Thermal Behavior and Cured Products of Bis(4maleimidodiphenyl)methane, Bis(isomaleimidodiphenyl)methane and 4,4'-Diaminodiphenyl Methane Mixtures

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ABSTRACT: The thermal behavior of mixtures of bis(4-maleimidophenyl) (A) with bis(4-isomaleimidophenyl)methane (C) and their mixture with 4,4'-diaminodiphenyl methane (D) were investigated by differential scanning calorimetry. The study of the binary system A/C in different proportions led us to determine an eutectic mixture at a molar fraction of C in the range of 0.7–0.9. The ternary ACD mixtures showed themselves able to participate in three principal reactions: polyaddition, ring-opening addition, and homopolymerization. In each mixture studied the addition of diamine changed the melting point and maximum polymerization temperatures in the sense of a general decrease. The properties of the networks were studied by thermal analysis and through evaluation of water absorption. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3547–3556, 2003

Key words: polyimides; calorimetry; processing; resins; thermal properties

INTRODUCTION

Bismaleimide resins are an important class of polyimides. They are known for their ease of use and excellent thermal, electrical, and mechanical properties, which explains why they are widely used in composite materials. Because of the aromatic nature and high crosslink density of the cured network, the fully cured resins are brittle. To increase the process management of the molten state, bismaleimides are reacted with different functionalized comonomers such as aromatic diamines,^{1–6} diallyl bisphenols,^{7,9} and bisdiene.¹⁰ The use of binary and ternary bismaleimide mixtures may be developed as a method for improving processibility in the molten state.^{11,12} We already have reported the thermal behavior of polyaminobismaleimide prepolymers by differential scanning calorimetry.¹³

This article describes the influence of bis(4-isomaleimidodiphenyl)methane on the curing behavior of the bis(4-maleimidodiphenyl)methane and its influence on the properties of poly[(amino-amido)maleimide] networks.

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena spectrophotometer using the KBr pellet

technique. Melting and softening points were determined with a Gallenkamp hot-block point apparatus. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calorimetry (DSC) measurements were done with a Mettler TA Instrument DSC 12E in nitrogen at a heating rate of 10°C/ min. To determine the equilibrium water absorption, polymer samples were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator whose 89% relative humidity (RH) was maintained by an oversaturated aqueous solution of KCl at 20°C, and they were periodically weighed.

Monomer synthesis

Bis(4-maleimidophenyl)methane (A) was obtained by cyclodehydration of the parent maleamic acid in the presence of acetic anhydride and triethylamine using magnesium acetate as a catalyst (Scheme 1).¹⁴ The final product was recrystallized from toluene and dried under vacuum ($mp = 156^{\circ}$ C–158°C).

Bis(4-*N*-isomaleimidophenyl)methane (C) was obtained by cycloaddition of the parent bismaleimic acid in the presence of *N*,*N'*-dicyclohexyl carbodiimide (DCCI) in dichloromethane according to a method described in the literature.¹⁵ The final product was recrystallized from a benzene–ethylether mixture and dried under vacuum [$mp = 150^{\circ}$ C- 152° C (145° C- 150° C¹⁰)].

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Scheme 1

Preparation of AC mixtures

Mixtures containing various concentrations of the two monomers A and C were prepared in solvent after dissolution in chloroform at room temperature and under magnetic stirring. All the resulting solutions were perfectly homogeneous. After evaporating the solvent and drying for several hours in an oven at 60°C, the resulting powders were ground very fine in order to obtain the finest mixture possible.

Preparation of ACD mixtures

Blending of various AC mixtures with 4,4'-diaminodiphenyl methane (D) was carried out in a solid state at room temperature using D:AC molar ratios of 0.271, 0.4, 0.58, and 1. Each mixture of the series was ground fine and placed in aluminum crucibles.

Preparation of AC and ACD networks

The AC mixtures (AC₀–AC₁₀; Table I) and ACD mixtures (AC_iD_j, i = 1-10, j = 1-4; Table II) were cured by heating in shallow aluminum dishes at 220°C for 60 min in air.

RESULTS AND DISCUSSION

The influence of bis(4-*N*-isomaleimidophenyl)methane (C) on the thermal curing of bis(4-maleimidophenyl)methane (A) and their mixture with 4,4'diaminodiphenyl methane (D) was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis. The DSC diagrams of each AC mixture, recorded after a first dynamic run in the same conditions as the temperature gradient (10°C/ min), are shown in Figure 1; the melting temperature (T_m), polymerization onset temperature (T_0), exotherm maximum (T_{exo}), polymerization heat (ΔH_{polim}), and activation energy (E_a) are listed in Table I.

Processing thermal data as a function of the stoichiometric ratio of the mixture is shown in Figure 2. The performed thermal analysis revealed that endothermal transitions from the melting of A and C alone occurred at 160°C and 154°C, respectively. The addition of large quantities of C to the mixtures, that is, concentrations of x_C of 0.05, 0.1, 0.2, 0.3, and 0.5, resulted in the appearance of two melting points. The first endotherm remained around 130°C and corresponded to the melting temperatures of the eutectic (Te) and stayed independent, regardless

			Thermal stability					
Mixture	Molar fraction (x_C)	<i>Tm</i> ₁ (°C)	<i>Tm</i> ₂ (°C)	<i>T</i> ₀ (°C)	T _{exo} (°C)	$\Delta H_{ m polym}$ (J/g)	IDT (°C)	Т ₁₀ (°С)
AC ₀	0	_	160	190	240	262	418	475
AC_1	0.05	132	160	170	237	300	395	468
AC_2	0.1	131	158	165	233	304	390	464
AC_3	0.2	133	152	160	235	318	385	462
AC_4	0.3	131	148	157	235	308	382	458
AC_5	0.5	132	141	155	237	300	380	430
AC_6	0.6	132	140	152	237	296	380	425
AC_7	0.7	130	135	152	233	288	380	423
AC ₈	0.8	128	128	138	221	285	379	420
AC_9	0.9	128	141	150	234	298	378	418
AC_{10}	1.0		154	162	251	311	370	410

TABLE I

of the AC ratio. However, the intensity of this first endothermal peak depended on the C concentration. The area of the second endotherm, corresponding to the A monomer, also varied with concentration, but above all it was reduced to the point that it furnished a single and homogeneous melting signal with the first endotherm. The unique melting temperature corresponded to the so-called eutectic composition zone, in which the molar fraction of C ($x_{\rm C}$) in the mixture was 0.6, 0.8, and 0.9.

Processing melting data (T_{m1} and T_{m2}) as a function of the composition of the mixture (Table I) enabled a phase diagram to be constructed (Fig. 2). In this representation a relationship between the melting and the

TABLE II DSC Thermal Characteristics of ACD Mixtures as Function of Molar Fraction C (x_c) and D (x_{DC})

	raa	reb	χ _{D46} ^c	Tm_{π}	Tm_{2}	Tm	Ter	Τ.	Too	Τ.,	ΔH_1	ΔH_2	TGA	
Mixture	(%)	(%)	(%)	(°C)	(°C)	(°C)	(°C)	$(^{\circ}C)$	(°C)	(°C)	(J/g)	(J/g)	IDT (°C)	T ₁₀ (°C)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
AC_0D_1	0	0	0.27	80		146		_	192	238	94	290	370	426
AC_1D_1	0.05	5.40	0.27	80	_	150	_	_	183	237	104	265	392	428
AC_2D_1	0.10	2.70	0.27	85	134	156	_	_	177	227	84	189	385	431
AC_3D_1	0.20	1.35	0.27	88	132	154	65	92	165	218	67	189	350	433
AC_4D_1	0.30	0.90	0.27	90	128	154	60	92	160	221	62	149	335	438
AC_6D_1	0.60	0.54	0.27	90	130	134	60	93	158	223	48	118	333	413
AC_8D_1	0.80	0.45	0.27	92	145	_	60	93	150	232	_		342	408
AC_0D_2	0	0	0.4	81	_	142	_	_	188	227	99	235	350	423
AC_1D_2	0.05	8.16	0.4	84	_	145	_	_	172	226	93	228	374	417
AC_2D_2	0.10	4.08	0.4	86	_	150	70	72	168	225	77	190	368	419
AC_3D_2	0.20	2.04	0.4	85	138	160	68	90	165	223	56	150	340	422
AC_4D_2	0.30	1.35	0.4	90	124	160	70	94	162	225	67	106	333	428
AC_6D_2	0.60	0.68	0.4	91	130	_	75	94	159	227	39	159	332	408
AC_8D_2	0.80	0.49	0.4	91	145	_	75	100	148	237	—	_	340	402
AC_1D_3	0.05	11.46	0.58	80	_	138			184	225	111	219	340	420
AC_2D_3	0.10	5.71	0.58	86	_	143	_	_	160	234	102	222	342	410
AC_3D_3	0.20	2.85	0.58	87	133	144	75	95	160	225	71	172	338	405
AC_4D_3	0.30	1.90	0.58	90	126	155	75	94	158	216	31	112	335	402
AC_6D_3	0.60	0.95	0.58	90	131	_	75	94	157	226	—	_	339	400
AC_8D_3	0.80	0.71	0.58	90	145	_	92	95	150	236	—	_	342	398
AC_0D_4	0	0	1	80	122	_			148	218	_	213	340	408
AC_1D_4	0.05	19.98	1	81	131	_	_	_	146	216	83	169	339	405
AC_2D_4	0.10	9.98	1	84	130	_	_	_	145	196	88	142	339	404
AC_3D_4	0.20	4.99	1	87	130	_	75	94	145	197	70	122	338	403
AC_6D_4	0.60	1.66	1	92	130	_	60	95	145	157	_	_	338	400
AC_8D_4	0.80	1.20	1	94	134	_	70	98	141	154	—	_	338	394
$AC_{10}D_4$	1	1	1	95	136		62	100	155	162			315	308

^a Molar fraction C/A

^b Molar fraction D/C

^c Molar fraction D/(A+C)



Figure 1 DSC diagrams of A and C monomers alone and in mixture as a fraction of the molar fraction of C.

solubility of each component of the binary AC system can be shown via different liquid–solid phases, while retaining the eutectic concept introduced by Nagai et al.¹⁶ In the present case of a eutectic and in terms of melting equilibriums, there are four particular zones, specific for each state, whether liquid, solid, or both at the same time. These domains are delimited by three curves passing through E (eutectic point) characterized by a unique temperature, Te, for all compositions of A and C ($x_c = 0.8$). The four domains (Fig. 2) are specific to one or another of the states: domain 1 corresponds to A and C in the liquid state; domain 2 concerns the two compounds in the solid state; and domains 3 and 4 correspond to equilibriums of binary solution plus solid A and binary solution plus solid C, respectively.

Thermal studies also showed an effect of the mixture composition on the polymerization temperature, T_{0} , as well as T_{exo} , noted as the maximum of the exothermal peaks (Table I). The polymerization onset temperature decreased with an increasing proportion of C in the mixture, and this decrease became maximal for concentrations corresponding to the eutectic composition zone. The result was most significant at point E because at this eutectic concentration ($x_c = 0.8$), T_0 (138°C) was at its lowest and on the same order as that noted for C alone (154°C), considering the temperature gradient chosen for the study (°C/min).

The same comment is valid for T_{exo} temperatures. As the concentration of C in the mixture was increased, there was a significant decrease that became maximal at the eutectic point ($x_c = 0.8$) T_{exo} = 221°C. When the proportion became higher than that at point E, reactivity changed with the increasing of T_0 and T_{exo} . These data are consistent with the results of Varma and Tiwari¹⁷ and Marie Florence Grenier-Loustalot,⁶ who observed a low value of the exotherm maximum in a precise mixture, but are inconsistent with those of Nagai et al.,¹⁶ who reported no change in the exothermal peaks in the eutectic mixture. The polymerization heats of the AC mixture varied between 262.2 and 318 J/g. The thermal stability of the networks obtained by heating of the AC mixtures at 250°C for 60 min are presented in Table I. The initial decomposition temperature (IDT) and the temperature at which there was 10% weight loss (T_{10}) decreased with the increasing of the proportion of C in the mixture, and



Figure 2 Phase diagram: melting equilibrium with the formation of a eutectic: (1) domain 1, (2) domain 2, (3) domain 3, (4) domain 4.





these occurred in ranges between 370°C and 418°C for IDT and between 410°C and 475°C for T_{10} .

Ternary bismaleimide/bisisomaleimide/diamine systems (ACD)

Ternary ACD systems contain bismaleimide/bisisomaleimide mixtures AC and 4,4'-diaminodiphenyl methane (D) in various concentrations. The compositions of ternary ACD mixtures and their thermal characteristics are given in Table II. The moltenstate polymerization of bismaleimide and bisisomaleimide (AC) mixtures with aromatic diamines is governed by three reactions (Scheme 2). The first reaction involves copolymerization of the aromatic diamine with isomaleimide functions via a ringopening polyaddition reaction [Scheme 2(a)]; the second reaction involves the Michael addition reaction of diamine to the double bonds of maleimide [Scheme 2(b)]; and the third reaction involves homopolymerization of double bonds of maleimide or maleamide functions [Scheme 2(c,d)] by a thermally

induced radical opening of the maleimide double bonds (Scheme 2). We have already reported the thermal behavior of the bismaleimide–diamine mixture.¹³

Correlating DSC data for a dynamic regime with isothermal data, we reached the conclusion that the optimum polyaddition temperature ranged between 150°C and 160°C.¹³



Figure 3 DSC thermograms of $AC_{10}D_4$ mixture in molar ratio D:C = 1:1 in N₂. Heating rate is 5°C/min.



The thermal behavior of bisisomaleimide (C) and diamine (D) in an equimolecular mixture $(AC_{10}D_4)$ in the molten state was investigated by DSC measurements (Fig. 3). The first DSC thermogram dynamic run at temperature gradient (5°C/min) indicated two exotherms. The exotherm in the low-temperature regime was attributed to the ring-opening polyaddition reaction of melting diamine to bisisomaleimide with the forming of bisamines [Scheme 3(a)]. The T_{exo} peak at around 140°C-150°C was assigned to the continuing reaction to form the bisamide and the polymaleamides [Scheme 3(b)]. The second run of the mixture, $AC_{10}D_4$ (with a peak at around 344°C), may be attributed to the polymerization reaction of the maleamide double bonds [Scheme 2(d)] or the polymaleimide chain fragmentation with the obtaining of the new reactive species (Scheme 4).

The IR spectra of the $AC_{10}D_4$ mixture at molar ratio C:D = 1:1, after heat treatment at various temperatures are shown in Figure 4. According to the assignment of bands reported by Nagarathinan and colleagues,¹⁸ the bands at 1785 and 1670 cm⁻¹

(corresponding to the five lactone rings and the C=N) and at 1080 cm⁻¹ (as a result of the -Ostretch) disappeared, and new frequencies appeared at 3300, 1650, and 1540 cm^{-1} (corresponding to NH stretch vibration, amide I, C=O bond, and NH deformation). The absorptions at 1415 and 830 cm^{-1} were assigned to in-plane and out-of-plane deformations of the ethylenic double bond, >C=C<, with a cis configuration [Fig. 4(b)]. The IR spectra of the AC₁₀D₄ mixture after thermal treatment at 170°C for 60 min and at 350°C for 30 min showed additional bands at 1720, 1385, and 1180 cm^{-1} , assigned to the succinimide rings [Fig. 4(b,c)]. Figure 4(c) shows the decreasing of the bands at 1650, 1540, and 1325 cm⁻¹ accompanying an increasing of the bands at 1720, 1385, and 1180 cm^{-1} . This demonstrates that the formation of the aspartimide units continued by increasing the temperature.

In accordance with spectral studies of polymaleimides reported by Nagarajan and colleagues,¹⁹ it is possible that a fragmentation mechanism occurred for the degradation of the polymaleimides with the



Scheme 4



Figure 4 IR spectra of $AC_{10}D_4$ mixture: (a) uncured mixture, (b) cured mixture at 170°C for 60 min, (c) cured mixture at 350°C for 30 min.

formation of the aspartimides by the polyaddition reactions, which is presented in Scheme 4.

The IR spectra of the ternary mixture AC_8D_4 after thermal treatment at 100°C, 200°C, and 350°C have the same shape (Fig. 5). Depending on the ternary system composition one or more reactions may have occurred (Scheme 2). At concentration x_{DC} , lower than 1, the ring-opening polyaddition reaction (a) was predominant. That determined the appearance of the second polymerization maximum in the ACD mixtures, with $x_C > 0.2$ and $x_{DC} < 3$, which ranged between the melting temperature of the diamine and that of the bisisomaleimide (80°C–95°C). At the molar ratio x_{DC} > 1, the diamine excess reacted with bismaleimide by the Michael addition reaction (b). In this case, the system would be characterized by the reactions of the a, b, c, and d types.

For the AC_xD_4 mixture with a molar ratio of D/(A+C) = 1 (Fig. 6), it was observed that the melting temperature of the diamine corresponding to the first endotherm increased from 80°C in the equimolecular mixture of the bismaleimide–diamine to 95°C in the equimolecular mixture $AC_{10}D_4$. The diamine formed an eutectic mixture with bismaleimide in the mixture with $x_c < 0.2$. At a con-

centration greater than 0.2 the melting of this eutectic mixture could not be observed because of the appearance of the isomaleimide ring-opening reaction. The high exotherm peak increased with the bisisomaleimide concentration, and the temperature corresponding to the Michael addition process and the homopolymerization (T_{exo2}) decreased from 218°C to 155°C for the eutectic mixture AC₈D₄ (Fig. 6). At a molar ratio lower than 1, an increasing of the temperature corresponding to the exotherm (T_{exo2}) with the bisisomaleimide concentration (x_c) was observed. So, the temperature increased from 223°C to



Figure 5 IR spectra of AC_8 and AC_8D_4 mixtures: (a) AC_8 uncured mixture, (b) AC_8D_4 uncured mixture, (c) AC_8D_4 cured at 100°C for 60 min, (d) AC_8D_4 cured at 200°C for 60 min, (e) AC_8D_4 cured at 350°C for 30 min.



Figure 6 DSC thermograms of ACD_4 mixtures (molar ratio D/A+C = 1) with various x_C rations.

237°C for the AC_xD_3 mixtures, from 225°C to 236°C for the AC_xD_2 mixtures, and from 218°C to 232°C for the AC_xD_1 mixtures (Fig. 7). As shown in Figure 8, for the AC_8D_x mixtures (which are eutectic mixtures between bismaleimide and bisisomaleimide and various molar ratios of the diamine), two melting endotherms were observed that corresponded to the diamine and the AC mixture and to one polymerization exotherm. The temperature corresponding to the ring-opening reaction was about 95°C–100°C and that of the homopolymerization was 220°C–237°C.

The thermal stability of cured ACD mixtures was investigated by TGA in dynamic conditions (Table II and Fig. 9) and in isothermal conditions at 275°C (Fig. 10).

The initial decomposition temperature (IDT) and the temperature at which there was 10% weight loss (T_{10}) decreased with an increasing proportion of C and D in the mixture and occurred between 315°C and 392°C for IDT and 388°C and 438°C for T_{10} (Table II).

The effect of the ACD mixture composition (x_C) on temperature T_{10} is shown in Figure 9. T_{10} decreased with increasing x_C and x_{DC} ratios. The same behavior

also was observed by measuring in the isothermal conditions (Fig. 10).

The absorption of water from the atmosphere at a constant humidity is shown in Figure 11. As can be seen, the absorbed water amount increased with increasing amine and isomaleimide concentrations in the system.

CONCLUSIONS

This article has presented the results of the work on the reactivity of bismaleimide (A), bisisomaleimide (C), and their mixtures (AC) in the molten state. The DSC study of the AC mixture enabled a phase diagram to be constructed that contained an eutectic in which a relationship between the melting and solubility of each constituent (A and C, respectively) could be described.

The study of the ternary bismaleimide–bisisomaleimide–diamine system (ACD) in the molten state



Figure 7 DSC thermograms of ACD₃ mixtures (molar ratio D/A+C = 0.58) with various x_C rations. Heating rate is 10°C/min.



Figure 8 DSC thermograms of eutectic mixture AC_8 with various diamine concentrations

showed the influence of bisisomaleimide concentration, $x_{C''}$ on the thermal behavior and the properties of the uncured and cured ACD mixtures.

The molten-state polymerization of ACD mixtures was governed by three principal reactions: copoly-



Figure 9 The temperature variation corresponding of the 10% weight loss from ACD resins depending on the molar ratio $x_C = C/A$ and $x_{DC} = D/(A+C)$



Figure 10 Isothermal weight-loss curves at 275°C for ACD resin by thermal cured at 220°C for 60 min.



Figure 11 The absorption of water from atmosphere at constant humidity of 89%.

merization of bisisomaleimide with diamine by ring-opening polyaddition; Michael polyaddition reaction of diamine to bismaleimide; and homopolymerization of maleimide or the maleamide double bond.

The presence of bisisomaleimide in a proportion greater than 50% in the mixture with bismaleimide led to a decrease in the melting temperature and its properties (thermal stability, absorption of water).

References

- 1. Mandric, G.; Chiriac, C.; Gherasim, G.; Sava, M.; Pecincu, S. Materiale Plastice 1980, 18(3), 133.
- 2. Tungare, A. V.; Martin, G. C. J Appl Polym Sci 1992, 46, 1125.
- 3. Wang, C.-S.; Len, T.-S.; Hsu, K.-R. Polymer 1998, 39, 2921.
- 4. Varma, I. K.; Sangita, Gupta, S. P.; Varma, D. S. Thermochim Acta 1985, 93, 217.
- 5. Wu, W.; Wang, D.; Ye, C. J Appl Polym Sci 1998, 70, 2471.
- 6. Grenier-Loustlat, M. F.; da Cunha, L. High Perform Polym 1998, 10(3), 285.
- Morgan, R. J.; Shin, E. E.; Rosenberg, B.; Jurek, A. Polym 1997, 38, 639.

- 8. Phelan, J. C.; Paik Sung, C. S. Macromol 1997, 30, 6845.
- 9. Gouri, G.; Reghunadhan Nair, C. P.; Ramaswamy, R. High Perform Polym 2000, 12, 497.
- 10. Abbate, M.; Martuscelli, E.; Musto, P.; Rogosta, G. J Appl Polym Sci 1997, 65, 979.
- 11. Series, A.; Feve, M.; Pascault, J. P. J Appl Polym Sci 1993, 48, 257.
- 12. Nagai, A.; Takahashi, A.; Katagond, M.; Mukoh, A. J Appl Polym Sci 1990, 41, 2241.
- Gaina, V.; Gaina, C.; Sava, M. Polym Plast Technol Eng 2001, 40(1), 89.
- Dix, L. R.; Ebdon, J. R.; Flint, N. J.; Hodge, P.; O'Dell, R. Eur Polym J 1995, 31, 647.
- 15. Cotter, R. J.; Sourrs, C. K.; Whelan, J. M. J Org Chem 1961, 26, 10.
- 16. Nagai, A.; Takahashi, A.; Suzuki, M.; Katagud, M.; Mukoh, A. J Appl Polym Sci 1990, 41, 2241.
- 17. Varma, I. K.; Tiwari, R. J Thermal Anal 1987, 32, 1023.
- 18. Nagarathinam, R.; Viswanathan, S. J Macromol Sci Pure Appl Chem 1988, A25, 1675.
- Nagarajan, E. R.; Rajeswari, N.; Viswanathan, S. J Macromol Sci Pure Appl Chem 1997, A34(6), 1055.