THERMAL BEHAVIOUR OF BISITACONIMIDE AND REACTIVE DILUENT BLENDS

A. Solanki, V. Choudhary and I. K. Varma[*]

Centre for Polymer Science and Engineering, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi-110016, India

Abstract

Thermal behaviour of blends based on N,N'-bis(4-itaconimidophenyl) ether (IE) and 4,4'-bis(4-allyl-2-methoxyphenoxy) benzophenone (R_1) or 4,4'-bis(2-allylphenoxy) benzophenone (R_2) are described in this paper. The reactive diluent content was varied from 5–50% (mass/mass) in these blends. A decrease in the melting point and exothermic peak temperature was observed with increasing mass percent of reactive diluent. Thermal stability of blends was affected at high mass percentage of reactive diluents.

Keywords: bisitaconimides, blends, curing, reactive diluents, thermal stability

Introduction

Addition polyimides exhibit outstanding thermo-oxidative stability, exceptional dielectric properties and excellent resistance to humidity at elevated temperatures. However, these materials are inherently brittle due to the high cross-link density and aromatic structure and are liable to microcrack in their composites when subjected to thermal cycling.

Copolymerisation of addition polyimides with reactive diluents and elastomers has been employed successfully for improvement of toughness characteristics of these resins. Curing and thermal behaviour of bismaleimides with triallyl cyanurate [1, 2], divinyl benzene, fluoroelastomers [3], amino terminated acrylonitrile butadiene rubber (ATBN) [4], vinyl ester resin [5] and allyl type toughening agents [6, 7] have been described in the literature.

Such studies with bisitaconimide resins which are more reactive than bismaleimide resins due to the presence of 1,1-disubstituted double bond have not been reported in the literature [8, 9]. In this paper curing and thermal behaviour of blends based on N,N'-bis(4-itaconimidophenyl) ether (IE) with varying amounts (5–50% mass/mass) of 4,4'-bis(4-allyl-2-methoxyphenoxy) benzophenone (R_1) or 4,4'-bis(2-allylphenoxy) benzophenone (R_2) are described. The structures of IE resin, R_1 and R_2 are given in the Scheme 1.

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[*]   Author for correspondence: E-mail: ikvarma@hotmail.com
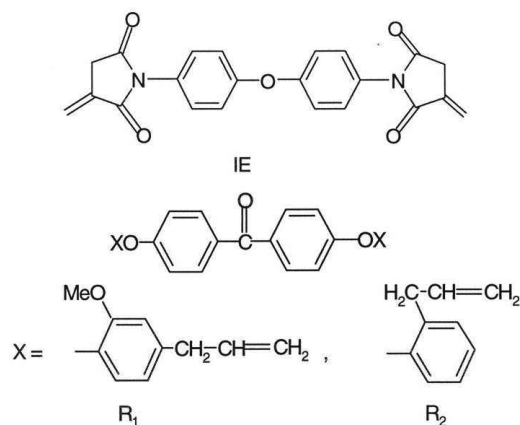
Scheme 1 Structures of IE resin and reactive diluents (R$_1$ and R$_2$)

Experimental

Materials

4,4'-diaminodiphenyl ether (Fluka), 4,4'-difluorobenzophenone, itaconic acid (Aldrich), 4-allyl-2-methoxy phenol (eugenol) (CDH), 2-allyl phenol (Lancaster), chloroform (Qualigens), dimethyl acetamide, phosphorus pentoxide and sodium hydroxide (Merck) were used as received.

Acetone (Qualigens) was kept over anhydrous potassium carbonate (Qualigens) for 24 h and distilled before use. Acetic anhydride (BDH) was distilled before use. Anhydrous sodium acetate (Sarabhai chemicals) was fused by heating and stored in a dessicator. Itaconic anhydride was prepared from itaconic acid by use of P$_2$O$_5$ as a dehydrating agent and chloroform as solvent [8]. The synthesis and characterization of bisitaconimide IE was done according to the procedure reported in literature [8].

Synthesis of reactive diluents (R$_1$ and R$_2$)

The reactive diluents R$_1$ and R$_2$ were synthesized (Scheme 2) using similar procedures. In a typical synthesis of R$_1$, 0.12 mol eugenol (4-allyl-2-methoxy phenol) and 0.13 mol of anhydrous potassium carbonate were taken in a round bottom flask, dissolved in 20 mL DMSO and the contents were heated at 100°C in nitrogen atmosphere. Then 0.06 mol of 4,4'-difluorobenzophenone was added and the reaction was continued for 5 h. The contents were then poured in 5% sodium hydroxide solution, washed with water and dried. The viscous material was then purified by using silica column and chloroform as eluent (yield=70%). The reactive diluent R$_2$ (4,4'-bis(2-allyl phenoxy) benzophenone) (yield=75%) was a white, sticky solid whereas R$_1$ was a viscous, transparent brown liquid.
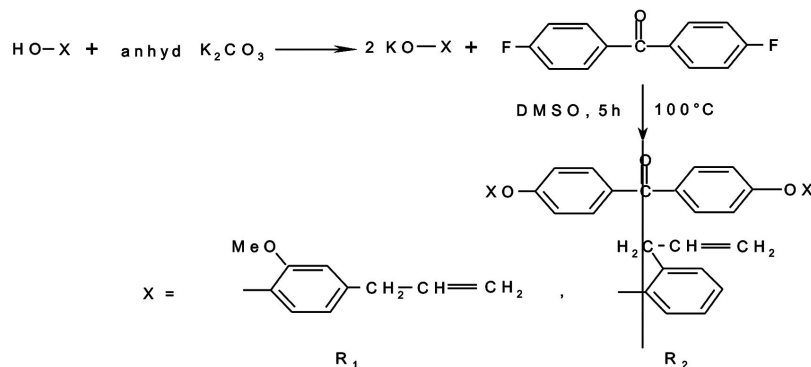
Scheme 2 Reaction scheme for synthesis of reactive diluents

Preparation of blends

Blends of bisitaconimide (IE) and reactive diluents R_1 and R_2 were prepared by solution method using chloroform as a solvent. The reactive diluent content was varied from 5–50% (mass/mass) in these blends (Table 1). The solution was stirred for sometime and then solvent was removed under ambient conditions.

Table 1 Sample designations of bisitaconimide: reactive diluent blends

Sample No.	Bisitaconimide/%	Reactive diluent R_1 or R_2/%	Designation of blends
1	95	5	IE-$R_1$0.5 (IE-$R_2$0.5)
2	90	10	IE-$R_1$1 (IE-$R_2$1)
3	80	20	IE-$R_2$2
4	70	30	IE-$R_2$3
5	60	40	IE-$R_1$4
6	50	50	IE-$R_1$5

Characterisation

Structural characterisation was done using Biorad Digilab FTS-40 FT-IR spectrometer, and Bruker AC 300 MHz ^{1}H-NMR spectrometer using CDCl$_3$ as solvent and tetramethyl silane as an internal standard.

TA 2100 thermal analyzer having a 910 DSC module and 951 TG module was used for the thermal characterization. DSC scans were recorded in static air atmosphere using 7±2.5 mg of sample in the temperature range of 50–350°C. TG studies were carried out in nitrogen atmosphere (flow rate 60 cm^3 min^{-1}) at a heating rate of 10°C min^{-1} (sample mass 10±2 mg).

Results and discussion

Characterisation of reactive diluents

In the FT-IR spectra of R_1 and R_2 (Fig. 1) absorption bands were observed at 1655 due to C=O (aromatic ketone), 1240 ± 2 and 1033 ± 1 cm^{-1} (due to ether linkage) and 930 cm^{-1} (due to alkene groups).
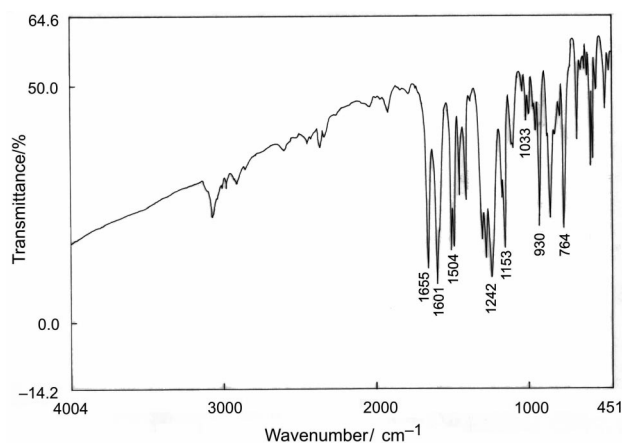

Fig. 1 FTIR spectrum of R_2

In the ^{1}H-NMR spectra of reactive diluents R_1 and R_2 (Fig. 2) the proton resonance signals were observed at 3.1–3.3 ppm (4H, methylene protons), 5.6–5.9 ppm (2H, methine protons) and 4.8–5.0 ppm (4H, vinylidene protons). The signals due to aromatic protons were observed at 6.7–7.6 ppm. In case of R_1 an additional signal was observed at 3.5 ppm (6H, methoxy protons).
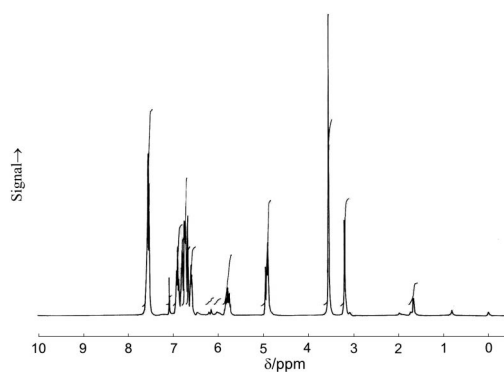

Fig. 2 ^{1}H-NMR spectrum of R_2

Thermal studies

The DSC scans of blends are shown in Fig. 3. A melting endotherm was observed below 200°C in all the samples. This was followed immediately by an exothermic transition (above ~200±6°C) due to the curing. The melting point of IE was at 196°C while exothermic peak temperature was 206°C. A systematic decrease in T_m and T_{exo} was observed by an increase in the content of reactive diluent (Table 2). Figure 4 shows the dependence of T_{exo} on the mole% of itaconimide in the blend. Decrease in T_{exo} is indicative of co-curing of itaconimide double bond and reactive diluent (Scheme 3).
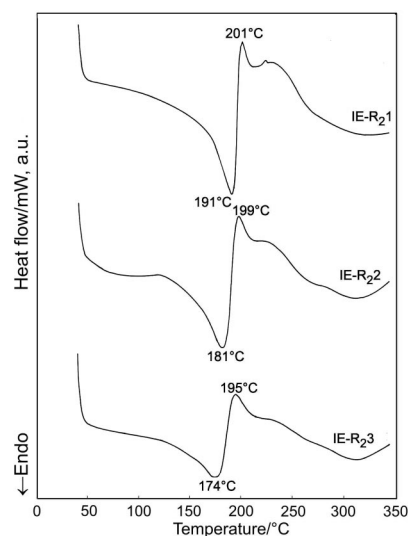

Fig. 3 DSC scans of IE:R_2 blends

Table 2 DSC results of bisitaconimide (IE): reactive diluent R_1/R_2 blends

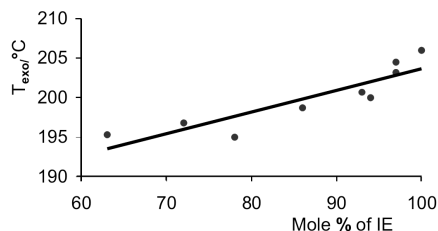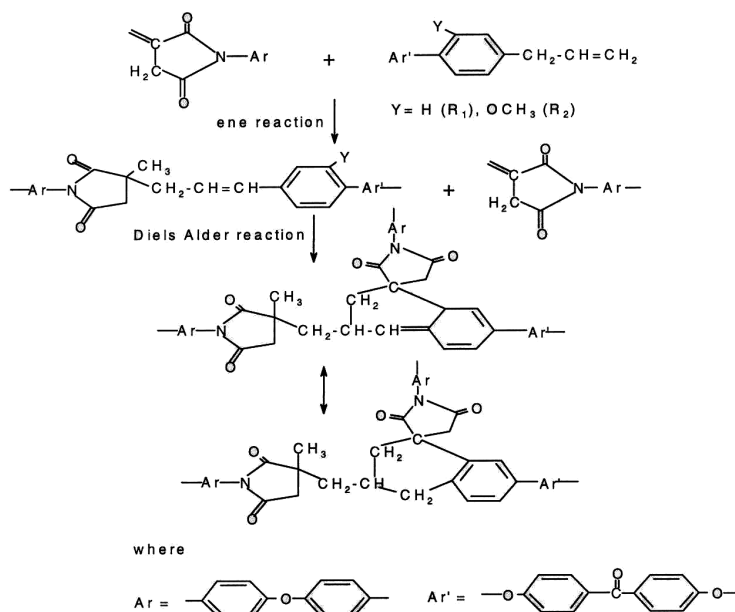| Sample No.	Sample	IE in blends mole/%	T_m/°C	T_{exo}/°C
1	IE	100	196.0	206.0
2	IE-$R_1$0.5	97	191.5	200.0
3	IE-$R_1$1	94	188.0	200.0
4	IE-$R_1$4	72	183.0	196.8
5	IE-$R_1$5	63	182.0	195.3
6	IE-$R_2$0.5	97	191.6	203.2
7	IE-$R_2$1	93	190.6	200.7
8	IE-$R_2$2	86	181.3	198.7
9	IE-$R_2$3	78	174.1	195.0

Fig. 4 Plot of mole% of IE *vs.* exothermic peak temperature (T_{exo}) in IE:R$_1$/R$_2$ blends

Scheme 3 Reaction scheme depicting co-curing of reactive diluents and bisitaconimide IE (based on scheme proposed by Stenzenberger *et al*. [6, 10]

Isothermal curing of resin blends was done at 200°C for 2 h. During isothermal curing a mass loss of 3–10% was observed depending upon the blend composition. These cured resin samples were stable upto 220°C and started losing mass above this temperature. The TG traces (Fig. 5) of isothermally cured blends (200°C for 2 h) showed two-step decomposition. The first step was in the temperature range of 224–450 and second was above 450°C. A decrease in the Ti was observed in the blends compared with the pure bisitaconimide IE. The mass loss in the first step increased as the % of reactive diluent increased. The plots of mole% of IE in the blends vs. % mass loss in the first step (from the TG results) are given in Fig. 6. The observed increase in % mass loss in the first step on increasing the reactive diluent content may be due to the presence of methyl, methylene and methine groups in the cross-linked network as depicted in Scheme 3.
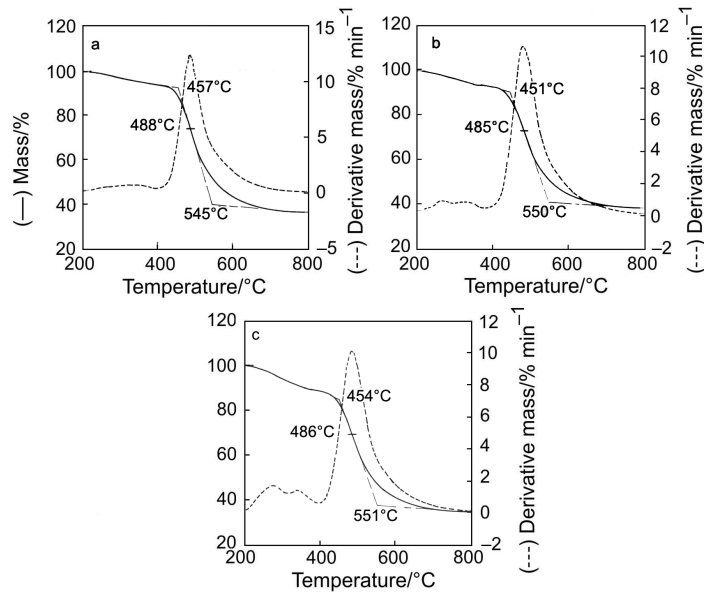
Fig. 5 TG/DTG traces of a – IE-R$_2$1; b – IE-R$_2$2 and c – IE-R$_2$3
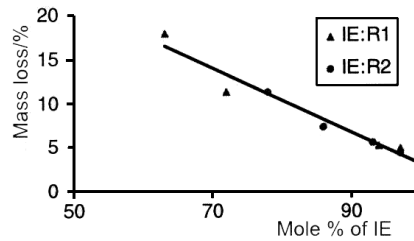

Fig. 6 Plot of mole% of IE *vs.* mass loss in the first step of IE:R$_1$/R$_2$ blends

Char yield of the blends at 800°C in nitrogen atmosphere decreased in case of samples having high concentration of reactive diluent. However at low % of reactive diluent only a marginal influence in char yield was observed. As is evident from the plot of mole% of IE in the blend vs. % char yield (Fig. 7) no significant change in the char yield of IE was observed on incorporation of reactive diluents (upto 40%). A sig-
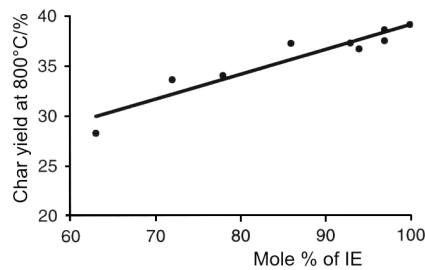

Fig. 7 Plot of mole% of IE *vs.* % char yield at 800°C of IE:R$_1$/R$_2$ blends

nificant decrease in char yield (28%) was observed in the presence of R1 diluent at higher concentrations. The TG results of the blends are given in Table 3.

Table 3 TG/DTG results of bisitaconimide: reactive diluent R_1/R_2 blends

Sample	Decomposition temperatures/°C			Mass loss/%	Char yield at 800°C/%
	T_1	T_{max}	T_f		
IE	290.0	323.0	395.0	3.0	39.0
	448.0	482.0	542.0	58.0	
IE-$R_1$0.5	253.9	348.3	465.2	4.90	38.5
	465.2	496.6	550.7	55.76	
IE-$R_1$1	245.0	290.0	370.7	5.33	36.6
	452.0	483.7	546.8	58.06	
IE-$R_1$4	250.0	294.0	359.5	11.33	33.6
	448.0	476.6	526.6	54.99	
IE-$R_1$5	269.6	317.0	359.5	17.86	28.3
	461.0	480.2	516.6	53.81	
IE-$R_2$0.5	251.6	348.3	457.7	4.4	37.4
	457.7	490.7	550.7	55.3	
IE-$R_2$1	236.0	–	379.7	5.48	37.2
	456.6	487.7	545.0	57.30	
IE-$R_2$2	227.0	–	366.2	7.26	37.2
	451.4	485.4	550.1	55.48	
IE-$R_2$3	224.7	–	375.2	11.26	34.0
	453.9	485.6	551.0	54.77	

Conclusions

From the DSC studies it showed co-curing of the itaconimide with allylic double bond of the reactive diluents. This leads to a decrease in the melting and curing temperatures of the blends. The char yield (%) decreased at higher mass percentage of reactive diluent (50%).

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