Thermal Studies on Chain Extended Bismaleimides-II

C. Thamaraichelvi[1], A. Vanangamudi[2],
M. Dhanalakshmi[3] and C.T. Vijayakumar[3,✉]

ABSTRACT

4,4'-Bismaleimidodiphenyl methane (BMIM) was synthesized by chemical imidization. Using three different aromatic diamines (4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M) and 4,4'-diaminodiphenyl sulfone (S)) chain extended BMIM were prepared. The scope of present work is to study the curing and degradation studies of different chain extended BMIM resins using differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Friedman (FRD) methods were followed to calculate apparent activation energy for curing and degradation studies. Exothermic transition indicative of curing was observed in DSC traces in the temperature range of 50-450 °C. Melting point and also the amount of heat released during thermal curing was considerably reduced in the chain extended BMIM. The initiation of curing reactions at temperature lower than pure BMIM's melting point can be easily identified by the non-presence of melting peak in the chain extended BMIM. The apparent activation energy values for the thermal degradation of the chain extended bismaleimides are significantly reduced compared to pure BMIM. From this, it is concluded that the chain extension using (4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl sulfone) plays an important role in pure BMIM degradation mechanism. Char yield was not significantly affected when pure bismaleimides were extended by aromatic diamines.

KEYWORDS

Bismaleimides, Chain extension, Thermal analysis, Curing kinetics, Degradation kinetics.

Author affiliations:

[1]Department of Chemistry, The Standard Fireworks Rajaratnam College for Women, Sivakasi-626 123, India

[2]Department of PG & Research Centre in Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi West-626 124, India

[3]Department of Polymer Technology, Kamaraj College of Engineering & Technology, S.P.G.C. Nagar, K. Vellakulam-625 701, India

✉To whom correspondence to be addressed:

E-mail: ctvijay22@yahoo.com; thamjaw2007@gmail.com

INTRODUCTION

Polymer materials in nowadays add value to the quality of life by involving in the production of all household appliances, insulating materials in industries, textiles, construction, electronics, medical implants and more over. Among polymers, polyimides technical requirements are of more importance. They have $CO\text{-}NR_2$ functional group known as imides. The free electron of nitrogen atoms and π electrons of the carbonyl group conjugates which makes them resistance to moisture and most chemical agents. Polybismaleimides have very good physical, chemical, mechanical and dielectric stability at temperatures ranging from 150 to 250 °C. These polyimides are vastly used in aerospace field as membranes. Rigid-rod aromatic polybismaleimides have very good thermo-oxidative stability,

rigid mechanical properties, strong dielectric strength and dimensional stability [1,2]. This pulls more audience towards rigid rod aromatic polyimides.

However, on the other side the pure bismaleimide resins have a major brittleness problem due to their high crosslinking density which affects material durability. Due to hydrophilic nature, bismaleimide composites cannot perform at temperature higher than 200 °C and cause the delamination of the composites. The brittleness of bismaleimides has been improved by various techniques such as dispersion of nanoparticles into bismaleimide resin systems, copolymerization with functionalized compounds such as epoxies, cyanates, allyl-phenols, Michael addition reaction of bismaleimides [3-5].

Varma and Tiwari [5] prepared 3,3'-bismaleimidophenyl sulfone (BS) and 4,4'-bismaleimidophenyl methane (BM) in solution using weight ratios 1:3 (MS13), 2:1 (MS21), 1:2 (MS12) and 3:1 (MS31). They also prepared the chain extended bis-maleimide resins by treating 3,3'-bismaleimidophenyl sulfone (BS)/4,4'-bismaleimidophenyl methane (BM) with 4,4'-diamino-diphenyl ether in molar ratios of 1:0.3 (BM-E and BS-E resins).

By using differential scanning calorimetry, the curing characteristics were evaluated for the resins blended with bismaleimides. The reduction in the melting and curing temperature is caused by the increase in BM content in BM:BS blends or increase in chain extended bismaleimide content in BM-E: BS (or) BS-E: BM blends. Thermogravimetric analysis of samples isothermally cured at 180 °C and 220 °C (1 h each) was carried out in inert atmosphere. They reported that the thermal stabilities of chain extended bismaleimides improved on blending.

The chain extension reaction studies of bismaleimides with aromatic diamines yields greater interest. In this paper we addressed the effect of chain extension of BMIM by calculating the apparent activation energies (E_a) using three different model free kinetic methods (KAS, FWO and FRD). The curing process and degradation process were studied using DSC, TGA and DTA techniques and the results are reported and discussed.

Kinetic studies: The solid-state reactions rate can be explained using the following equation:

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

where, $d\alpha/dt$ is the rate of the reaction, $k(T)$ is the rate constant and $f(\alpha)$ is the reaction model. According to Arrhenius's equation, the rate constant $k(T)$ is temperature dependent and it is explained using the following equation:

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

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 eqn. 3:

$$\alpha = \frac{W_o - W_T}{W_o - W_e} \tag{3}$$

Kissinger-Akahira-Sunose (KAS) method: This method is based on the expression [6-8]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT} \tag{4}$$

where, β = heating rate, T = temperature, A = pre-exponential factor, R = gas constant and E_a = apparent activation energy. The activation energy has been calculated from the slope $-E_a/R$ derived by plotting $\ln(\beta/T^2)$ *vs.* $1/T$ which gives straight line.

Flynn-Wall-Ozawa (FWO) method [9]: Dynamic kinetic analysis has been done using the Flynn-Wall-Ozawa method and it does not require any assumptions to be made about the conversion dependence. The temperature (T) related to a fixed value of degree of conversion (α) can be measured from the experiments at different heating rates, β.

The FWO method utilize Doyle's approximation and the equation is present as:

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

The activation energy has been calculated from the slope which equals $-0.457 E_a/R$ by plotting $\log \beta$ *vs.* $1/T$. The presence of a single step reaction can be concluded with certainty by observing that the E_a value is same for different α values.

Friedman (FRD) method: Friedman method is used to calculate the apparent activation energy and the equation is given below:

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

where, α is the reaction extent and z, is constant. The activation energy E_a of the system can be calculated from the slope $(-E_a/R)$ of the linear plot between $\ln(d\alpha/dt)$ *versus* $1/T$.

E X P E R I M E N T A L

Toluene, N,N'-dimethylformamide (DMF), *p*-toluene-sulfonic acid (*p*-TSA), maleic anhydride and acetone were procured from S.D. Fine Chemicals Pvt. Ltd., Mumbai. 4,4'-Diaminodiphenylether, 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenyl sulfone were purchased from Hi-media Pvt. Ltd., Mumbai, India.

Preparation of bisamic acid: 4,4'-Diaminodiphenyl methane (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 min of stirring, 12.36 g of powdered maleic anhydride was added in small portions, and allowed to stir for a further period of 0.5 h to obtain yellow precipitate of bisamic acid. Finally the precipitate was filtered, washed with cold acetone and dried. Bisamic acid was synthesized in as per reported procedure [10] (**Scheme-I**)

Preparation of 4,4'-bismaleimidodiphenyl methane (BMIM): By using the appropriate bisamic acid (21.8 g) the BMIM was synthesized in toluene medium. Toluene (105 mL) was used to form slurry of the bisamic acid and this slurry was constantly stirred using mechanical stirrer. After 10 min, 1.29 g of *p*-toluene sulfonic acid was added to the contents with continuous stirring. Then the container 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 h 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

Scheme-I: Formation of bisamic acid
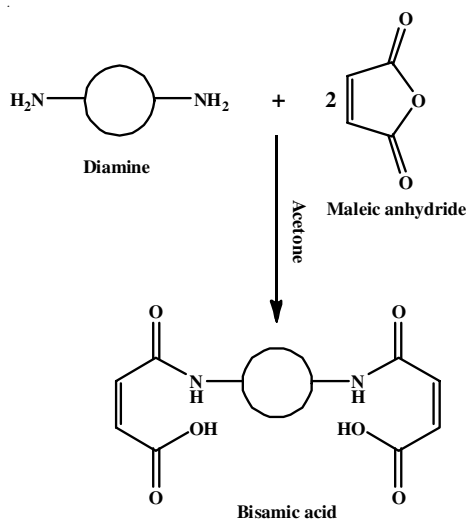
distillation and the concentrated reaction mixture was sufficiently cooled and poured into copious amount of crushed ice kept in a beaker. The precipitate was filtered and dried. Bismaleimide was synthesized as per the **Scheme-II**.

Scheme-II: Synthesis of bismaleimide
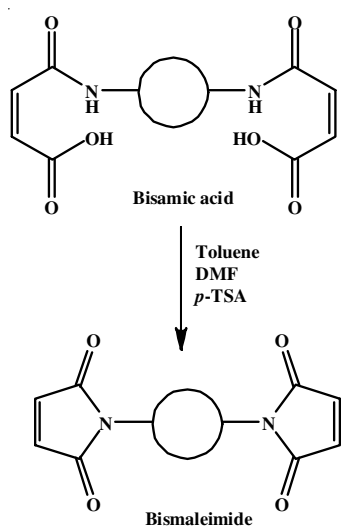
Synthesis of chain extended bismaleimides: Bismaleimide was taken in a 100 mL round bottom flask and made into a solution by dissolved it in 50 mL of acetone. The requisite quantity of the aromatic diamines (0.3 mol) was added to bismaleimide solution and the content was refluxed. After 5 h, acetone was distilled and the shinning powdery product of chain extended bismaleimide was obtained. By using bismaleimide (BMIM) and three different aromatic diamines (E, M and S), three different chain extended bismaleimides (BMIM-E, BMIM-M and BMIM-S) were synthesized.

Differential scanning calorimetry: Differential scanning calorimetric analysis has been done in DSC Q20 of TA instruments (New Castle, Delaware, USA) with nearly 2.4 mg of the sample. The DSC curves were obtained by heating the material at different heating rates (β = 10, 20 and 30 °C/min) from 50 °C to 350 °C in an inert nitrogen atmosphere (flow rate = 50 mL/min).

Thermogravimetric analysis: The degradation characteristics of the chain extended bismaleimides was studied using TG analyzer (model Q50, TA Instruments) with approximately 4-5 mg of the sample. The sample was flushed with nitrogen at the flow rate of 60 mL/min and 40 mL/min for the balance area. The samples are heated at different heating rates (10, 20 and 30 °C/min) ranging from 40 to 800 °C.

RESULTS AND DISCUSSION

DSC studies: The DSC curves of chain extended BMIM with three different diamines and pure BMIM were plotted at different heating rates (β = 10, 20 and 30 °C min^{-1}). The DSC curves for BMIM and BMIM-S plotted at different heating rates are shown in Fig. 1. The DSC curves of pure BMIM and chain extended BMIM are recorded at 20 °C min^{-1} heating rate (Fig. 2). Table-1 shows the values derived from the DSC curves such as melting point (T_m), curing temperatures and enthalpy of fusion (ΔH_f), at different heating rates for BMIM and chain extended BMIM.

TABLE-1
DSC PARAMETERS FOR BMIM AND CHAIN EXTENDED BMIM

Material	Heating rate (°C/min)	T_m (°C)	T_s (°C)	T_{max} (°C)	T_e (°C)	ΔH_c (J/g)
BMIM	10	159	164	237	339	149
	20	155	197	269	344	242
	30	156	198	279	338	183
BMIM-E	10	75	89	120	185	66
	20	80	103	128	197	45
	30	76	107	125	200	17
BMIM-M	10	78	93	125	202	29
	20	89	111	130	203	37
	30	80	108	166	340	38
BMIM-S	10	130	150	212	285	340
	20	130	148	225	307	570
	30	130	150	235	316	647

BMIM shows a sharp melting point at 155 °C and the material is found to be stable till 197 °C. The thermal polymerization starts around 197 °C where the material starts to cure and over at around 344 °C. Its maximum is located at 267 °C. The enthalpy of curing for the polymerization of BMIM is 242 J/g. The area under the exothermic represents 100 % of cure. Similarly, the compounds BMIM-E, BMIM-M and BMIM-S shows sharp melting points at 80, 89 and 130 °C, respectively. It starts to cure at around 160, 150 and 163 °C and the thermal polymerizations are over at around 197, 203 and 307 °C. T_{max} at 128, 130 and 225 °C respectively. The enthalpy of curing for the polymerization of BMIM-E, BMIM-M and BMIM-S are 45, 37 and 570 J/g, respectively. The differences in the nature and extent of the cure reaction followed by the difference in the structure of the cross-linked molecular network [11] may be attributed by the variation in ΔH_c values at different heating rates.

In all the cases, there is a considerable decrease in the curing onset maximum and end set temperatures of BMIM-E, BMIM-M and BMIM-S when compared to pure BMIM. This is due to the chain extension of bismaleimides.
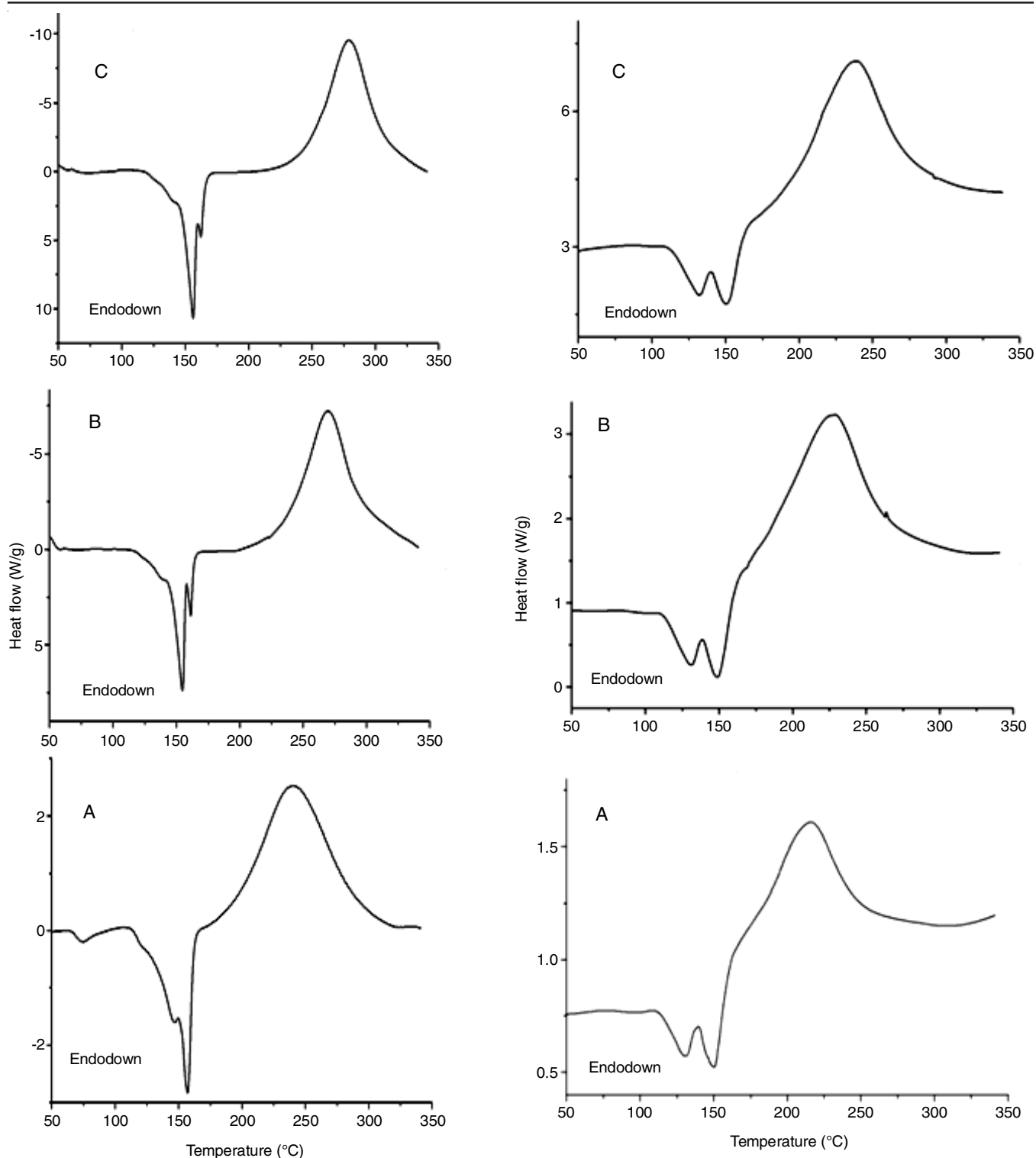
Fig. 1. DSC curves for BMIM and BMIM-S at A = 10, B = 20 and C = 30 °C min^{-1}

Cure kinetics: Experimental data derived from the DSC curves of the BMIM and chain extended BMIM's at various heating rates (10, 20, 30 °C/min) are used in the kinetic studies of its curing behaviour.

The apparent E_a of the curing process has been arrived using KAS, FWO and FRD model free kinetic methods. Out of which FRD belongs to differential approximation method and the other two are integral approximation methods. For various reaction extents (α) ranges from 0.2 to 0.8 the value

of apparent E_a is calculated. According to Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry, the relative experimental errors in the kinetic data become larger at the lowest and highest conversions; hence it recommends limiting analysis beyond certain ranges.

KAS, FWO and FRD plots for the samples BMIM, BMIM-M and BMIM-E are represented in Fig. 3. For the system given, the straight lines in the plots indicate the validity of the KAS, FWO and FRD analysis. The single reaction mechanism can
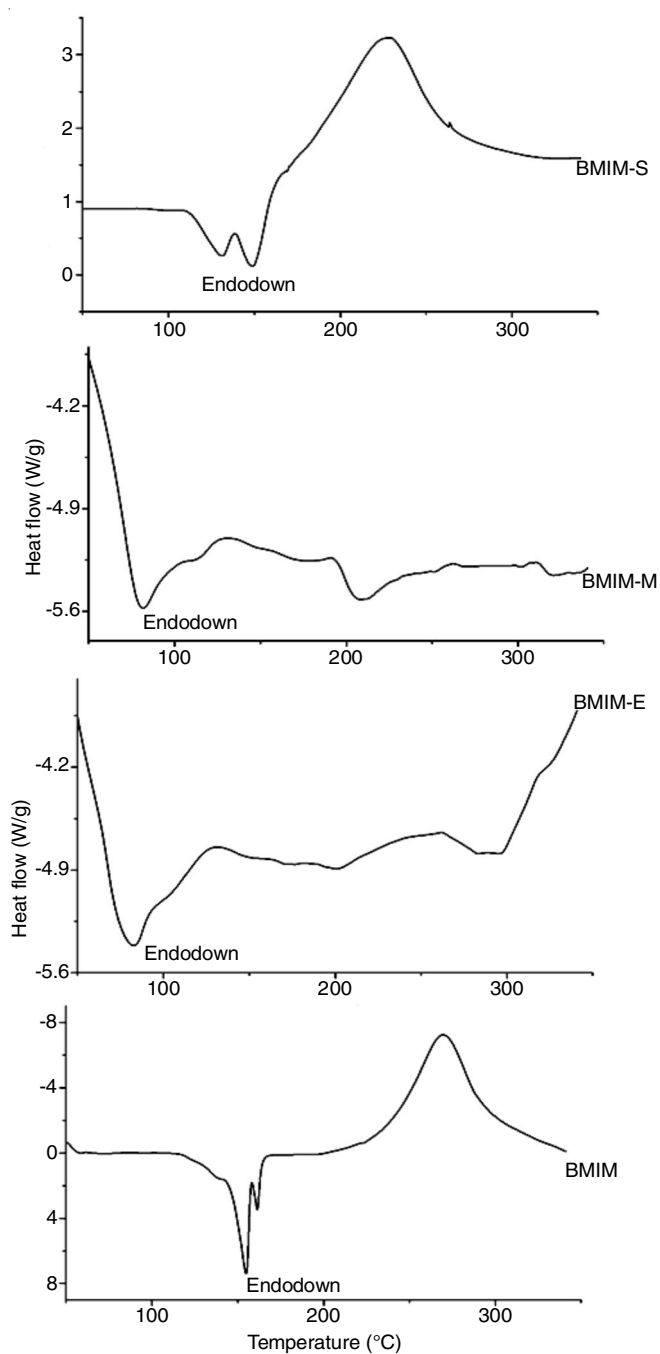
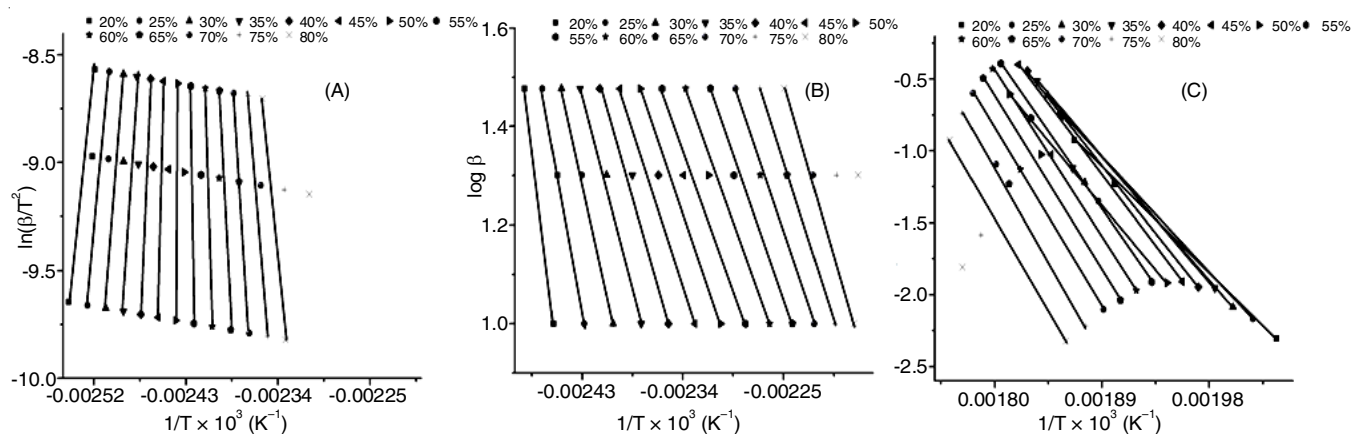Fig. 2. DSC curves for BMIM and chain extended BMIM at 20 °C/min

be visualized easily from the parallel lines in the FRD plots which are found up to 45 % conversion. For the curing of BMIM and chain extended BMIM, the apparent activation energy developed can be derived from the three different methods and shown in Table-2.

In common, all the curing process (or) reactions involving thermoset resins, have undergo gelation *i.e.*, from liquid to rubber and finally vitrification like rubber to glass transitions. The molecular mobility has been reduced by the cross linking process and thus changing the reaction from kinetically controlled to a diffusion controlled one. Hill and coworkers [12] investigated the kinetics and curing mechanism of bismale-imide-diamine thermosets matrix systems. They concluded that, up to 70 % conversion the excellent fit to the experimental data for the consumption of primary and secondary amines was obtained with the kinetic rate laws, whereas at higher conversions, a negative deviation from the predicted rates was found. This contributes to vitrification, which shown the element of diffusion control in the reaction.

The plots below had shown the different α value *vs.* corresponding E_a value for the compounds BMIM and BMIM-M in Fig. 4. The E_a value and its variation trend with respect to α were found very much the same in both the integral methods (KAS and FWO). Even though the differential method (FRD) gives E_a values within the particular range, there are slight deviations and the same is attributed to the initial approximations made.

Fig. 5 shows the trend of activation energy *vs.* reaction extent for the curing of the samples derived using KAS method. 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. The KAS studies shown that the calculated apparent activation energies of BMIM increase gradually (50-80 KJ/mol) with increase in the extent of reaction (α) from 0.2-0.8. At first the polymerization occurs rapidly due to the higher concentration of monomer and thereby required very low energy for the reaction to takes place. But as the reaction continues, the availability of monomer decreases, simultaneously the viscosity increases and this made the cross linking polymerization reaction not easy.

In the non-isothermal experiments, the linear increase in temperature causes the increase in chain mobility thereby it

Fig. 3. (A) KAS plot for BMIM-E, (B) FWO plot for BMIM-M and (C) FRD plot for BMIM

TABLE-2
ACTIVATION ENERGIES FOR THE CURING OF BMIM AND CHAIN EXTENDED BMIM

| Sample	α	E_a values (KJ/mol)												
		0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80
BMIM	KAS	42	44	46	48	51	53	56	58	61	65	68	71	74
	FWO	48	50	52	54	56	59	61	64	67	70	73	76	79
	FRD	67	67	72	73	86	84	78	98	95	99	107	98	92
BMIM-E	KAS	303	355	420	508	597	587	365	129	247	219	159	112	78
	FWO	294	344	405	489	593	564	354	116	128	201	144	100	68
	FRD	392	438	533	653	750	706	395	280	429	386	296	210	183
BMIM-M	KAS	210	184	162	141	126	116	109	104	101	99	98	98	100
	FWO	193	169	148	127	113	104	97	92	89	87	86	86	88
	FRD	329	273	234	196	166	148	134	114	102	92	86	84	67
BMIM-S	KAS	150	159	162	165	163	159	149	133	118	110	112	113	99
	FWO	150	159	162	165	163	159	149	133	118	110	112	113	99
	FRD	211	190	185	177	154	142	152	125	97	119	114	96	74
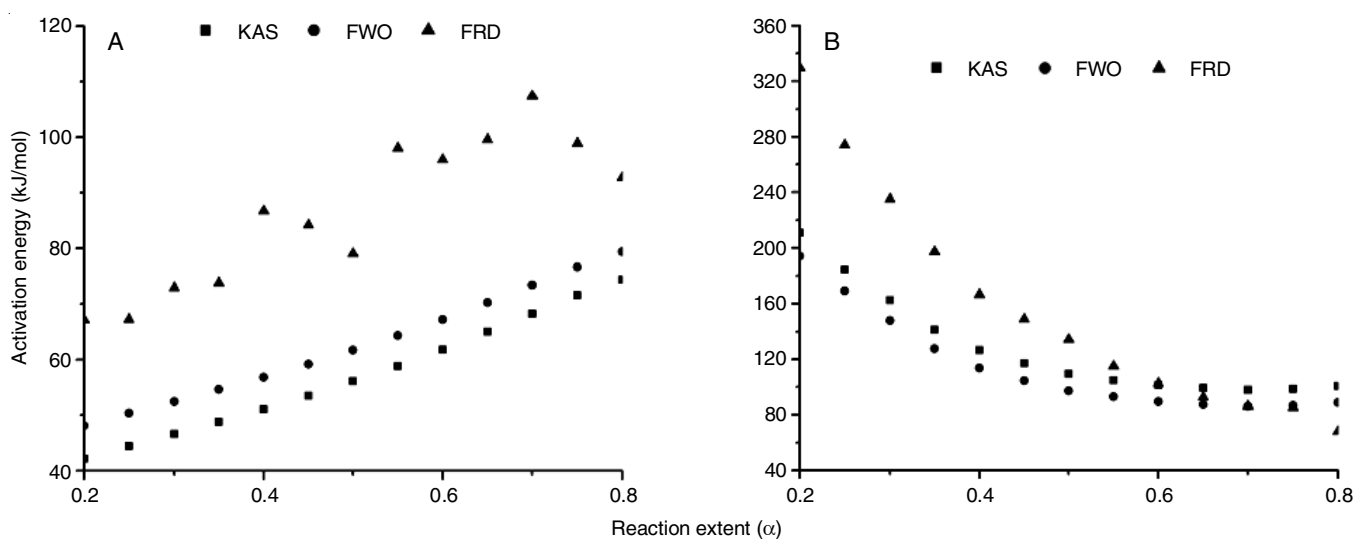
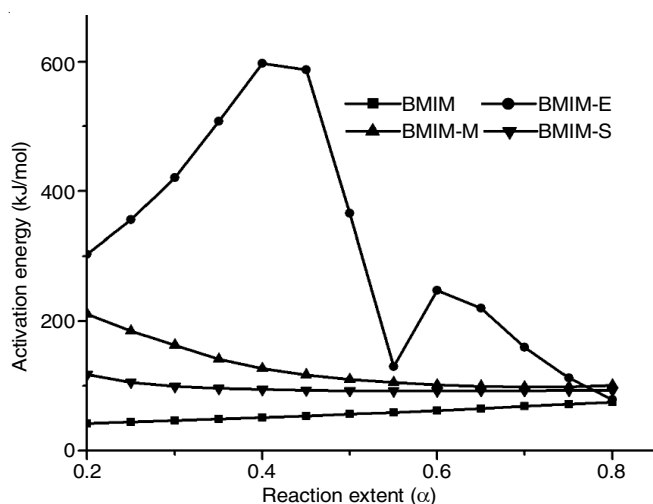Fig. 4. KAS, FWO and FRD plots for A = BMIM and B = BMIM-M

Fig. 5. Activation energies calculated for different conversions of BMIM and chain extended BMIM using KAS method

reactivating the chemical reactions. This causes the activation energy to increase or the higher reaction extent levels. Hence at this time the polymerization reaction requires higher energy and shown a gradual increase in the apparent energy. This phenomenon is exhibited in the BMPM/diallylbisphenol A

resin system. In the BMPM/diallylbisphenol system, ene type reaction is occur between the allyl phenol compounds and BMPM which gives a linear chain extension followed by a Diels-Alder reaction at a higher temperature. The reaction becomes complex with multiplet reactions and formation of succinimide groups by the conversion of maleimide moieties occurs. The activation energy shows a steady increase 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) 2011 [13] for valid reasons mentioned.

The apparent E_a values for BMIM-E tends to increase (300-500 kJ/mol) drastically with the increasing extent of reaction (α) (0.2-0.5). After the reaction extent (0.5), the apparent E_a is suddenly decreased. The activation energy shows a rapid decrease at higher reaction extent levels which can be easily explained by the changes in the reaction mechanism from kinetically controlled to diffusion controlled one. This caused the monomer molecules to freeze in their position (in the glassy state) and considerably reduced the chemical reaction which acts as the virtual cessation of the reaction. Thus it

clearly indicates that molecular mobility can be decreased dramatically by vitrification, correspondingly the effective activation energy also decreases with increasing extent of reaction.

The apparent E_a of BMIM-M decreases during the curing process up to the reaction extent (0.2-0.6), after that the apparent E_a is more or less same. The chain extension using diamino diphenylmethane must have some influence in the BMIM. BMIM-S system shows decreasing in the apparent E_a up to 0.3 reaction extent after that there is no change in activation energy values up to the higher reaction extent.

TGA and DTG studies: Both the TG and DTG curves for thermally cured BMIM and chain extended BMIM are plotted at various heating rates (10, 20 and 30 °C min^{-1}) under nitrogen atmosphere (Fig. 6). All the thermograms showed a shift to higher temperatures with increasing heating rates. The T_i, T_{max} and T_e values for the degradation and char residue obtained at 800 °C for all the samples noted at multiple heating rates 10,20 and 30 °C min^{-1} are shown in Table-3.

The DTG curve of thermally cured BMIM and chain extended BMIM are shown in Fig. 7. The overlapping of two degradation
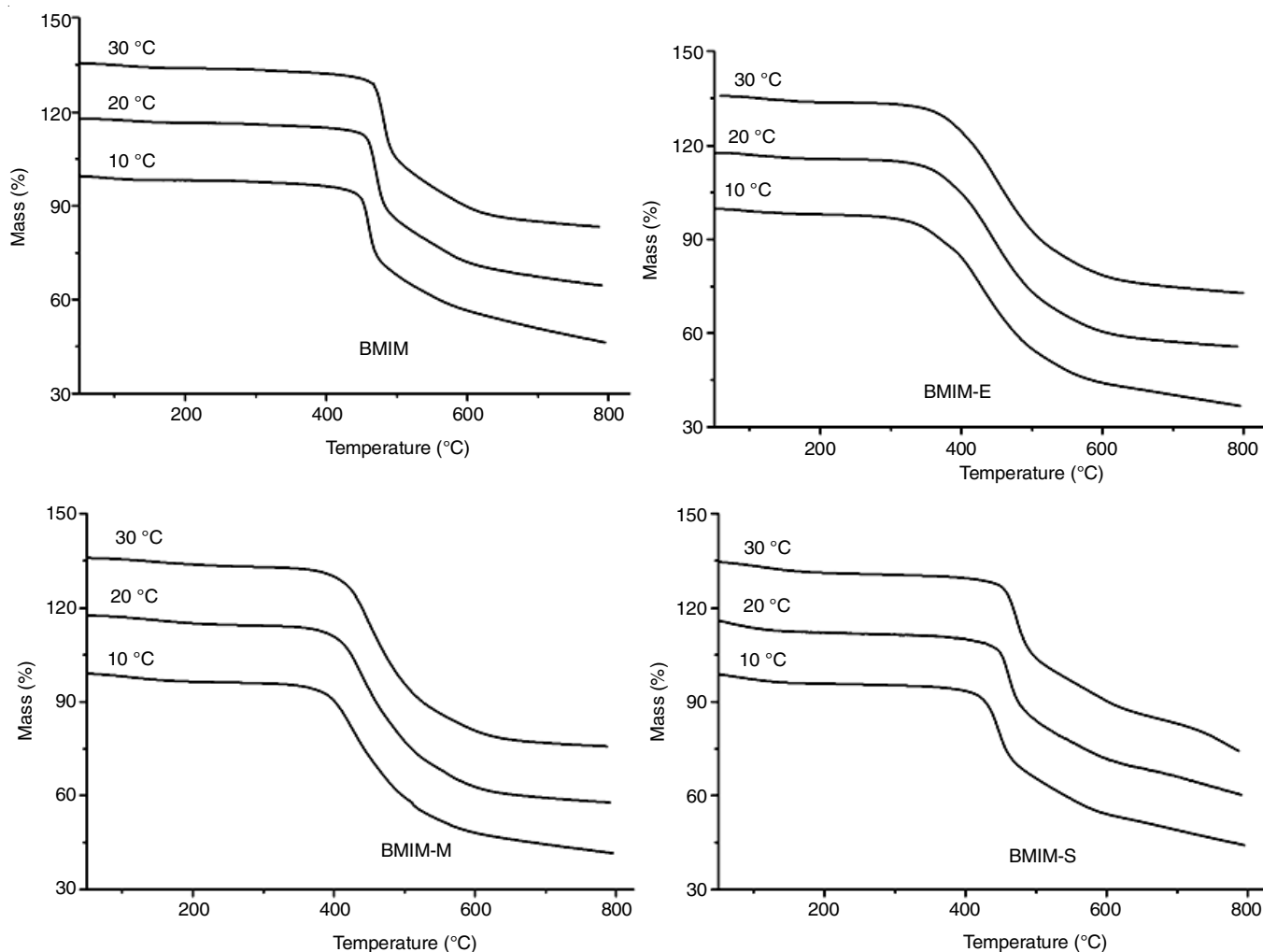

Fig. 6. TG curves of BMIM and chain extended BMIM

TABLE-3
DATA FROM THE TG CURVES OF THERMALLY CURED PURE BMIM AND CHAIN EXTENDED BMIM

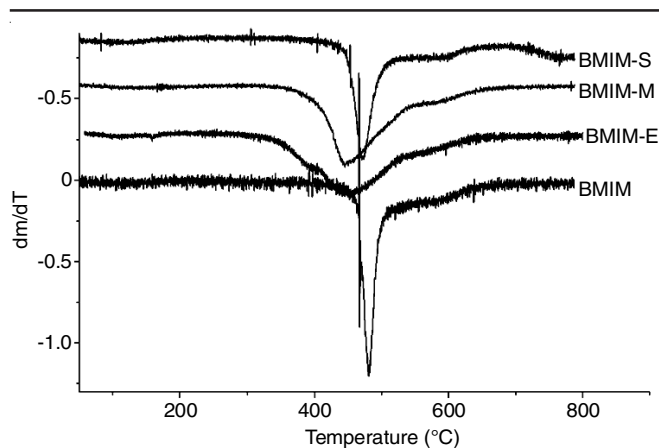| Material	Heating rate (°C/min)	Onset T_s (°C)	Maximum T_{max} (°C)	Endset T_e (°C)	Char value at 800 °C (%)
BMIM	10	420	450	620	45
	20	425	460	610	44
	30	440	475	600	45
BMIM-E	10	375	420	600	38
	20	380	430	620	38
	30	380	450	620	39
BMIM-M	10	390	420	600	39
	20	395	430	620	40
	30	395	440	625	40
BMIM-S	10	465	440	615	49
	20	470	450	620	49
	30	470	470	620	48

Fig. 7. DTG curves of BMIM and chain extended BMIM at 20 °C min⁻¹

curves of BMIM clearly indicates that the second degradation starts well before the completion of the first degradation. At around 395 °C the first weight loss occurred followed by the second weight loss which starts at 500 °C. The quantity of left over char is found to be 45 % at 710 °C. The introduction of aromatic diamines in pure BMIM along with the polymers produced from them by thermal curing of BMIM-E, BMIM-M and BMIM-S shifts the initial degradation temperature to 360, 370 and 400 °C respectively, at a heating rate of 20 °C min⁻¹.

The DTG curves evidenced the fast degradation of BMIM-E and BMIM-M among the different chain extended BMIM. The authors investigated the thermal properties of structurally different bismaleimides which are thermally cured. From all the investigated materials one can finalized the presence of two overlapping degradations which shown bismaleimide matrix systems are having nearly similar degradation mechanisms. At up to 520 °C, the first stage decomposition occurred accounting for 20 % weight loss, which may be due to the loss of diamine *via* Michael addition when compared to BMIM.

Kinetic analysis: Kinetic analysis of the degradation of all the thermally cured materials are studied from the TG curves at three different heating rates (β = 10, 20, 30 °C min⁻¹). The apparent activation energies for the degradation of thermally cured samples are studied (Table-4) and compared by utilizing the three model-free iso-conversional kinetic methods (KAS, FWO and FRD) shown in Fig. 8. The plot of ln ($\beta/T2$) *vs.* 1/T,

log β *vs.* 1/T and ln (dα/dt) *vs.* 1/T gives a straight line for KAS, FWO and FRD respectively, indicates the validity of the three methods for the present systems. The possibility of a single reaction mechanism is shown from the parallel lines in the plots up to 65 % degradation. But above 65 % degradation, complex reaction occurs which are reflected by the non-parallel lines. Similar for other cured materials investigated the same trend is noticed. There is a difference in the apparent activation energy values calculated by FRD method for the degradation of cured samples, whereas the other two methods KAS and FWO give the same value. The difference is because of the different methods involved in the calculation of activation energy that is KAS and FWO methods are integral and FRD is differential one.

Fig. 9 shows the plots of activation energy *versus* reaction extent for the degradation of cured samples calculated using KAS method. The activation energy values calculated using KAS and FWO methods are comparatively similar and the E_a can be considered as having almost constant average value up to 90 % conversion for the thermal degradation of aliphatic polyester, polyethylene adipate [14]. The apparent activation energy for the degradation studies of thermally cured BMIM shows decrease up to the reaction extent 0.65 after that it increases. Using GC-MS technique thermal pyrolysis products of polymerized bismaleimide, 4,4'-bismaleimido diphenyl methane at 500, 600 and 700 °C in air and 500 and 600 °C in nitrogen are analyzed by Torrecillas *et al.* [15]. They found that aniline and phenyl isocyanate occur in the first phases of degradation (500 °C) as the main substance, whether under air or nitrogen. They also suggested the degradation mechanism for the formation of isocyanate derivatives from cross-linked polybismaleimides which releases CO, CO_2 and H_2O molecules.

Xie *et al.* [16] studied the thermal properties of polymerization of four different monomeric reactants (PMR) polyimides using TG/FTIR/MS. They found that carbon dioxide is released in two stages as a major compound from polyimides. The detection of CO_2 before CO indicates that both CO and CO_2 are the direct products from the decomposition of polyimides and phenyl isocyanates as the other major product. The cleavage of carbonyl group in the imide rings is confirmed by the presence of benzonitrile using TG-MS. Lastly they finalized that CO is obtained directly from the degradation of imide

TABLE-4
ACTIVATION ENERGIES FOR THE THERMAL DEGRADATION OF BMIM AND CHAIN EXTENDED BMIM

| Sample		E_a values (KJ/mol)												
	α	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80
BMIM	KAS	252	249	284	288	259	276	335	454	184	609	525	407	243
	FWO	251	248	250	253	258	274	330	443	187	566	486	373	218
	FRD	213	231	246	279	314	397	620	731	186	734	333	346	169
BMIM-E	KAS	210	240	249	256	269	284	305	335	368	407	407	133	97
	FWO	210	355	248	254	267	281	302	330	361	399	399	138	80
	FRD	168	160	169	164	197	207	228	245	247	247	254	179	284
BMIM-M	KAS	198	205	220	237	256	295	342	413	482	616	1415	1322	3899
	FWO	199	206	221	237	255	292	336	404	470	597	1357	1244	3692
	FRD	218	237	254	274	290	399	387	402	560	782	1799	823	5002
BMIM-S	KAS	150	159	162	165	163	159	149	133	118	110	112	113	99
	FWO	154	162	166	168	166	163	153	138	125	117	120	121	108
	FRD	211	190	185	177	154	142	152	125	97	119	114	96	74
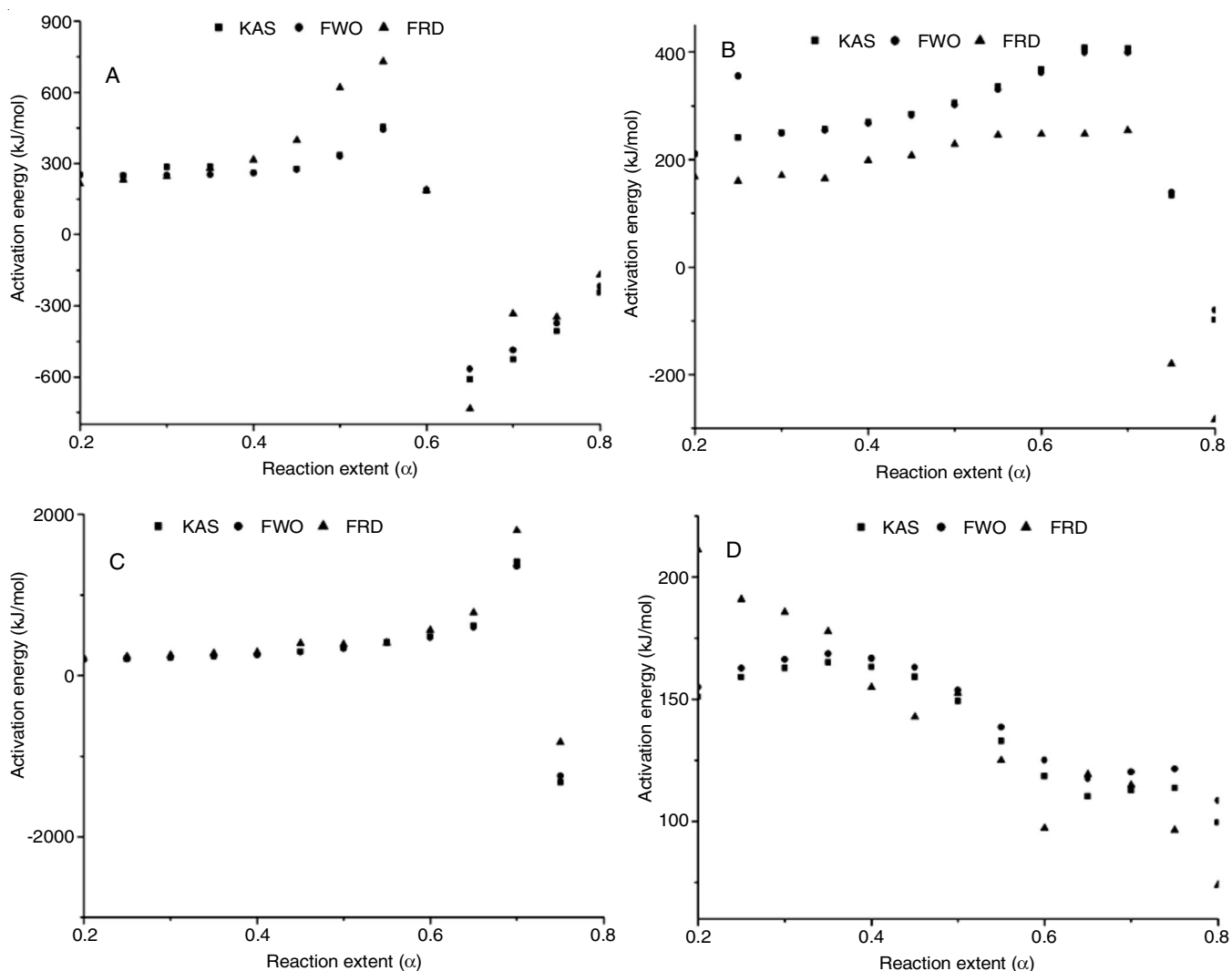
Fig. 8. Plots between the activation energy *vs.* reaction extent for the degradation of thermally cured A = BMIM, B = BMIM-E, C = BMIM-M and D = BMIM-S
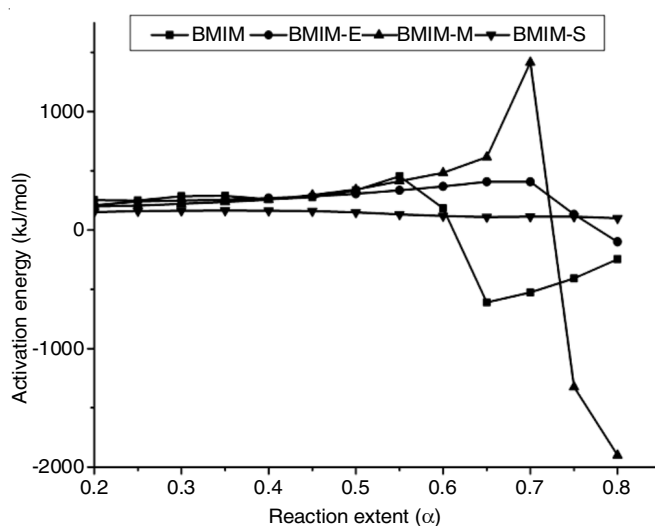

Fig. 9. Plots between the activation energy and reaction extent for the degradation of thermally cured BMIM, BMIM-E, BMIM-M and BMIM-S

ring and CO_2 is produced by the further combination of the formed CO with oxygen radicals during pyrolysis of hydrocarbon polymers.

The above results concluded that amine and isocyanate are formed as a corresponding major degradation product during the thermal degradation of polybismaleimide by the release of carbon monoxide and carbon dioxide. The increase in the activation energy confirms the formation of aniline and phenyl isocyanate during the degradation of BMIM. Reasonable amounts of CO and CO_2 is released from the degrading polymerized BMIM before the reaction extent 0.55 causing the destruction of imide rings and the presence of favourably structured degrading BMIM requires considerably less energy for degradation after $\alpha = 0.55$. Further degradation of BMIM is restricted by the formation of coke which creates a surface layer of protective char at the reaction extent value of 0.65. Thus for further degradation the system requires additional energy, thereby raise the activation energy.

The variation in activation energy for the degradation of the material BMIM-E is different from BMIM. After the reaction extent 0.40 the activation energy increases due to the formation of aniline and phenyl isocyanate during the degradation of BMIM-E till $\alpha = 0.7$ and then it decreases. The activation energy values for the degradation of BMIM-M is similar to that of BMIM up to the reaction extent 0.55. But after the reaction

extent 0.65 the activation energy for the total degradation process of BMIM-M increases by nearly 500 kJ/mol and then decreases. The observed steep 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 BMIM using aromatic methylene diamines. The variation in activation energy noted for the degradation of the material BMIM-S is different from the other three materials. Its activation energy is 100 kJ/mol less when compared to pure BMIM. After the reaction extent of 0.6 there is no change in the activation energy values up to the reaction extent 0.8. By observing the activation energy trends of BMIM-E and BMIM-M, authors conclude that the chain extension using E and M plays a vital role in the degradation mechanism of the pure BMIM.

Varma *et al.* [17] 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). 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 and 220 °C (1 h each) was carried out in nitrogen atmosphere. They reported that thermal stabilities improved on blending of chain extended bismaleimides.

Rajasekaran *et al.* [18] studied the effect of polyether sulfone and N,N'-bismaleimide-4,4'-diphenylmethane on the epoxy resins. In order to develop 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). 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 concluding that the degradation temperature was increased with increasing BMI concentrations as observed in the case of polyethersulfone modified systems and this may because of the rigidity and enhanced crosslink density imparted by bismaleimide.

Conclusion

The three different chain extended bismaleimides were prepared using three different aromatic diamines. DSC analysis was used to investigate the curing behaviour of 4,4'-bismaleimidodiphenyl methane (BMIM) and chain extended BMIM. Chain extension considerably reduces the melting point and also the amount of heat released during the thermal curing in BMIM-E and BMIM-M. The absence of a melting peak in the chain extended BMIM can thus be accounted by the initiation of curing reactions at temperatures lower than the melting point of pure BMIM. 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. Detailed thermogravimetric analysis of thermally cured pure BMIM and chain extended BMIM reveals the initial degradation temperature lies in the range between 360-400 °C. The apparent activation energy values for the thermal degradation of the BMIM-S are significantly reduced when compared to pure BMIM. Char yield was not significantly affected when pure bismaleimides were extended by aromatic diamines.

REFERENCES

1. A. Georgiev, D. Dimov, E. Spassova, J. Assa, P. Dineff and G. Danev, Chemical and Physical Properties of Polyimides: Biomedical and Engineering Applications, In: High Performance Polymers-Polyimide Based-from Chemistry to Applications, InTech Open, Chap. 4, pp. 65-84 (2012); https://doi.org/10.5772/53918.

2. E.S. Guerra and E.V. Lima, Handbook of Polymer Synthesis, Characterization and Processing, Wiley & Sons (2013).

3. R. Girase, R. Jaiswal, L. Chaudhari, S. Bhattacharya and D. D'Melo, Studies on Unsaturated Polyester Composites for High-Temperature Applications, *J. Vinyl. Addit. Technol.*, **18**, 46 (2012); https://doi.org/10.1002/vnl.20282.

4. H. Stenzenberger and P. Konig, New Functionalized Poly(arylene-ether ketone)s and Their Use as Modifiers for Bismaleimide Resin, *High Perform. Polym.*, **5**, 123 (1993); https://doi.org/10.1088/0954-0083/5/2/004.

5. I.K. Varma and R. Tiwari, Cyclodehydration of Bismaleamic Acids, *Macromol. Mater. Eng.*, **157**, 59 (1988); https://doi.org/10.1002/apmc.1988.051570106.

6. T. Ozawa, A New Method of Analyzing Thermogravimetric Data, *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965); https://doi.org/10.1246/bcsj.38.1881.

7. H.E. Kissinger, Reaction Kinetics in Differential Thermal Analysis, *Anal. Chem.*, **29**, 1702 (1957); https://doi.org/10.1021/ac60131a045.

8. T. Akahira and T. Sunose, Method of Determining Activation Deterioration Constant of Electrical Insulating Materials, *1969th Res. Report, Chiba Inst. Technol. (Sci. Technol.)*, **16**, 22-31 (1971).

9. J.H. Flynn and L.A. Wall, *Polym. Lett.*, **4**, 323 (1966); https://doi.org/10.1002/pol.1966.110040504.

10. C.T. Vijayakumar, R. Surender, K. Rajakumar and S. Alam, Synthesis and Thermal Studies of Bisphenol-A based Bismaleimide, *J. Therm. Anal. Calorim.*, **103**, 693 (2011); https://doi.org/10.1007/s10973-010-1020-5.

11. G. Pitchaimari and C.T. Vijayakumar, *J. Therm. Anal. Calorim.*, **114**, 1351 (2013); https://doi.org/10.1007/s10973-013-3174-4.

12. D.J.T. Hill, G.A. George and D.G. Rogers, A Systematic Study of the Microwave and Thermal Cure Kinetics of the TGDDM/DDS and TGDDM/DDM Epoxy-Amine Resin Systems, *Polym. Adv. Technol.*, **12**, 169 (2001); https://doi.org/10.1002/pat.139.

13. S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu and N. Sbirrazzuoli, *Thermochim. Acta*, **520**, 1 (2011); https://doi.org/10.1016/j.tca.2011.03.034.

14. R. Surender, A. Mahendran, A. Thamaraichelvan, S. Alam and C.T. Vijayakumar, Curing Studies of Bisphenol A based Bismaleimide and Cloisite 15a Nanoclay Blends using Differential Scanning Calorimetry and Model-Free Kinetics, *J. Appl. Polym. Sci.*, **128**, 712 (2013); https://doi.org/10.1002/app.38219.

15. R. Torrecillas, N. Regnier and B. Mortaigne, Thermal Degradation of Bismaleimide and Bisnadimide Networks-Products of Thermal Degradation and Type of Crosslinking Points, *Polym. Degrad. Stab.*, **51**, 307 (1996); https://doi.org/10.1016/0141-3910(95)00197-2.

16. W. Xie, W.-P. Pan and K.C. Chuang, Thermal Characterization of PMR Polyimides, *Thermochim. Acta*, **367-368**, 143 (2001); https://doi.org/10.1016/S0040-6031(00)00698-5.

17. I.K. Varma and R. Tiwari, Thermal Characterization of Bismaleimide Blends, *J. Therm. Anal.*, **32**, 1023 (1987); https://doi.org/10.1007/BF01905158.

18. R. Rajasekaran, M. Alagar and C.K. Chozhan, Effect of Polyethersulfone and N,N′-Bismaleimido-4,4′-diphenyl methane on the Mechanical and Thermal Properties of Epoxy Systems, *Express Polym. Lett.*, **2**, 339 (2008); https://doi.org/10.3144/expresspolymlett.2008.40.