal, L. Chaudhari, S. Bhattacharya, and D.D. Melo, *J. Vinyl. Addit. Technol.* 18, 46 (2012).
4. H.Stenzenberger and P.Konig, *High Perf. Polym.*, 5, 123(1993).
5. I.K Varma and R. Tiwari, Angew. "Cyclodehydration of bismaleamic acids", *Macromolecular Materials and Engineering*,157, 1 (1988).
6. T. Ozawa, *Bull. Chem. Soc. Jpn*., 38, 1881-1886(1965).
7. J. H. Flynn and L. A. Wall, *Polym. Lett.*, , 4, 323-328(1966).
8. Kissinger, H.E. 'Reaction kinetics in differential thermal analysis,' *Analytical Chemistry*, 29(11), 1702-1706(1957).
9. Akahira, T. and Sunose, T. 'Method of determining activation deterioration constant of electrical insulating materials,' *Res.Report, Chiba.Inst.Technol. (Sci.Technol.)*, 16, 22-31(1971).
10. Pichaimari. G, Vijayakumar. C.T, Functionalized monmers based on N-(4-hydroxyphenyl)maleimide, *J Therm Anal Calorim*, 3174,4(2013).
11. Vyazovkin S, Burnhamb AK, Criadoc JM, et al. ICTAC kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta*.,520, 1–19(2011).
12. Vyazovkin SV and Lesnikovich AI. An approach to the solution of the inverse kinetic problem in the case of complex processes:part 1. Methods employing a series of thermoanalytical curves. *Thermochim Acta.*, 165, 273–280(1990)..
13. C.T. Vijayakumar, R. Surender, K. Rajakumar, and S.Alam, *J. Therm. Anal. Calorim.*, 103, 693 (2010).
14. R. Surender, A. Mahendran, A. Thamaraichelvan, S. Alam, and C.T. Vijayakumar, *J. Appl. Polym. Sci.* 128, 712 (2013).
15. D.Rajamani, R.Surender, S.Alam, S.Muthusuburamanian, C.T.Vijayakumar, Bismaleimide/rice husk silica blends-Kinetics of Curing by DSC . *Science Jet 2013*, 1-8.
16. R. Surender, A. Mahendran, A. Thamaraichelvan, S. Alam,and C.T. Vijayakumar, *Thermochim. Acta.*, 562, 11 (2013).
17. S. Vinayagamoorthi, C.T. Vijayakumar, S. Alam, and S.Nanjundan, Eur. *Polym. J.*, 45, 1217 (2009).
18. J.L. Hopewell, G.A. George, and D.J.T. Hill, *Polymer*, 41, 8231 (2000).
19. N. Guigo, A. Mija, L. Vincent, and N. Sbirrazzuoli, *Phys.Chem. Chem. Phys*., 9, 5359 (2007).
20. G. He, B. Riedl, and A.A Kadi, *J. Appl. Polym. Sci.*, 87,433 (2003).
21. Jankovic B, Adnadevic B, Jovanovic J. ,*Thermochim Acta*. 452, 106–15(2007).
22. Chrissafis K. Kinetics of thermal degradation of polymers: complementary use of isoconversional and model fitting methods.J Therm Anal Calorim. 2009;25:273–83.
23. Torrecillas R, Regnier N, Mortaigne B. Thermal degradation of bismaleimide and bisnadimide networks: products of thermal degradation and type of crosslinking points. Polym Degrad Stab.1996;51:307–18.
24. Xie W, Pan WP, Chung KC. Thermal characterization of PMR polyimides. Thermochim Acta. 2001;367–368:143–53.
25. I.K Varma and R.Tiwari,*J.Thermal Analysis*,32,1023-1037(1987).
26. R.Rajasekaran, M.Alagar, C.Karikal Chozhan,eXPRESS polymer letters,2;5,339-348(2008)