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Thermal Degradation Kinetics of Structurally Diverse Poly(bispropargyl ethers-bismaleimide) Blends*

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Abstract Structurally diverse bispropargyl ethers using resorcinol, quinol, 4,4′-dihydroxy biphenyl, bisphenol-A, 4,4′-dihydroxy diphenyl ketone, 4,4′-dihydroxy diphenylsulphone, trimethyl indane bisphenol and tetramethyl spirobiindane bisphenol were prepared by using phase transfer catalyst. Synthesized materials were separately blended with 4,4′-bismaleimido diphenyl methane (BMIM) in mole ratios (0.5:0.5). The materials were thermally cured and the structural characterisation and the thermal properties of these cross-linked materials are investigated using Fourier-transform infrared (FTIR) spectrophotometer and thermogravimetric analyzer (TGA). Among the different materials investigated polyMRPE, polyMBPEBPA and polyMSPE show higher onset degradation temperature of 300 °C indicating higher thermal stability. The degradation kinetics is investigated using Flynn-Wall-Ozawa (FWO), Vyazovkin (VYZ) and Friedman (FRD) methods. Amongst the various cured materials investigated, the activation energy (E_a-D) values obtained for polyMRPE and polyMKPE were observed to increase continuously from $\alpha = 0.2$ to 0.8 and the values range from 199 kJ/mol to 245 kJ/mol and 153 kJ/mol to 295 kJ/mol respectively. The crosslinked materials resulting from these bispropargyl monomers definitely need more energy for bond cleavage due to the presence of more aromatic units. The volatile products obtained during the thermal degradation of the polymers were analyzed using thermogravimetric-Fourier transform infrared analyses (TG-FTIR). The phenols, substituted phenols, carbon monoxide, carbon dioxide and small amount of aniline were found to be the major products during thermal degradation of these cured blends.

Keywords: Bispropargyl ethers; Bismaleimide; TG; Degradation kinetics; TG-FTIR.

INTRODUCTION

High temperature resistant materials have attracted a great deal of interest in aerospace and microelectronics industries[1]. Temperature changes can stimulate a variety of chemical and physical processes in polymer systems. Important examples of these processes include glass transition, crystallization, crosslinking, thermal degradation, *etc*. The overall or macroscopic kinetics of these processes are conveniently measured by using thermal analysis methods such as differential scanning calorimetry (DSC), thermogravimetry (TG) and other techniques[2, 3]. A thermal analysis method, mainly thermogravimetric method is extensively used to study the thermal degradation of the polymers. The kinetic parameters such as the activation energy (E_a), pre exponential

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factor (*A*) and reaction model (*n*) of thermal degradation of polymers give an idea regarding the decomposition mechanism of the materials[4–6].

The bispropargyl derivatives of bisphenols have been developed as one of the high performance resins and they possess good thermal stability and moisture resistance[7, 8]. These bispropargyl derivatives are attractive from the point of view of the ease of synthesis and polymerization. In addition the materials are polymerized without any volatiles, which make them possible to get void free materials without high pressure[9, 10]. Thermosetting bismaleimide resins are used as matrices for advanced composites in aerospace and electronic industries. They possess excellent thermal and oxidative stability, flame retardation and low propensity to moisture absorption. Bismaleimides can be also cured without the evolution of volatiles.

In many cases, certain properties of a polymer can be enhanced by blending it with one another. Blending of thermosets is one of the ways to reduce cost and/or to improve mechanical performance of the material, but also to reduce negative environmental impact. The properties of a thermoset and composites made out of it are greatly influenced by addition of the second component. Many studies have devoted to blend allyl derivates of phenols, such as 2,2′-diallyl-bisphenol A, allyl ether novolac with bismaleimide. The results indicated that the blend resins exhibited better toughness and high heat resistance[11]. Owing to the similar chemical property of propargyl group and allyl group, it is expected that the thermal properties can be sufficiently improved by blending bispropargyl ether with bismaleimide. The blends of bispropargyl ethers and bismaleimide are having good thermal stability and have good physico-chemical attributes of the two resin systems. The unsaturated bonds present in the both systems are polymerized without forming any volatiles[12].

In the previous study[13] the authors reported on the curing kinetics E_a-C of structurally diverse bispropargyl ethers (BPEs) and their blends with bismaleimide. The detailed curing studies of the synthesized different bispropargyl ethers and their blends with BMIM were performed using DSC and it was found out that the addition of BMIM affected the melting and curing behavior of the bispropargyl ethers. Hence, it is reasonable to expect that the addition of BMIM in bispropargyl ethers shows some influence during the degradation process of the cured different bispropargyl ethers. The variation of the activation energy with the extent of conversion helps to reveal the complexity of multiple reactions taking place during thermal degradation of materials[14].

Hence in the present work it is intended to investigate the variation in the apparent activation energy for the thermal degradation (E_a-D) of the thermally cured bispropargyl ethers blended with 4,4′-bismaleimido diphenyl methane (0.5:0.5 mol). The three model free kinetic methods Flynn-Wall-Ozawa (FWO), Vyazovkin (VYZ) and Friedman (FRD) are used to evaluate the apparent activation energies for the degradation and the results are presented and discussed.

EXPERIMENTAL

Preparation of BPEs and BMIM

The synthetic procedures for the preparation of structurally diverse bispropargyl ethers (BPEs) using resorcinol (RPE), quinol (QPE), 4,4'-dihydroxy biphenyl (BPPE), bisphenol-A (BPEBPA), 4,4'-dihydroxy diphenyl ketone (KPE), 4,4'-dihydroxy diphenylsulfone (SPE), trimethyl indane bisphenol (IPE) and tetramethyl spirobiindane bisphenol (SPIPE) were already presented in detail in the previous work[13]. 4,4'-Bismaleimido diphenyl methane (BMIM) was obtained from ABR Organic Ltd, Hyderabad, India. The structures of BPEs and BMIM are shown in Fig. 1.

Blending of Bispropargyl Ethers (BPEs) with BMIM

The different BPEs were separately blended with BMIM (0.5:0.5 mol) in an agate mortar and the mixture was ground repeatedly to have effective mixing. The mixture was then dried in a vacuum oven and preserved for polymerization. The following blends were made: MRPE (0.5 mol RPE + 0.5 mol BMIM), MQPE (0.5 mol QPE + 0.5 mol BMIM), MBPPE (0.5 mol BPPE + 0.5 mol BMIM), MBPEBPA (0.5 mol BPEBPA + 0.5 mol BMIM), MKPE (0.5 mol KPE + 0.5 mol BMIM), MSPE (0.5 mol SPE + 0.5 mol BMIM), MIPE (0.5 mol IPE + 0.5 mol BMIM), MSPIPE (0.5 mol SPIPE + 0.5 mol BMIM).

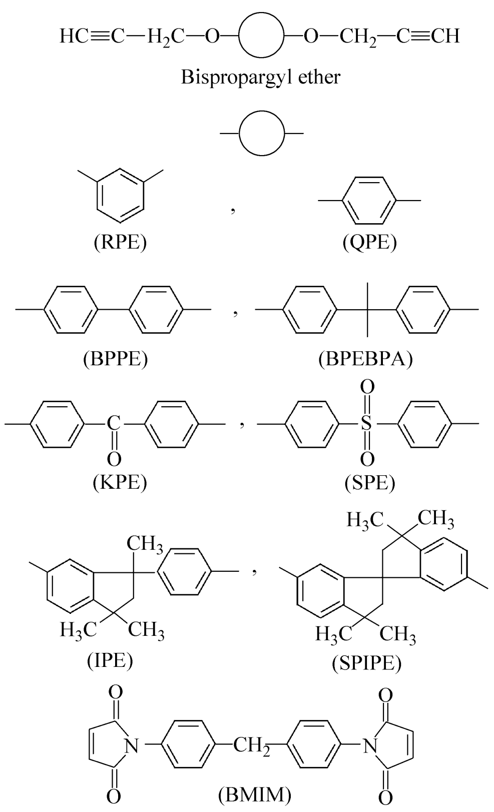


Fig. 1 Structures of bispropargyl ethers and BMIM

Thermal Curing

The materials MRPE and MQPE and BMIM were separately taken in micro test tubes and flushed with dry oxygen-free-nitrogen. The materials were thermally polymerized at 210 °C for 6 h. The blends MBPPE, MBPEBPA, MKPE, MSPE, MIPE and MSPIPE were taken in micro test tubes separately and flushed with dry oxygen-free-nitrogen. The materials were thermally polymerized at 240 °C for 6 h. After the polymerization, test tube was cooled and the sample were removed from the micro test tube, ground to coarse powder, packed and stored for further analysis.

Methods

The FTIR spectra of the cured materials were recorded using a Shimadzu Fourier Transform Infrared Spectrophotometer-8400S, Japan by employing KBr disc technique. The TG curves for all the thermally cured materials were recorded in a TA Instruments TG Q50 system. The samples were heated at different heating rates (20, 30 and 40 K/min) from ambient to 800 °C in nitrogen atmosphere. Generally 2 mg to 3 mg of the sample was used with a balance flow of 40 mL/min and a sample flow of 60 mL/min. The TG-FTIR studies for all the materials cured blends were carried out in a TA instruments TGA Q5000V3.10 Build 258 system using a heating rate of 10 K/min from ambient to 800 °C. Nearly, 2–3 mg samples were used for the analysis in nitrogen atmosphere (balance flow: 10 mL/min and sample flow: 25 mL/min) and the FTIR of the degraded products were recorded for every 30 s.

Kinetic Analysis

The rate of solid-state reactions can be described as

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

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 temperature-dependent rate constant, $k(T)$ is defined as

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

where A is pre-exponential factor, E_a is the activation energy, R is the gas constant and T is temperature. The reaction extent for the degradation reaction is shown in the following equation

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

where W_o is the weight at initial, W_T is the weight at the particular temperature, W_e is the weight at the end of the degradation process.

Flynn-Wall-Ozawa Method (FWO)

The FWO method is widely used for dynamic kinetic analysis and does not require any assumptions to be made about the conversion dependence[15]. The equation used for this method is given as follows

$$E_a = \frac{-R\Delta\ln\beta}{1.052\Delta(\frac{1}{T})} \tag{3}$$

where E_a is the apparent activation energy, R is the gas constant, β is the heating rate and T is the temperature. In this method, plots of $\ln\beta$ versus $1/T$ give parallel lines for each α value. The slope of these lines gives apparent activation energy (E_a), as per the following expression

$$\text{Slope} = -0.4567\left(\frac{E_a}{R}\right) \tag{5}$$

Vyazovkin Method (VYZ)

The activation energy can be determined at any particular degree of conversion by finding the value of E_a for which the objective function Ω is minimized[16].

$$\Omega = \sum_{i=1}^{n}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{I(E_a, T_{\alpha i})\beta_j}{I(E_a, T_{\alpha j})\beta_i} \tag{6}$$

with

$$I(E_a, T_{\alpha i}) = \int_0^{T_{\alpha i}}\exp\left(\frac{-E_a}{RT}\right)dT \tag{7}$$

Theory and application of model free kinetic approaches, starting from basic rate equations and ending in activation energy prediction are discussed in the literature[17]. Since every kinetic method has different error, the use of more than one method can give a range of values for the activation energy at very particular value of the extent of reaction (α)[18].

Friedman Method (FRD)

This is one of the differential methods used to calculate E_a and the equation[19] is given below

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln z + n\ln(1-\alpha) - \left(\frac{E_a}{RT}\right) \tag{8}$$

From the slope ($-E_a/R$) of the linear plot between $\ln(d\alpha/dt)$ versus $1/T$, where z is a constant, E_a of the system can be calculated.

RESULTS AND DISCUSSION

FTIR Studies

The FTIR spectra of thermally polymerized different bispropargyl ethers-BMIM blends are shown in Fig. 2. The appearance of a new broad band at 3433 cm^{-1} indicates the formation of phenol entities during the curing process and the appearance of a band around 1605 cm^{-1} indicates the conversion of the propargyl group to chromene structure. The disappearance of $\equiv$C—H stretching band at 3263 cm^{-1} and C$\equiv$C stretching band at 2121 cm^{-1} confirms the polymerization of bispropargyl ethers[20]. The FTIR spectrum of all the thermally polymerized materials shows the appearance of a new band at around 1607 cm^{-1} which is due to the chromene ring present in the polymerized compounds. The FTIR spectrum of thermally cured BMIM shows the disappearance of maleimide =CH peak at 3095 cm^{-1} and appearance of aliphatic C—H peak at 2931 cm^{-1}, which indicates the curing process is near completion. Thermally polymerized materials show an absorption band at 1504 cm^{-1} attributed to the phenyl nucleus stretching. The presence of a band at around 1705 cm^{-1} confirms the presence of the cyclic imide ring structure in the cured thermosets.

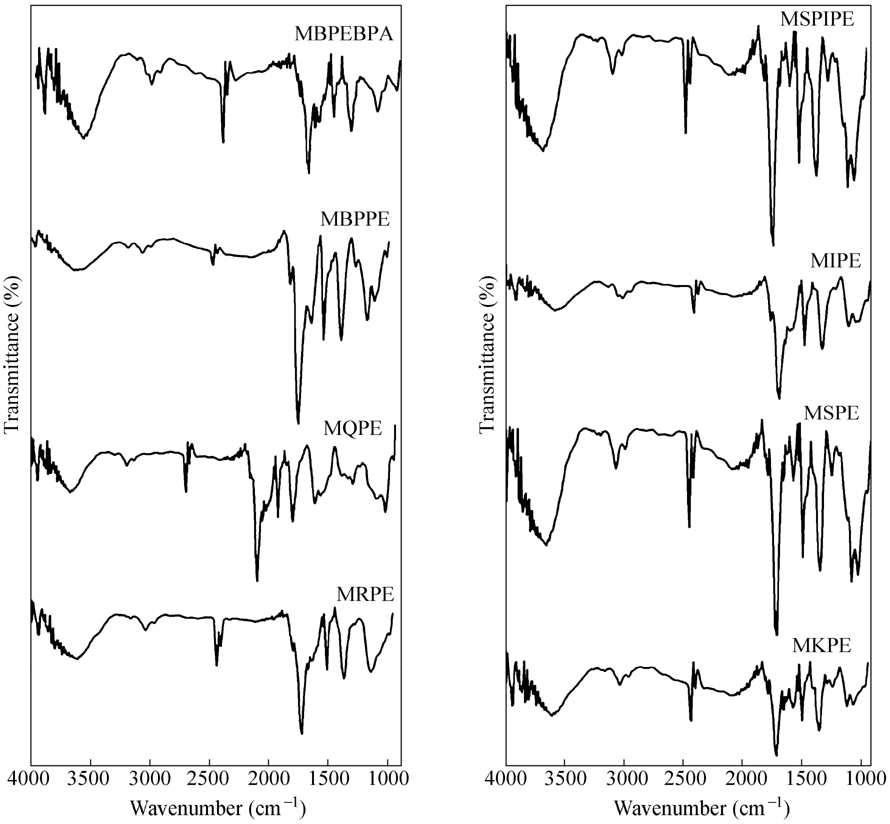


Fig. 2 FTIR spectra of thermally cured different bispropargyl ethers-BMIM blends

Curing of the bispropargyl ether-bismaleimide blends (240 °C for 6 h) shows remarkable decrease of the band at 3263 cm^{-1} ($\equiv$C—H) and band at 2121 cm^{-1} (C$\equiv$C). The absorption band pertaining to the C—N—C group (1388 cm^{-1}) changed slightly. This indicated that more propargyl groups were consumed than maleimide groups in co-cure reactions. After that the absorption of propargyl groups and maleimide both disappeared, which confirms the complete polymerization of the materials[10].

The FTIR spectra of the thermally cured different bispropargyl ethers-BMIM blends show the absorption bands corresponding to the cured pure bispropargyl ethers and indicating that the blending of propargyl ether with bismaleimides does not affect the basic polymerization mechanism of the cured pure materials. Zhao *et al.*[21] studied the thermal properties of propargyloxy phenylmaleimides and reported that in the FTIR spectra of the polymerized materials, the percentage transmittance noted for the peaks corresponding to maleimide and propargyl groups are decreasing in the same manner and this indicates that the consumption rates of the two groups might be close in curing reactions.

Surender *et al.*[22] studied the isothermal curing behavior of bispropargyl ether and bismaleimide blends. The blends of BPEBPA and 4,4′-bismaleimido diphenyl ether (BMIE) having different weight ratios (80:20, 60:40, 40:60, 20:80) were made and the pure monomers and blends were isothermally polymerized at 200 °C for different time intervals (0, 3, 6, 9, 12 h). The FTIR studies of the blends reveal that the addition of BMIE is not affecting very much the absorption peaks specific for BPEBPA. The FTIR spectra of the cured blends (BPEBPA and BMIE) at different time intervals clearly show the formation of a broad absorption peak at 3450–3550 cm^{-1} indicating the presence of phenolic groups in the cured blend. This hints that the addition of BMIE is not affecting the polymerization mechanism of BPEBPA.

From the above observations, it is concluded that the blending of BMIM with structurally different bispropargyl ethers is not interfering with the polymerization of the propargyl groups *i.e.*, the Claisen rearrangement of the propargyl groups, the conversion to the chromene structure followed by the addition polymerization of the double bond present in the chromene ring.

TG and DTG Studies

The TG and DTG curves for thermally cured different bispropargyl ethers-BMIM blends recorded at 20 K/min in nitrogen atmosphere are shown in Fig. 3 and for clarity the TG curves are shifted uniformly in the *Y* axis and the DTG curves are also shifted in the *Y* axis uniformly. The TG and DTG traces for polyMSPIPE recorded at different heating rates (20, 30 and 40 K/min) in nitrogen atmosphere are shown in Fig. 4. All the thermograms are shifted to higher temperatures with increasing heating rates. The onset (T_S), maximum (T_{max}), endset (T_E) temperatures for the degradation and the char residue obtained at 700 °C for all the samples noted at 20 K/min are tabulated in Table 1. The detailed observations of the thermogravimetric data for all the cured materials obtained at a heating rate of 20 K/min are discussed below.

The DTG curves (Fig. 3) of thermally cured MRPE, MBPPE, MBPEBPA, MSPE and MIPE show double stage degradation and thermally cured MQPE, MKPE and MSPIPE show overlapping multi stage degradations in which before the completion of a particular stage of degradation of the material the next stage of degradation begins and thus the degradation is complex[23]. The initiation of the second stage degradation reaction for the following materials polyMQPE, polyMKPE and polyMSPIPE was nearly in the same temperature region and was found in the range of 500–510 °C.

Table 1. The degradation parameters for the thermally cured structurally different bispropargyl ethers-BMIM blends and polyBMIM (Heating rate 20 K/min)

Samples	T_S (°C)	T_{max} (°C)			T_E (°C)	Char residue at 700 °C (%)
		I	II	III		
PolyMRPE	310	465	–	560	750	56
PolyMQPE	268	458	508	598	745	48
PolyMBPPE	254	445	–	575	750	58
PolyMBPEBPA	300	440	–	572	725	48
PolyMKPE	275	438	510	558	750	60
PolyMSPE	298	405	–	542	748	54
PolyMIPE	288	445	–	582	740	48
PolyMSPIPE	268	458	504	582	750	43
PolyBMIM	430	470	–	–	532	49

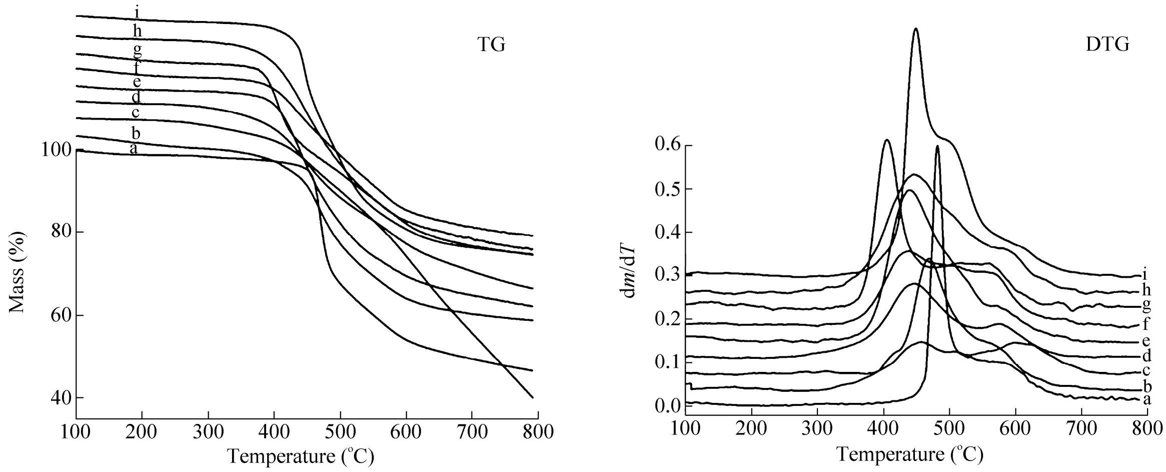


Fig. 3 TG and DTG traces of thermally cured different bispropargyl ethers-BMIM blends (heating rate = 20 K/min): (a) polyBMIM, (b) polyMRPE, (c) polyMQPE, (d) polyMBPPE, (e) polyMBPEBPA, (f) polyMKPE, (g) polyMSPE, (h) polyMIPE and (i) polyMSPIPE (For clarity TG and DTG curves are shifted uniformly in the *Y* axis.)

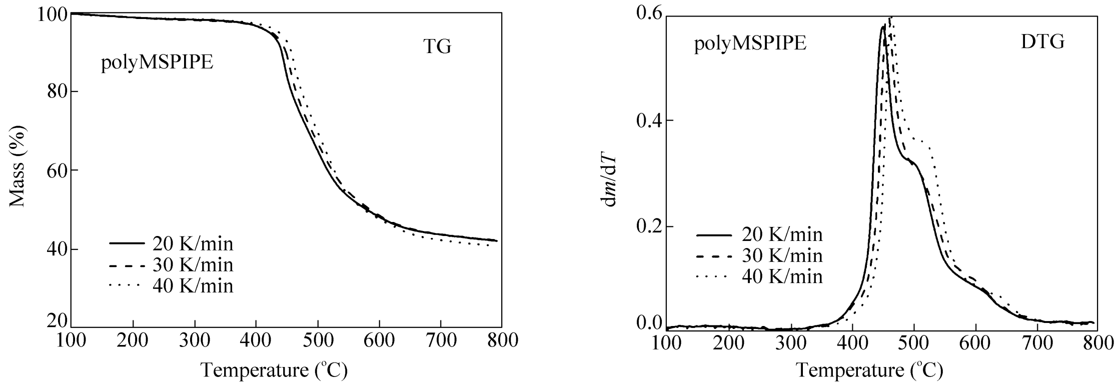


Fig. 4 TG and DTG traces of thermally cured MSPIPE at different heating rates (20, 30 and 40 K/min)

The thermally cured MRPE shows the onset degradation temperature at 310 °C and the maxima for the two stages of degradation were found to be at 465 and 560 °C respectively. The degradation nearly ends at 750 °C and the char residue at 700 °C is 56%. Thermally cured MBPEBPA shows the onset degradation temperature at 300 °C and the degradation was found to have maxima at 440 and 572 °C respectively. The thermal degradation was nearly over by 725 °C, and the char residue at 700 °C is 48%. The onset degradation for the thermally cured MSPE was found at 298 °C. The first and the second degradation stages were found to have maxima at 400 and 540 °C. The degradation was nearly complete by 748 °C, and the char residue at 700 °C is 54%. Taking into consideration the initial degradation temperature as the main criterion for the thermal stability, from Table 1, one can easily identify that among all the materials investigated, polyMRPE, polyMBPEBPA and polyMSPE materials are showing better thermal stability than other materials investigated. A plausible explanation for this observation is the presence of highly crosslinked network resulting from the thermal curing process.

The thermally cured MKPE and MIPE show the onset degradation around 280 °C whereas the thermally cured MQPE, MBPPE and MSPIPE show slightly lower onset degradation temperature (260 °C). The degradation maxima for cured MQPE, MBPPE and MSPIPE were found between 450 °C and 585 °C and were found to be between 440 and 570 °C for the materials polyMKPE and polyMIPE. The degradation was found to be complete for these materials at around 750 °C. The char residues at 700 °C are 48, 58 and 43 for polyMQPE, polyMBPPE and polyMSPIPE respectively. The char residues for polyMKPE and polyMIPE at 700 °C are 60%

and 48% respectively.

Ping Chen *et al.*[24] studied the cure behavior of the mixer of bismaleimide containing phthalide cardo structure (BMIP) and 2,2-diallyl bisphenol A (DABPA) and reported the kinetics and thermal properties of the mixture. They reported that the cured network of bismaleimide containing phthalide cardo structure (BMIP) and 2,2′-diallyl bisphenol A (DABPA) underwent two-stage decomposition reaction, and the inflection temperatures of the two stages are 476 and 534 °C, respectively. The first stage could be due to the degradation of the aliphatic chain structures derived from allyl groups, and the second stage should be attributed to the aryl and the heterocyclic structures derived from maleimide in the cured resins.

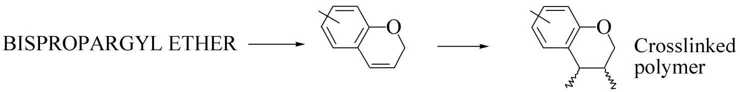
The thermally cured MIPE shows onset degradation at 288 °C which is higher than that of the thermally cured MSPIPE which shows onset at 268 °C as evidenced from Table 2. Vijayakumar *et al.*[25] studied the thermal properties of structurally diverse bisbenzoxazines. They reported the increased thermal stability of PIBPB, poly(indane bisphenol bisbenzoxazine), when compared to PSBIB, poly(spirobiindane bisphenol bisbenzoxazine), and concluded that the high temperature curing of SBIB may lead to the breakage of the spirobiindane unit, which may be the probable reason for the lower thermal stability of PSBIB.

Table 2. Apparent activation energy (E_a-D) values for thermally cured structurally diverse bispropargyl ethers-BMIM blends (VYZ method) at different reaction extents (α)

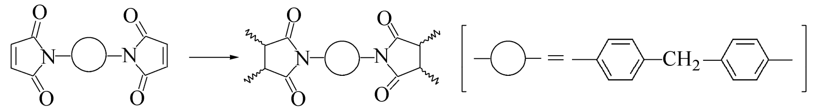
Samples	E_a-D (kJ/mol)												
	a = 0.20	a = 0.25	a = 0.30	a = 0.35	a = 0.40	a = 0.45	a = 0.50	a = 0.55	a = 0.60	a = 0.65	a = 0.70	a = 0.75	a = 0.80
poly MRPE	199	199	197	203	211	212	234	235	245	245	245	245	245
poly MQPE	100	100	100	100	109	124	146	168	195	215	233	245	245
poly MBPPE	125	108	100	100	100	100	100	100	115	138	166	209	245
poly MBPEBPA	149	156	155	158	165	177	196	218	233	245	245	245	295
poly MKPE	153	153	166	172	195	211	234	245	255	265	270	285	295
poly MSPE	134	138	138	143	148	157	169	182	193	194	214	233	245
poly MIPE	100	104	111	121	127	142	152	175	210	245	245	245	245
poly MSPIPE	155	154	147	146	147	153	164	172	192	207	237	245	245
poly BMIM	100	100	100	100	100	103	108	121	158	214	245	245	295

Feng Liu *et al.*[10] synthesized bispropargyl ether bisphenol A (PBPA) and blended with 4,4′-bismaleimide diphenyl methane at different molar ratios. The authors concluded from the TG results that the cured blends presented much better thermal stability than cured PBPA, which was beneficial from the addition of the 4,4’-bismaleimide diphenyl methane.

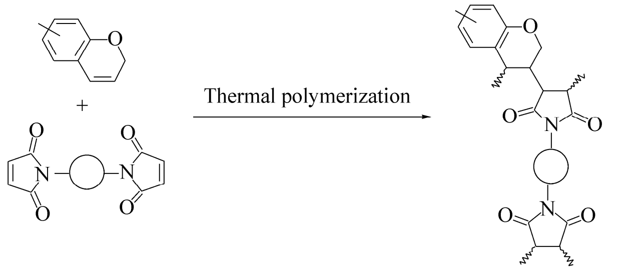
Polymers obtained by thermal polymerization of the blended materials MRPE, MBPEBPA and MSPE recorded the highest degradation onset temperatures at 300 °C. This indicates that among the thermally cured materials polyMRPE, polyMBPEBPA and polyMSPE exhibit higher thermal stability. During the polymerization of blended materials (BPEs + BMIM), apart from the polymerization of the rearranged propargyl ether entities and the maleimide units, the reaction between the double bond present in the chromene unit with the double bond present in the maleimide unit is inevitable. Hence it is reasonable to expect much complex structure (Fig. 5) for the thermally polymerized bispropargyl ethers blended with BMIM. Among the blended materials MBPPE and MKPE exhibit higher char residue (~60%) at 700 °C.



Thermal polymerization of bispropargyl ether



Thermal polymerization of bismaleimide



Thermal polymerization of bispropargyl ether-bismaleimide blend

Fig. 5 Possible polymerization of bispropargyl ethers, BMIM and bispropargyl ether-BMIM blend

As we all know, the properties of the cured resins are dependent on the cross linked structure of the cured resins. It is very interesting to discuss what kind of network formed during the cure imparts the cured materials excellent thermal properties. In addition the excellent properties of the cured materials should derive from interesting molecular structure. It is evident that the degradation processes of the blends (BPEs+BMIM) discussed here are very complex. Since during thermal degradation process, products of degradation of bispropargyl ether moiety, bismaleimide and the copolymer resulting from these structurally different thermosetting monomers will be formed.

In a separate study the authors investigated the degradation kinetics (E_a-D) of structurally diverse pure polybispropargyl ethers. The detailed thermal stabilities of different polybispropargyl ethers were investigated using TG. The onset degradation temperature of thermally cured RPE, QPE, BPPE, BPEBPA, KPE, SPE, IPE and SPIPE are 310, 235, 223, 260, 220, 272, 285 and 256 °C respectively. In the present work it is (Table 1) found that the onset degradation temperature of bispropargyl ether blended with BMIM shifts to higher region than that of pure polybispropargyl ethers. The TG results imply that the cured blends presented much better thermal stability than the cured pure bispropargyl ethers. In addition the aromatic spacer present in the different bispropargyl ethers plays a predominant role during thermal degradation process.

Kinetics of Thermal Degradation

The apparent activation energy for the degradation of all the polymers was determined by three different model-free kinetic (FWO, VYZ and FRD) methods. The apparent activation energy values for all the materials obtained by VYZ method is tabulated in Table 2. The plots between the apparent activation energy for degradation and the reaction extent values (α) of polyMSPE by the three methods are shown in Fig. 6. The plots between the apparent activation energy and the reaction extent (α) values for all the thermoset materials investigated by VYZ method are shown in Fig. 7. Although the apparent activation energy values calculated for the degradation of cured samples by these methods are different, the trends noted in the variation of apparent activation energy for the degradation of cured samples obtained by these three kinetic methods are the same. This difference in activation energy is due to the methods by which the apparent activation energy was calculated that is FWO and VYZ are integral methods whereas FRD is a differential method.

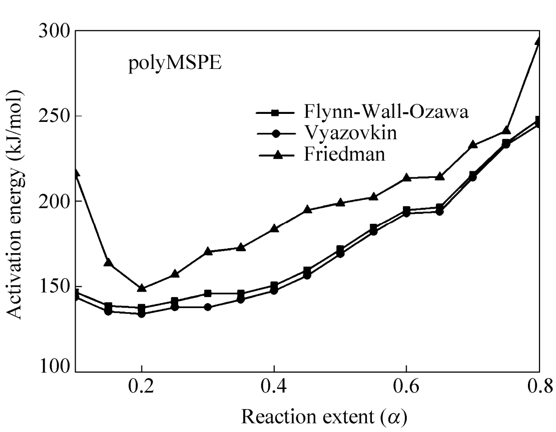


Fig. 6 Relative reaction extent versus apparent activation energies of polyMSPE by FWO, VYZ and FRD methods

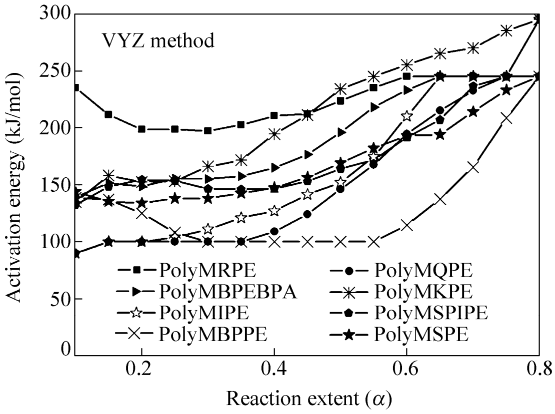


Fig. 7 Relative reaction extent versus apparent activation energies of thermal degradation (E_a-D) of thermosets resulting from the thermal polymerization of structurally diverse bispropargyl ethers-BMIM blends (VYZ method)

The trends noted in the apparent activation energy for the thermal degradation of the materials agree very well for the methods FWO and VYZ. But, different values are noted for FRD method and it is due to the way in which the apparent activation energy is calculated[13]. The apparent activation energy for thermal degradation (E_a-D) obtained using Vyazovkin method for thermally cured structurally diverse bispropargyl ethers-BMIM blends is considered for discussion.

From Fig. 7 it is obvious that the materials studied can be grouped into three distinct categories. The apparent activation energy of the thermally cured materials MRPE and MKPE increases gradually with increasing extent of reaction. The thermally cured materials MQPE, MBPPE and MIPE have constant activation energy in the initial stage of degradation. The apparent activation energy of these materials shows a gradual increase with increase in the value of reaction extent in the later stages of degradation. The apparent activation energy of thermally cured materials MBPEBPA, MSPE and MSPIPE shows a slight variation in the initial stage of degradation and increases constantly for further reaction extent levels.

The apparent activation energy for the degradation of polyMRPE varies from 199 kJ/mol to 245 kJ/mol. A slight decrease in apparent activation energy is noted for the initial reaction extent levels and increases constantly up to the reaction extent level $\alpha = 0.3$–0.6, then no change in the activation energy, almost constant activation energy is noted for the further reaction extent levels. Among the materials investigated polyMRPE shows the highest activation energy at the initial stage of thermal degradation process. It indicates that the *meta* disposition of the groups in this bispropargyl ether and the blended BMIM results in a complex network structure wherein the structural entities need sufficiently higher energy for the release of the degradation products.

From Fig. 7, it is interesting to note that as the degradation of the polyMRPE is initiated; the E_a value progressively increases, indicating the need for higher energy for the breakage of several weak links in the cross-linked network polymer. In the temperature region of 310–400 °C, the mass loss amounts to 10%. After the initial degradation owing to the favourable situation present in the degrading polymer matrix, the elimination of molecules results in faster mass loss, a process which shows a constant apparent activation energy.

The apparent activation energy value for the degradation of cured MKPE varies from 153 kJ/mol to 295 kJ/mol for increasing values of reaction extents (α = 0.2–0.8). A steep increase in the apparent activation energy values is noticed. Similarly Pitchaimari *et al.*[26] reported the studies on thermal degradation kinetics of thermal and UV cured *N*-(4-hydroxy phenyl) maleimide derivatives. The apparent activation energy values for the degradation of poly(*N*-(4-methacryloyloxyphenyl) maleimide) (MAX) with *N*-vinyl-2-pyrrolidone (NVP) as a comonomer (TDMAX) increased from 84 kJ/mol to 156 kJ/mol gradually with increasing extent of reaction (α = 0.1–0.9). The initial lower value of the activation energy is most likely associated with the initiation process that occurs at these weak links. As these weak links are consumed, the limiting step of degradation shifts toward the degradation initiated by random scission, which typically has greater activation energy. The very high values of E_a-D calculated at large extents of degradation explain the large amount of solid residue remained. An increase of E_a-D with α has been also reported in literature for other types of polymers[27, 28].

The apparent activation energy (E_a-D) values for the degradation of cured MQPE, MBPPE and MIPE varies from 100 kJ/mol to 245 kJ/mol. The E_a-D values for polyMQPE systems remain constant for the reaction extent level α = 0.2–0.35 and then a sudden increase is noted for further reaction extent levels. The material polyMBPPE shows a slight decrease in apparent activation energy for the initial reaction extent levels (α = 0.2–0.3), nearly constant apparent activation energy is noted for the reaction extent levels 0.3 to 0.55 and then the E_a-D values increase steeply for further reaction extent levels ($\alpha > 0.55$).

The E_a-D values are constant for the material polyMIPE up to the reaction extent level of α = 0.4 and then a sudden increase is noted for further reaction extent levels. A similar trend of apparent activation energy is evidenced from Fig. 7 for polyMQPE and polyMBPPE due to the existence of structural similarities between these materials. Hence it is reasonable to assume that these materials (polyMQPE, polyMBPPE and polyMIPE) are having the possibility of undergoing degradation through a common degradation route involving similar type of bond cleavages.

The apparent activation energies for thermally cured MBPEBPA, MSPE and MSPIPE vary from 145 kJ/mol to 260 kJ/mol. The cured materials have a minimal variation in the E_a-D values for the reaction extent levels around α = 0.2–0.3 and the activation energy values increases gradually with increasing extent of reaction (0.3–0.8). The initial decrease in E_a-D values was attributed to the existence of weak points in the polymer chains whereas the higher E_a-D values at the later stages of degradation were associated with high degrees of random scission of the main chain. Shamim *et al.*[29] studied the curing characteristics and thermal degradation aspects of structurally different bisbenzoxazines. They reported that the apparent activation energy value for the thermal degradation (E_a-D) of polyspirobiindane benzoxazine shows a gradual increase in E_a-D with respect to increase in reaction extent levels. The same trend existed for the polybisphenol-A bisbenzoxazine. Similar results are obtained for the materials polyMBPEBPA and polyMSPIPE.

Krongauz[30] reported similar results for the crosslink density dependence of polymer degradation kinetics in photo crosslinked acrylates. The rotation of polymer segments is consistent with the low apparent activation energy of polyacrylate degradation. As the crosslinking density increases, an increase in the activation energy is noted. Change from degradation due to rotation of polymer segments at low temperatures to degradation through direct bond scission at higher temperatures may also explain the increase in apparent activation energy with temperature.

Among the different thermosets investigated, the materials polyMRPE and polyMKPE show continuous increase in the apparent activation energy (E_a-D) for the thermal degradation with increasing reaction extent values. During thermal degradation owing to the formation of highly crosslinked network structures along with the charring phenomenon, the apparent activation energy for the thermal degradation increased as the extent of degradation of the materials increased. In general, aromatics do not want to lose their cyclic conjugated system resulting in an unusual stability.

TG-FTIR Studies

Thermogravimetric (TG) analysis combined with Fourier transform infrared (FTIR) analysis of evolved products has proven to be a powerful technique for characterization of coal, source rock, heavy hydrocarbons, biomass, waste materials, and plastics. The TG-FTIR method can be used to determine the resource potential of a material, *i.e.*, the types of products a material is likely to produce when subjected to processing by pyrolysis or combustion. From the FTIR spectra recorded for the volatiles evolved during the TG analysis, the type and functionality of the degradation products can be studied. The major volatiles evolved during the thermal degradation of these materials and the amount that is evolved are dictated by the structural features of the material.

The TG-FTIR spectra of the degradation products obtained at various temperatures for polyMBPEBPA and polyMIPE are shown in Fig. 8.

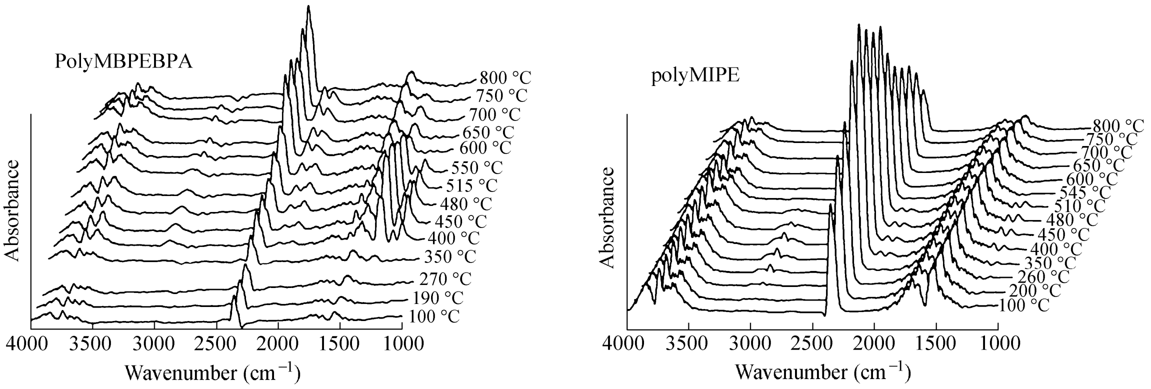


Fig. 8 TG-FTIR curves for polyMBPEBPA and polyMIPE

The release of carbon dioxide (CO_2) and carbon monoxide (CO) from the degrading cured different bispropargyl ethers-BMIM blends were confirmed by the appearance of a band at 2340 cm^{-1} (C—O stretching). As the temperature increases the intensity of the evolved gases (CO_2 and CO) increases and shows a gradual decrease for polyMBPPE and polyMIPE whereas for all other cured blends the intensity of the evolved CO_2 and CO was observed distinctly at the later stages of degradation.

Generally polyBMIM degrades with the elimination of CO_2 and CO. Many studies have reported the formation of the diamine, aniline, toluidine from the degrading polyBMIM. Further a small amount of carbodiimides through the formation of isocyanate has been reported by Vijayakumar *et al*[31]. They studied thermal degradation of poly(*N*-arylmaleimide) using GC-MS technique and they reported carbon dioxide as the major gaseous product formed during the thermal degradation of polyimide and offered two different mechanisms for its release. The imide-isoimide rearrangement and the formation of isocyanates from the polymer chains are followed by dimerization of the isocyanate which yields a carbodiimide with the release of carbon dioxide.

Similarly Torrecillas *et al.*[32] studied the 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 using GC-MS technique. They found that the main substances formed are aniline and phenyl isocyanate, which occur in the first phases of degradation (500 °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 release of detectable amounts of phenols from all the cured blends observed over 350 °C is confirmed by the increase in the —OH stretching band (3550 cm^{-1}). The possibility of presence of free phenolic groups in the thermally cured different blends is less as confirmed by the TG-FTIR curves.

The band noted at 3010 cm^{-1} indicates the release of aliphatic hydrocarbons (—CH stretching) from the degrading cured material. The release of hydrocarbons (—CH stretching) was observed around 480–700 °C for polyMRPE, polyMBPPE, polyMKPE and polyMSPE. The other materials such as polyMBPEBPA and polyMSPIPE release aliphatic hydrocarbons (—CH stretching) around 400–600 °C where as polyMIPE liberates aliphatic hydrocarbons in the temperature range 350–480 °C.

From this one can conclude that maximum release of aliphatic hydrocarbon is noticed in the later stage of degradation for the cured materials such as polyMRPE, polyMBPPE, polyMKPE and polyMSPE. From the cured materials polyMBPEBPA, polyMIPE and polyMSPIPE the release of aliphatic hydrocarbon was evidenced after the initial stage of degradation. Among the materials the polyMQPE shows negligible release of aliphatic hydrocarbon.

The appearance of band at 1120 cm^{-1} to 1172 cm^{-1} is attributed to the release of ether group ($-O-CH_2$) bearing volatiles. A small amount of release of ether products is noticed in the temperature range from 400 °C to 600 °C for polyMBPPE, polyMBPEBPA, polyMKPE, polyMSPE, polyMIPE and polyMSPIPE and is noticed in negligible amounts from polyMRPE and polyMQPE. The band pertaining to the release of the ether groups is sufficiently intense in the case of polyMBPEBPA and polyMSPE. The absorbance band pertaining to the ether products ($-O-CH_2$) obtained from the degradation of the thermally cured bispropargyl ethers-BMIM blends especially polyMRPE and polyMQPE is overlapping with the peak particular for the compounds having C=C units.

The appearance of a band at 1500 cm^{-1} indicates the evolution of compounds having olefinic group (C=C). The release of such degradation products (C=C) is observed distinctly in the temperature region 400 °C to 550 °C for polyMBPEBPA and for all other cured materials the intensity of the band was not prominent. From the above results, one can conclude that the obtained gaseous degradation products should be able to liberate by a cleavage at activated benzylic (or) propargylic site[33]. The possible polymerization and the probable structural entity of the cured network of pure bispropargyl ethers, pure BMIM and bispropargyl ethers-BMIM blends are shown in Fig. 5. The possibility of isomerisation of the propargyl group to allene units followed by polymerisation is already presented in our previous work[34].

The possibility of forming hydrocarbons, aromatic and aliphatic olefin is negligible. Consider the case of all the bispropargyl ethers investigated and may be broadly classified into three major categories. They are (1) polyMRPE, polyMQPE and polyMBPPE (2) polyMKPE and polyMSPE (3) polyMBPEBPA, polyMIPE and polyMSPIPE. Generally bispropargyl ethers undergo Claisen rearrangement followed by cyclisation and polymerization. Therefore the formation of chromene and the polymerization of the double bond present in the chromene are already established[20].

During thermal degradation the possibility of forming olefinic groups from the chromene end is also minimal. Hence it is reasonable to conclude that olefins and olefinic related compounds are evolved from the spacer entity. Among the categories discussed the release of olefinic groups is minimal for the materials polyMREP, polyMQPE and polyMBPPE. The materials polyMKPE and polyMSPE show the formation of olefins in trace levels. In the materials polyMBPEBPA, polyMIPE and polyMSPIPE the possibility of release of olefins is more probable.

From the material polyMBPEBPA, the release of olefins having the structural unit [$CH_2=CH-C(CH_3)-(p\text{-}C_6H_4)-$] is reasonable (Fig. 9). The material polyMIPE and polyMSPIPE also release the structurally favoured aromatic olefins during thermal degradation. Hence the spacer unit present in the bispropargyl ether is the major source for the liberation of olefins from the polybispropargylether-BMIM blends.

In addition to that, small quantities of aniline and 4,4′-diamino diphenyl methane are also registered among the degradation products due to the existence of BMIM in the cured network structures. The possible degradation products obtained from bispropargyl ethers-BMIM blends are shown in Fig. 10.

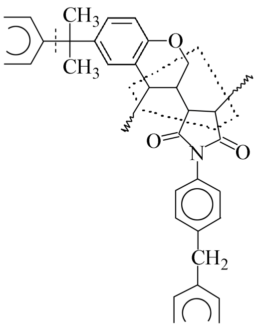


Fig. 9 Cured network structure of polybispropargyl ether-BMIM blend

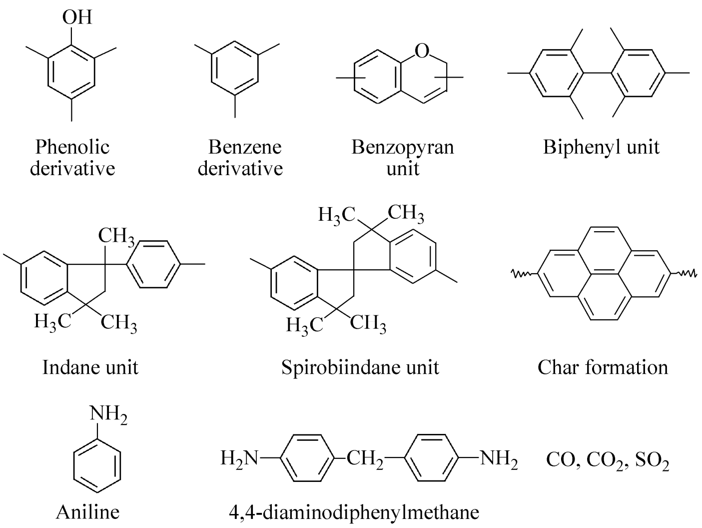


Fig. 10 Possible degradation products obtained from polybispropargyl ethers-BMIM blends

Vinayagamoorthy *et al.*[33] studied the polymerization and the thermal degradation of bismaleimide/propargyl terminated resin system. Off-line isothermal degradation in nitrogen atmosphere was carried out for the thermally polymerized samples and the pyrolysis products were separated and identified using gas chromatograph-mass spectrometer (GC-MS). They reported the cured blend of BPEBPA-BMIE on isothermal degradation produces wide variety of compounds. The major compounds identified are phenol, cresol and ethyl methyl phenols, the products derived from the bispropargyl monomer part of the blend. Small quantities of aniline and 4,4′-methanedianiline are also registered among the degradation products.

Detailed TG-FTIR studies of cured materials showed the evolution of phenols, substituted phenols, aromatic ethers, CO_2 and CO and small amount of aniline from cured bispropargyl ether-BMIM blends. The release of such degradation products was observed in different temperature regions and in varying amounts and is a manifestation of the difference in the architecture of the network structure comprising of the structural units pertaining to the aromatic central skeleton and to the influence of the added BMIM.

CONCLUSIONS

From various bisphenols and propargyl chloride, the structurally different bispropargyl ethers were prepared. The synthesised materials were blended with BMIM (0.5:0.5 mol) and thermally cured. The polymerization of the materials was confirmed by FTIR studies. The detailed thermal stabilities of different cured bispropargyl ethers-BMIM were investigated using TG. The DTG curves of the thermally cured MRPE, MBPPE, MBPEBPA, MSPE and MIPE shows bimodal degradation and thermally cured MQPE, MKPE, and MSPIPE show an overlapping multi stage degradation pattern. Among the different materials investigated polyMRPE, polyMBPEBPA and polyMSPE shows higher thermal stability. Crosslinked network and the central skeleton may result in the differences in the degradation parameters. The degradation kinetics of the cured thermoset materials was studied using two integral and one differential approximation methods. Among the various blended materials polyMRPE (199 kJ/mol to 245 kJ/mol) and polyMKPE (153 kJ/mol to 295 kJ/mol) need higher apparent activation energies for thermal degradation process. From this one can conclude that the nature of the aromatic ring present as a spacer in between the propargyl groups influences the apparent activation energy for the thermal degradation. The evolved gases were analyzed using TG-FTIR technique. From these results, it was concluded that more volatiles are released during the second stage of degradation. Phenols and substituted phenols were found to be the major products and were released during the later stage of degradation. Detectable amounts of aniline were also found to be formed during the thermal degradation of these cured bispropargylether-BMIM blends.

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