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THERMAL CHARACTERISATION OF BISMALEIMIDE-DIAMINE ADDUCT POLYMERS

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ABSTRACT

The enthalpy change and the kinetic parameters for the thermal polymerisation of four bismaleimide-diamine adducts, prepared by reacting diamino diphenyl methane with 4,4'-Bismaleimido diphenyl methane, 4,4'-Bismaleimido diphenyl ether, 4,4'-Bismaleimido diphenyl sulphone and 3,3'-Bismaleimido diphenyl sulphone, were evaluated from their DSC curves. The kinetic parameters, viz., energy of activation E and pre-exponential factor A for the thermal decomposition of the cured adducts were calculated from their TG curves using four integral equations. The values of E and A and the thermal stability of polymers are inter-related.

INTRODUCTION

Bismaleimides are potential candidates as matrix resins for strong and light-weight fibre-reinforced structural composites, usable at elivated temperatures. The low molecular weight imide prepolymers, end-capped with reactive maleimide rings, are thermally polymerised to obtain highly cross-linked heat resistant polymers, without the elimination of byproducts. Some aspects of the kinetics of their thermal decomposition and cure reaction have been reported by us recently [1]. The polymers made from bismaleimides are generally brittle in character. This problem is overcome to a cerain extent by chain extension of the imide by a Michael type addition reaction using diamines. Several studies on Michael addition reaction products of various aromatic diamines with bismaleimides have been recently reported [2,3].

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The present study is mainly concerned with the thermal characterisation of bismaleimide-diamine adduct, known as aspartimide, prepared from diamino diphenyl methane and four structurally different bismaleimides, viz., 4,4'-Bismaleimido diphenyl methane, 4,4'-Bismaleimido diphenyl ether, 4,4'-Bismaleimido diphernyl sulphone and 3,3'-Bismaleimid diphenyl sulphone (These adducts are numbered I, II, III, and IV respectively).

EXPERIMENTAL

The method for synthesis of the bismaleimides is given in our earlier publication [1]. The adducts were prepared by refluxing the bismaleimide with diamino diphenyl methane in 1:0.3 mole ratio in DMF for 4-5 hrs. The viscous solution was then poured into cold water and the precipitated adduct was washed with water and dried in vacuum at 50-60°C.

The IR Spectra were recorded in KBr pellets, using Perkin-Elmer model 283 infrared spectrophotometer. The inherent viscosity of the samples in DMF was measured at 30°C, using Cannon-Ubbelhode viscometer fitted with Wescan model 221 viscocity timer. Thermal analysis was carried out using a Dupont 990 Thermal Analyser with 951 TGA and 905 DSC; heating rate: 10°C min^{-1}, sample mass: 10±0.2 mg and atmosphere: nitrogen at a flow of 50 cm^3 min^{-1}.

RESULTS AND DISCUSSION

The IR Spectra of the samples have all the characterestic bands of the corresponding bismaleimide [1]. Additional bands were observed at 3380-3480 cm^{-1} (NH-str.) and 1630 cm^{-1} (NH-bend.), showing the formation of the adducts. The molecular weight build-up of the adducts is indicated from the inherent viscosity of the bismaleimides (0.03) and the adducts (0.06 to 0.09)

Heat and Kinetics of Polymerisation

The heat and the kinetics of the thermal polymerisation of the four bisimide-diamine adducts were evaluated from their DSC curves, using the methods described earlier [1] and the results are given in Table 1. The ΔH values are in the range of 7 to 16 cals g^{-1} which are lower than the values for the bisimides [1]. This is due to the lower number of double bonds in the imide-diamine adduct. The kinetic parameters for the cure reaction of the adducts are in the range: E = 30-38 kcal mol^{-1} and A= 10^{11} - 10^{13} s^{-1}. The values for the corresponding bismides are lower [1], showing that the chain extension has the effect of increasing the activation energy and the pre-exponential factor for the polymerisation reaction.

TABLE 1. Heat and Kinetics of Polymerisation of Bisimide-diamine Adducts.

Sample	ΔH cals g^{-1}	E kcal mol^{-1}	A s^{-1}
I	12.5	32.2	7.85×10^{11}
II	15.6	30.7	1.21×10^{11}
III	8.6	34.6	4.51×10^{12}
IV	7.4	37.9	5.64×10^{13}

Thermal Stability and Thermal Decomposition Kinetics

The decomposition termperatures obtained from the TG curves of the cured samples of the four adducts are: I = 370°C II = 380°C, III = 380°C and IV = 350°C By comparison to the corresponding temperatures of the bisimides [1], it can be seen that the adducts are thermally less stable than the polyimides. This is in agreement with the earlier reports that chain extension through Michael addition has the effect of decreasing the thermal stability of the polymer [4].

The kinetic parameters, viz., energy of activation E, pre-exponential factor A, and the order parameter n for the thermal decomposition of the cured samples were evaluated from their TG data. The order parameter n was first determined by an iteration method described earlier [5] and was found to be 2 in all the cases. The same value was obtained for the polyimides also [1]. Using this value of n, E and A were computed with four integral kinetic equations, viz., Coats - Redfern Equation [6], MacCallum - Tanner Equation [7], Madhusudanan - Krishnan - Ninan (MKN) Equation [8] and Horowitz - Metzger Equation [9].

The values of E and A and the corresponding correlation coefficients r for the linear plots are given in Table 2. From this table it can be seen that the first three kinetic equations give very close values of E and A, while the Horowitz-Metzer equation gives slightly higher values which can be attributed to the approximation method used in the derivation of the equation [5]. The kinetic parameters for the adducts are lower than the corresponding bisimides, which is due to the lower thermal stability of the former. This trend is also reflected in the comparison of the data for the para and

TABLE 2. Kinetic Parameters for the Thermal Decomposition of Bisimide-diamine Adducts.

Sample	Coats-Redfern			MacCallum-Tanner		
	E	A	r	E	A	r
I	41.91	6.21×10^{6}	0.9987	42.64	3.62×10^{7}	0.9988
II	48.32	1.18×10^{9}	0.9994	48.75	6.55×10^{9}	0.9996
III	78.32	4.33×10^{18}	0.9987	79.53	1.95×10^{19}	0.9988
IV	38.98	1.02×10^{6}	0.9987	39.80	5.76×10^{6}	0.9987

Sample	M.K.N.			Horowitz-Metzger		
	E	A	r	E	A	r
I	41.95	9.60×10^{7}	0.9989	44.65	1.38×10^{10}	0.9975
II	48.82	5.56×10^{10}	0.9995	50.67	2.32×10^{14}	0.9985
III	78.37	1.39×10^{19}	0.9987	80.22	1.08×10^{23}	0.9970
IV	39.52	2.68×10^{7}	0.9988	41.85	8.87×10^{9}	0.9975

(E in kcal mol^{-1} and A in s^{-1})

meta sulphone based polymers. Para substitution enhances the thermal stability [10]; between the para and meta sulphone aspartimides, the former has higher decomposition temperature, activation energy and pre-exponential factor.

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