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Characterization of thermal behavior of mixed bismaleimides for composites

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Three types of bismaleimides viz., 4,4′-bismaleimido diphenyl methane (BDM), 4,4′-bismaleimido diphenyl ether (BDE) and hexa-methylene bismaleimide (HMBI) were synthesized. The thermal behavior of these bis monomers in neat and blended forms was studied by thermoanalytical techniques. All the monomer systems undergo thermal polymerization after the completion of melting. An eutectic type single lowest melting point is obtained for 60 : 40 imide formulations of BDM + HMBI and BDE + HMBI. The heat and kinetic parameters of polymerization are composition dependent and they show an increasing trend with the increase of HMBI. The thermal stability and char content decrease with the increase of hexamethylene bismaleimide whereas the thermal degradation kinetics show a reverse trend. The flexural and shear storage modulus values of the glass composite laminates made with the bismaleimides are also composition and temperature dependent.

1. Introduction

Polyimides represent an important class of high temperature, solvent resistant polymers. They find extensive applications as matrix component of light weight fibre reinforced structural composites for aerospace applications, metal-to-metal adhesives, sleeve bearings, electrical insulations, microelectronics etc. [1, 2]. Often polyimides are formed by a two-stage process. The first step involves the polycondensation of an aromatic dianhydride and an aromatic diamine to form an intermediate poly(amic acid). Dehydration of the poly(amic acid) at elevated temperatures yields the polyimide structure. The cured polyimide is insoluble and infusible and has high temperature and oxidative stability and radiation resistance. A thermoset polyimide is one prepared by heating a fully imidized monomer having reactive functional groups at each end that can react with another monomer molecule. Bismaleimide, bisitaconimide and bisnadimide monomers are examples of network forming thermosetting addition polyimides. Synthesis and characterization of polyimides derived from aromatic and heterocyclic ring compounds, chain extended Michael addition products and copolymerized bisimides were studied in detail by us and several other researchers [3–7]. One of the most important polyimides is the bismaleimide whose repeating unit may represent a variety of aromatic structures. In many cases, certain properties of a polymer can be enhanced by blending it with one another. The incorporation of aliphatic bismaleimide reduces brittleness and stiffness of the bisimide and also improves the processability and flexibility of the resulting polymer blend.

Various thermoanalytical techniques such as thermogravimetry (TG), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are extensively used to study the physical and chemical properties of polymers and composites as functions of time and temperature [8]. The evaluation of thermal polymerization and degradation kinetics by thermoanalytical techniques provides rapid feedback of valuable information relating to optimum processing conditions, prediction of shelf life etc. The present study is chiefly concerned with the synthesis and thermal characterization of three classes of bismaleimides and their copolymerization products in neat and blended forms. Thermogravimetry, differential scanning calorimetry and dynamic mechanical analysis were employed to study their thermal behavior.

2. Experimental

2.1. Samples (Bisimide monomers)

The monomers viz., 4,4′-bismaleimido diphenyl methane (BDM), 4,4′-bismaleimido diphenyl ether (BDE) were prepared by the method described by us earlier [4, 5]. The solid imides were separated, washed and vacuum dried at 80 to 85 °C for 5 h. Hexamethylene bismaleimide (HMBI) was synthesized by the reaction of hexamethylene diamine and maleic anhydride in acetone. The yield of HMBI was slightly lower than the other two imides, because of the oligomerization of the maleimide during imidization. The oligomerized product is a resinous material which is insoluble in water. The water soluble imide monomer is separated out by cooling.

In order to study the effect of aliphatic HMBI on aromatic BDM and BDE, monomer mixtures of different compositions containing BDM + HMBI and BDE + HMBI were prepared (weight ratios = 100 : 0, 80 : 20, 70 : 30, 60 : 40, 40 : 60, 20 : 80 and 0 : 100) and used for the present study. Glass polyimide composites (15 × 10 mm) were also prepared using neat and 60 : 40 resin compositions. The DMA measurements were done on cured laminate samples at different temperatures.

2.2. Preparation of glass-polyimide composites

Glass cloth reinforced composites of BDM and BDE and their blends with HMBI (60 : 40 in both the cases) were prepared. 40% solutions of these monomers in dimethyl formamide were initially oligomerised by heating at 120–125 °C for 4 h and impregnated on silane-treated E-glass bidirectional cloth of 0.175 mm thickness. The solvent from the prepreg was removed under vacuum at 80 °C for 1 h. The prepreg was cut into 150 × 100 mm rectangles and 20 pieces were stacked and cured in an hydraulic press by applying 800 kPa pressure at the following temperature regime: RT to 150 °C at a linear heating rate of 5 °C/min; hold at 150 °C for 1 h; 150 to 220 °C at a heating rate of 5 °C/min; hold at 220 °C for 4 h for consolidation and complete curing. The cooling was also performed under pressure. The resin content of the composite was estimated by thermogravimetric analysis under flowing air atmosphere and was found to be in the range of 25–28%.

2.3. Instrumental

DSC experiments were carried out using a Mettler TA 3000 thermal analyser in conjunction with DSC-20 standard cell at a heating rate of 10 °C/min. TG experiments were carried out in a Dupont 951 thermogravimetric analyser in pure nitrogen atmosphere at a heating rate of 10 °C/min. Dynamic mechanical studies were performed with TA Instruments 983 DMA. The melting points of the monomers were determined by a Mettler FP-81 melting point apparatus. IR spectra of the three maleimides were recorded on a Perkin-Elmer model 283 IR spectrometer. Computational work was done on an IBM PC using FORTRAN 77 program.

3. Results and discussion

3.1. IR spectra

A typical IR spectrum of BDM is given in Fig. 1. The peak in the region 3000–3100 cm^{-1} for BDM is due to =CH stretch from the maleimide part as well as the aromatic region. The peak around 2900 cm^{-1} corresponds to −CH2 stretching vibrations. The asymmetric and symmetric C=O vibrations of the cyclic imide group are indicated at 1700–1800 cm^{-1}. The peaks at 1630, 1600 and 1580 cm^{-1} are assigned to C=C and aromatic vibrations respectively. The peak in the region 1490 cm^{-1} is due to −C−N−C− bending. The peaks at 1350 and 1380 cm^{-1} are due to −C−N− skeletal vibration and −CH2 bend. The peak at 820 cm^{-1} corresponds to the para substitution. The other two imides viz., BDE and HMBI differ only in the following spectral characteristics: For BDE, an additional band at 1000–1100 cm^{-1} corresponds to ether linkage. The additional band at 1440–1450 cm^{-1} for HMBI is due to −CH2 bending of the hexamethylene group.

3.2. Melting point

The DSC curves of the neat bisimides show single endothermic melting transition and their values are in agreement with the values determined by the melting point apparatus (BDM = 154–156 °C, BDE = 165–168 °C and HMBI = 130–134 °C). In mixed bisimides, small additional endothermic peaks were noticed due to the second minor component and they vanished at 60 : 40 composition for both BDM + HMDI and BDE + HMDI, indicating complete miscibility for both

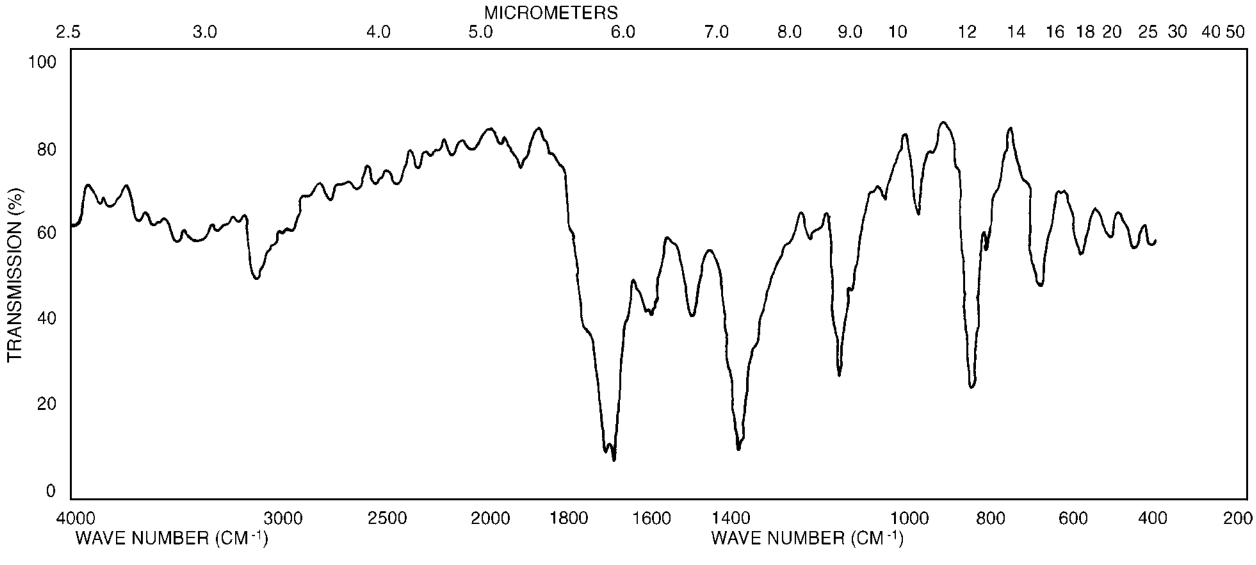

Figure 1 IR spectrum of BDM.

TABLE I DSC results of mixed bismaleimides

	BDM : HMBI			BDE : HMBI		
Composition	M.P (°C)	*T* (exo)	Δ*H* (J/g)	M.P (°C)	*T* (exo)	Δ*H* (J/g)
100 : 0	155	260	37.2	169	273	31.3
80 : 20	143	258	46.0	150	272	42.0
70 : 30	133	259	50.0	137	269	47.1
60 : 40	125	257	56.0	125	270	53.5
40 : 60	130	261	66.0	128	272	63.0
20 : 80	134	262	75.9	135	274	74.0
0 : 100	137	261	87.4	137	261	87.4

TABLE II Kinetics of polymerization

	BDM : HMBI						BDE : HMBI					
	Roger		MLR		MKN		Roger		MLR		MKN	
Composition	*E*	*A*	*E*	*A*	*E*	*A*	*E*	*A*	*E*	*A*	*E*	*A*
100 : 0	116.8	2.0×10^{9}	115.9	1.9×10^{9}	117.2	2.1×10^{9}	119.3	1.3×10^{10}	118.9	1.6×10^{9}	118.0	1.6×10^{9}
80 : 20	125.6	1.8×10^{10}	125.6	1.6×10^{10}	122.6	6.2×10^{9}	113.9	9.5×10^{8}	108.4	6.5×10^{8}	113.0	7.2×10^{8}
70 : 30	130.6	7.0×10^{10}	127.7	2.5×10^{10}	127.7	5.1×10^{11}	119.3	3.4×10^{8}	110.5	9.9×10^{9}	117.2	1.4×10^{9}
60 : 40	117.2	3.0×10^{10}	129.8	2.2×10^{10}	131.8	4.8×10^{10}	121.0	6.5×10^{9}	113.9	2.4×10^{9}	118.9	2.2×10^{10}
40 : 60	121.4	1.1×10^{10}	131.9	2.0×10^{10}	136.0	1.7×10^{12}	126.0	1.4×10^{10}	117.2	6.5×10^{9}	131.9	3.8×10^{10}
20 : 80	126.0	1.3×10^{10}	133.9	9.0×10^{10}	146.9	3.3×10^{12}	131.9	2.8×10^{10}	126.4	8.0×10^{10}	145.2	7.0×10^{11}
0 : 100	140.2	1.6×10^{11}	150.7	3.1×10^{12}	156.1	1.4×10^{13}	140.2	1.6×10^{11}	150.7	3.1×10^{12}	156.1	1.4×10^{13}

E in kJ/mol and A in s^{-1}.

the systems at this ratio. The melting points detected from DSC major peaks are given in Table I. From this Table it is observed that the melting points of the mixtures decrease with the increase of HMBI content in both types of monomer systems and a eutectic type single lowest melting point is obtained at 60 : 40 composition for both monomers. Thereafter, the melting points show a gradual increase with HMBI content.

3.3. Heat of polymerization

The neat and mixed bismaleimides undergo thermal polymerization immediately after melting. The peak exothermic temperatures (Texo) and the heat of polymerization (ΔH) computed from the DSC curves are also given in Table I. The peak exothermic temperatures are not much affected by blending whereas the ΔH of polymerization shows a systematic increasing trend with HMBI concentration in both monomer systems.

3.4. Kinetics of polymerization

The kinetic parameters viz., activation energy E, pre-exponential factor A and order parameter n for the cure reaction of the bismaleimides were calculated and tabulated (Table II). Three mathematical approaches viz., Rogers [9, 10], Multiple Linear Regression (MLR) [11] and Madhusudanan-Krishnan-Ninan (MKN) [12] were used for calculating the kinetic parameters. The fractional conversion α was calculated from DSC curves at different temperatures and corresponding $(1 - \alpha)$ and $g(\alpha)$ forms were calculated. The values of E and A were computed from the slopes and intercepts of ln $g(\alpha)$ vs. l/T plots. From Table II, it is found that though the values of the kinetic parameters obtained by the three methods are more or less comparable, the MKN equation shows a systematic trend of increase in the kinetic parameters with increase in HMBI content in both imides. Similar increasing trend is seen in the case of ΔH values also.

3.5. Thermal stability and thermal degradation

The thermal stability of the cured bismaleimides were evaluated from their TG curves. The resins undergo three stages of mass loss. The first stage corresponds to volatile/unreacted monomer loss in the temperature range of 50 to 300 °C. The second major stage corresponds to the degradation of the polymer in the temperature range of 350 to 550 °C and the slow process of the third stage above 550 °C is due to charring of the residue left in the polymer pyrolysis. The char residue at 700 °C is in the range of 53–54% for BDM and BDE whereas in the case of aliphatic HMBI it is only 23–25%. The char residue showed a decreasing trend with increasing concentration of HMBI in the mixed bismaleimides.

3.6. Thermal degradation kinetics

The Arrhenius activation parameters for the thermal degradation of neat and mixed imides were calculated from the thermogravimetric data. The order parameter n was first determined by an iteration procedure. Using the value of $n = 2$, E and A were calculated by Madhusudanan-Krishnan-Ninan and Coats-Redfern [13] equations. The values of E and A from the kinetic plots are given in Table III. It is found that these kinetic

TABLE III Kinetics of thermal degradation

	BDM : HMBI				BDE : HMBI			
	MKN		Coats-Redfern		MKN		Coats-Redfern	
Composition	E	A	E	A	E	A	E	A
100 : 0	324.0	6.0×10^{20}	324.0	8.5×10^{19}	320.6	4.8×10^{19}	320.2	4.4×10^{19}
80 : 20	304.3	5.2×10^{18}	303.9	4.8×10^{18}	298.0	4.2×10^{18}	297.2	3.6×10^{18}
70 : 30	311.0	4.9×10^{19}	311.0	4.1×10^{19}	315.6	8.3×10^{19}	311.9	5.4×10^{19}
60 : 40	313.9	2.3×10^{20}	313.9	2.1×10^{20}	319.8	1.7×10^{20}	319.8	1.6×10^{20}
40 : 60	318.6	7.2×10^{19}	317.7	6.8×10^{19}	325.2	8.3×10^{20}	324.0	6.9×10^{20}
20 : 80	323.6	6.5×10^{19}	323.2	6.1×10^{19}	329.4	3.5×10^{21}	327.8	3.3×10^{21}
0 : 100	333.6	2.3×10^{21}	333.6	2.2×10^{21}	333.6	2.3×10^{21}	333.6	2.1×10^{21}

E in kJ/mol and A in s^{-1}.

TABLE IV Dynamic mechanical analysis results of composites

	Sample							
	BDM		BDE		BDM : HMBI (60 : 40)		BDE : HMBI (60 : 40)	
Temp. ($^{\circ}$C)	E'	G'	E'	G'	E'	G'	E'	G'
35	10.27	3.60	10.05	3.55	8.87	3.08	8.40	2.95
50	10.09	3.50	9.95	3.46	8.80	3.07	8.34	2.90
100	9.60	3.33	9.53	3.31	8.31	2.90	7.86	2.76
150	9.19	3.17	9.13	3.17	7.64	2.66	7.03	2.40
200	9.00	3.10	8.66	3.10	6.69	2.34	5.66	1.97
250	8.83	3.17	8.69	3.07	5.86	2.03	4.55	1.69

$E' =$ flexural storage modulus and $G' =$ shear storage modulus are in GPa.

parameters of degradation show a systematic increase with the increase of HMBI content in both of the polymer blends, as seen in the case of heat and kinetics of polymerization.

3.7. Dynamic mechanical analysis

The dynamic mechanical properties viz., flexural storage modulus and shear storage modulus of neat bisimide composites and a 60 : 40 blends of both systems with HMBI were determined in the temperature range of 50 to 250 $^{\circ}$C (The 60 : 40 ratio was chosen as it gives the lowest melting transition). The DMA results are given in Table IV. The shear storage modulus (G') is approximately-one third the flexural storage modulus (E'). The modulus values of BDM composites are found to be slightly higher than those of BDE composites. Similar trend is shown in the case of their blends with HMBI also. This is attributed to the presence of comparatively more flexible ether linkage in BDE. Another interesting observation is the drastic reduction of modulus with the increase of HMBI content in both types of laminates. The reduction is attributed to the long chain aliphatic $-$CH2 group of HMBI.

4. Conclusion

The studies on blending of bismaleimides BDM and BDE with HMBI show marked influence on melting characteristics of the blends. A single eutectic type low melting point is observed in both of the systems at 60 : 40 composition. All other monomer mixtures show duel melting behavior. The heat and kinetic parameters of polymerization show a systematic increasing trend with the increase of HMBI content. The thermal stability and char content show decreasing trend with the increase of HMBI, while the kinetic parameters of degradation show a systematic increase with the increase of HMBI. The shear and flexural storage modulus values of BDM and BDE based composites are very close whereas the incorporation of HMBI reduces the modulus values especially at high temperatures.

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