ELSEVIER

PII: S0032-3861(97)10332-9

Polymer Vol. 39 No. 20, pp. 4923–4928, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

Curing behaviour and thermal properties of Epon 828 resin cured with diimide–diacid and phthalic anhydride

Wei-kuo Chin[a,*], Ja-jen Hwu[a] and Min-Da Shau[b]
[a]*Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan*
[b]*Department of Applied Chemistry, Chia Nan College of Pharmacy and Science, Tainan, Taiwan*
(Received 3 May 1996; revised 10 September 1997; accepted 25 November 1997)

A diimide–diacid (DIDA) curing agent of *N,N'*-(4,4'-diphenylsulfone) bis(trimellitimide) was synthesized. Through the spectral characterization of infrared (i.r.), ^{1}H n.m.r., ^{13}C n.m.r., and of elemental analysis (EA), the DIDA structure was confirmed. The curing behaviour and resultant thermal properties of epoxy resin (Epon 828) with DIDA were studied by differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.), respectively. In order to improve the processing ability, DIDA was partially replaced by phthalic anhydride (PA) in the formulations carried. The thermal resistance depended on the relative proportions of curing agents in the formulations. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: diimide–diacid; phthalic anhydride; epoxy)

INTRODUCTION

The properties and performance of a cured epoxy polymer are all dependent on the types of epoxy resin, curing agent and the curing conditions used. If the chemical structures of cured epoxy polymers are constituted with aromatic and/or heterocyclic rings, their thermal resistance is superior to those of constituents with flexible or aliphatic chains. Imide compounds and polymers, which contain aromatic and/or heterocyclic groups, can offer desirable high-temperature stability. Therefore, using imide groups to modify the structure of epoxy to enhance its thermal resistance has received great attention in the research community[1]. Imide-modified epoxy polymers can be used as organic insulators, adhesives/or coatings, and in composites, and microelectronics. Cádiz and co-workers synthesized a series of diimide–diacid (DIDA) compounds[2]. Synthesized DIDA compounds were then used to react with epochlorohydrin to produce a series of diglycidyl ester compounds containing imide rings[2–4]. The diglycidyl ester compound could be further reacted with amine, diamine, acid, or diacid compounds to form linear or crosslinked polymers[5–9]. Introducing imide groups into the backbone structure of epoxy resin, the difficulty of processing ability was encountered. Another way to improve the thermal resistance of epoxy is to use a curing agent containing imide groups, such as hydroxyl-terminated imide compounds[10,11], imide–acid[12,13], imide–amine, or imide–anhydride, etc. In this study, we used the diimide–diacid compound as an epoxy resin curing agent. The diimide–diacid (DIDA) curing agent of *N,N'*-(4,4'-diphenylsulfone) bis(trimellitimide) was synthesized, according to *Scheme 1*. In order to improve the processing ability, DIDA was partially replaced by phthalic anhydride (PA) in the formulations. The curing behaviour and resultant thermal resistance of epoxy cured with DIDA and DIDA/PA were studied and discussed in this paper.

EXPERIMENTAL

Reagents

N,N'-Dimethylformamide (DMF) and *N,N'*-dimethylacetamide (DMAc) solvents were dried by phosphoric anhydride first, and further purified by distillation under reduced pressure. Toluene was purified by distillation under atmospheric pressure. 4,4'-diamino diphenylsulfone (DDS), phthalic anhydride (PA), and trimellitic anhydride (TMA) were reagent grade from Merck and used without further purification. Diglycidyl ether of bisphenol A (DGEBA), Epon 828, was purchased from Shell Chemical Co.

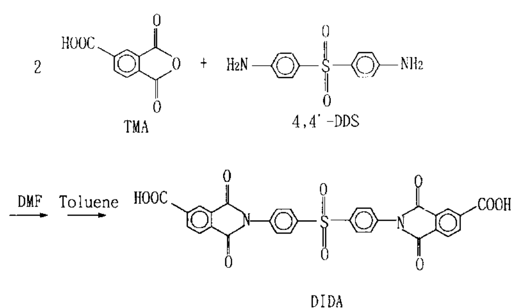
Synthesis of N,N'-(4,4'-diphenylsulfone) bis(trimellitimide) (DIDA)

A solution of trimellitic anhydride (39.3 g) in anhydrous *N,N'*-dimethylformamide (100 ml) was gradually added into a stirred solution of 4,4'-diaminodiphenylsulfone (24.83 g) in anhydrous *N,N'*-dimethylformamide (100 ml) under a nitrogen atmosphere and then stirred at 0°C for 2 h. An anhydrous toluene (65 ml) was added to the foregoing solution and heated up to 180°C for reaction. Stoichiometric water produced during the course of the reaction was collected by a Dean-Stark trap. The reaction mixture was then cooled to room temperature and precipitated in ice water and further washed with acetone. The obtained solid was recrystallized from *N,N'*-dimethylacetamide. The products were white and crystalline with a melting point near 300°C and the yield was 70%.

Characterization and measurements

The melting point was determined by a Yanaco MP-S3.

* To whom correspondence should be addressed



Scheme 1 Synthesis of DIDA

Elemental analysis was carried out on a Heraeus CHN-O Rapid Analyzer. Infrared (i.r.) and Fourier transform infrared (*FT*-i.r.) spectra were examined by using a Perkin-Elmer Model 983 and Bomen DA 3.002 FTS, respectively. ^{1}H n.m.r. and ^{13}C n.m.r. spectra were obtained using a Bruker AM-400 where samples were dissolved in DMSO-d6, with TMS employed as an internal standard. Curing conditions were determined through the dynamic and isothermal thermograms on a Du Pont 910 Differential Scanning Calorimeter (d.s.c.). Thermal resistance was evaluated by thermogravimetric analysis (t.g.a.) on a TGA Du Pont 2100 with a heating rate of 10°C/min. Dynamic mechanical analysis was performed on a Rheometrics Dynamic Spectrometer RDS-7760 with a heating rate of 3°C/min and a frequency of 1 Hz.

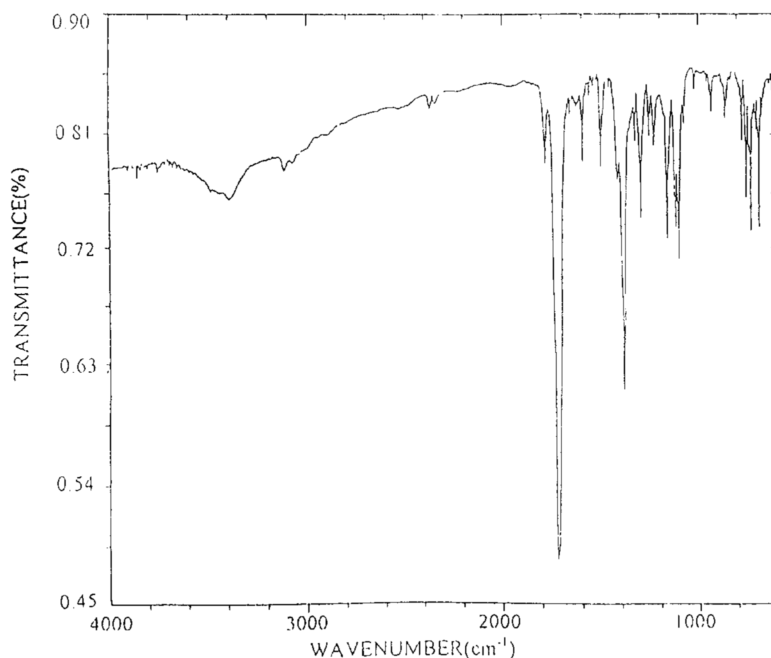


Figure 1 I.r. spectrum of DIDA

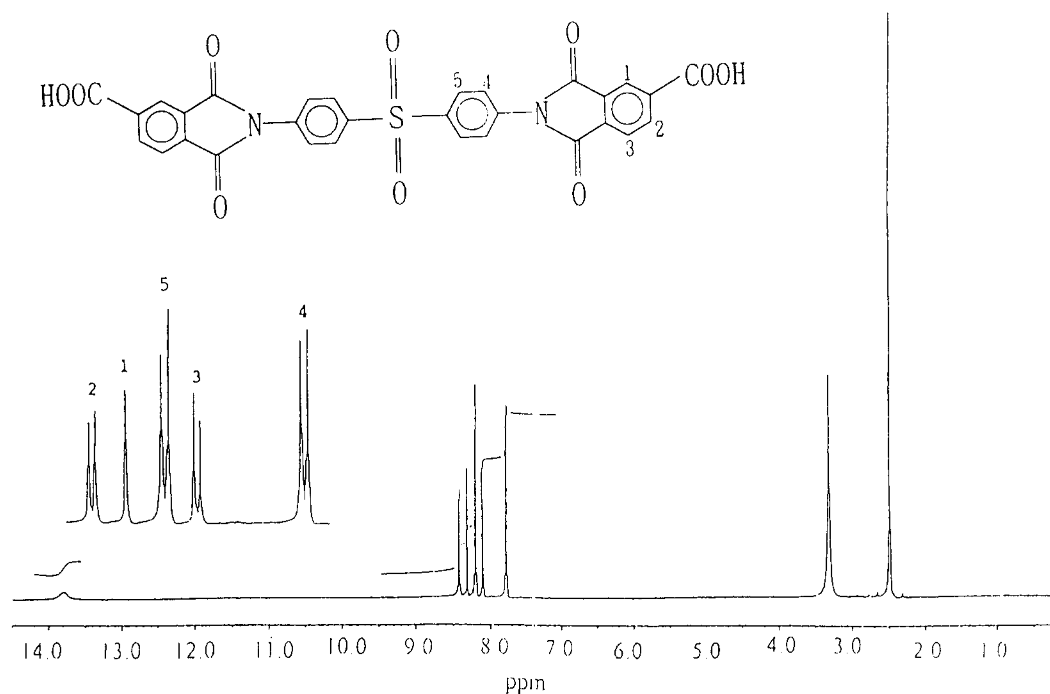


Figure 2 ^{1}H n.m.r. spectrum of DIDA

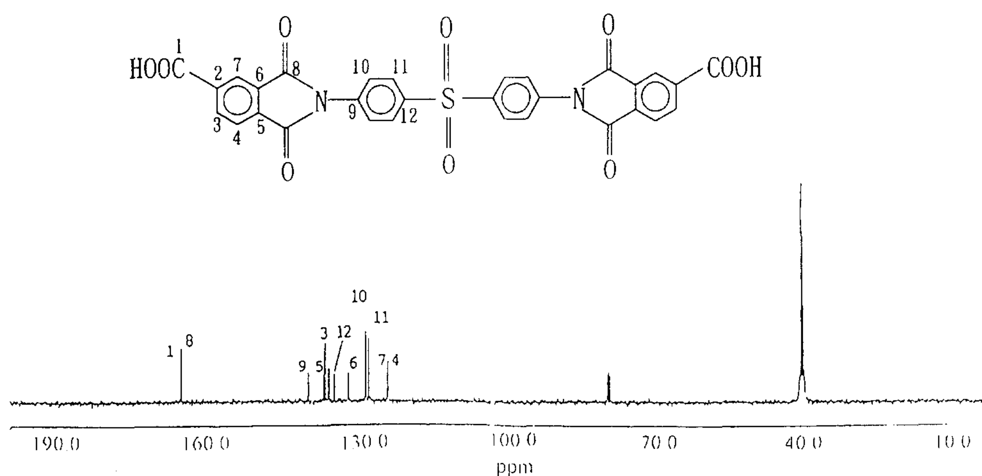


Figure 3 ^{13}C n.m.r. spectrum of DIDA

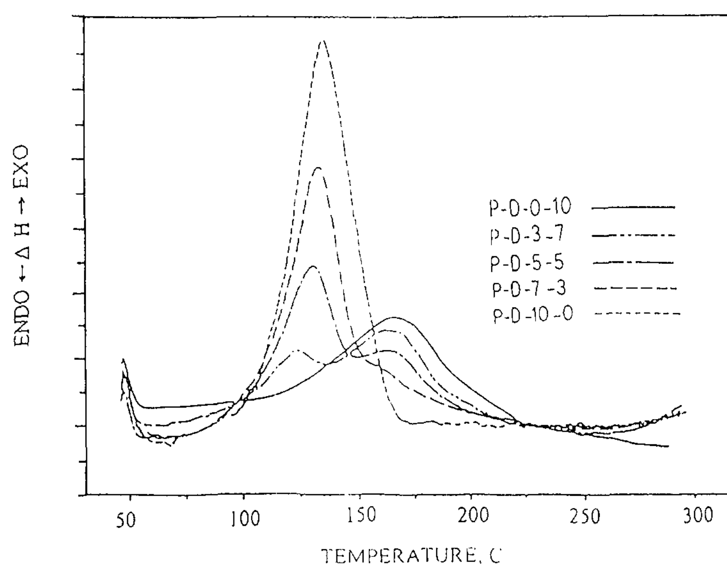


Figure 4 Dynamic d.s.c. thermograms of the Epon 828/PA-DIDA system. The heating rate is 10°C/min

Table 1 ^{1}H n.m.r. data of DIDA

	Type of Proton				
	1	2	3	4	5
Chemical shifts (ppm)	8.31 (2H,s)	8.39–8.41 (2H,dd)	7.78–8.08 (2H,d)	7.76–7.78 (4H,dd)	8.16–8.20 (4H,dd)

Table 2 ^{13}C n.m.r. data of DIDA

	Type of Carbon											
	Aromatic Carbons										Carboxyl Carbons	
	2	3	4	5	6	7	9	10	11	12	1	8
Chemical shifts (ppm)	135.66	136.40	123.74	136.79	131.76	123.95	139.82	127.63	128.31	134.57	165.67	165.60

Table 3 Formulations of the Epon 828/PA-DIDA system

Code	Eq. molar ratio		
	Epon 828	PA	DIDA
P-D-0-10	1	0	1
P-D-3-7	1	0.3	0.7
P-D-5-5	1	0.5	0.5
P-D-7-3	1	0.7	0.3
P-D-10-0	1	1	0

RESULTS AND DISCUSSION

Structural characterization of N, N′*-(4,4′-diphenylsulfone) bis(trimellitimide) (DIDA)*

The synthesized DIDA compound was characterized through the spectra of infrared (i.r.), ^{1}H n.m.r., ^{13}C n.m.r., and of elemental analysis (EA). The data of elemental analyses were found: 60.35% C, 2.76% H, 4.69% N, 26.74% O, and 5.33% S (calculated: 60.41% C, 2.70% H, 4.70% N,

Table 4 Normalized i.r. absorption ratio data of the Epon 828/PA-DIDA system during 125°C cure

Code	Functional group	$A_n*(t)/A_n*(0)$ Curing time (min):				
		0	7.5	15	22.5	30
P-D-0-10	P[a]	—	—	—	—	—
	D[b]	1.000	1.000	0.984	0.956	0.925
	E[c]	1.000	1.000	1.000	0.964	0.918
P-D-3-7	P	1.000	—	—	—	—
	D	1.000	0.973	0.917	0.919	0.868
	E	1.000	0.885	0.844	0.834	0.812
P-D-5-5	P	1.000	0.372	0.295	0.286	—
	D	1.000	0.988	0.988	0.974	0.941
	E	1.000	0.525	0.508	0.501	0.408
P-D-7-3	P	1.000	0.439	—	—	—
	D	1.000	1.000	1.000	0.974	—
	E	1.000	0.406	0.444	0.414	0.454
P-D-10-0	P	1.000	0.195	0.180	—	—
	D	—	—	—	—	—
	E	1.000	0.367	0.327	0.315	0.349

[a]P:C=O in anhydride (PA)
[b]D:C=O in carboxylic acid (DIDA)
[c]E:C–O in epoxide group (epoxy)

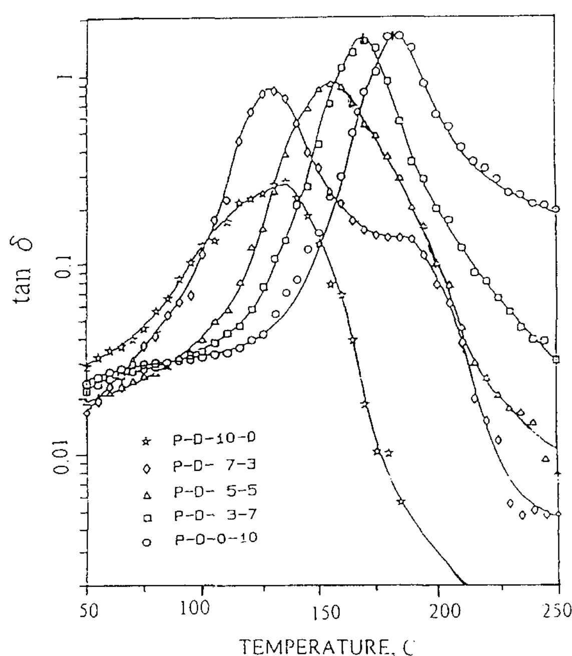


Figure 5 Damping behaviors of cured Epon 828/PA-DIDA polymer. The heating rate is 3°C/min and the frequency is 1 Hz

26.82% O, and 5.37% S). The i.r. spectrum of DIDA is shown in *Figure 1*. The peak at 3400 cm^{-1} shows the broad O–H absorption of carboxylic acid. The peak at 3095 cm^{-1} is the =C–H stretch absorption of the aromatic ring. Peaks at 1736 and 1719 cm^{-1} represent the stretch absorptions of C=O in imide group and carboxylic acid, respectively. The peak at 1384 cm^{-1} indicates the asymmetric stretch absorption of S=O. The ^1H and ^{13}C n.m.r. spectra of DIDA in DMSO-d6 are shown in *Figures 2* and *3*, respectively. The chemical shifts of characterized protons and carbons are listed in *Table 1* and *Table 2*, respectively. These shifts are based on the assigned labels of proton in *Figure 2* and carbon in *Figure 3*. Through the structural characterization of EA, i.r., ^1H n.m.r., and ^{13}C n.m.r., the synthesized compound was confirmed to be DIDA.

Curing behaviour of Epon 828/PA-DIDA system

Introducing the imide group into the structure of the curing agent, the thermal resistance of cured epoxy polymer can be improved. However, processing difficulty arose due to the high solid content of DIDA in the formulation. In order to improve the processing ability, DIDA was partially replaced by phthalic anhydride (PA) in the formulations carried. *Table 3* lists the formulations of Epon 828/PA-DIDA system used. The equivalent molar ratio of epoxy and curing agent is 1:1, and the ratio of PA and DIDA are varied from 0:1 to 1:0. *Figure 4* shows the dynamic d.s.c. thermograms of the Epon 828/PA-DIDA system. The PA and DIDA reacted with epoxies at lower and higher temperature, respectively. Using a mixed curing agent of PA and DIDA, the resin showed two exothermic peaks, as shown in *Figure 4*. Therefore, two curing steps were chosen. The chosen curing temperatures for PA and DIDA were 125 and 185°C, respectively. The reactivities of PA and DIDA with epoxies were qualitatively evaluated through the absorption change of *FT*-i.r. spectra during the thermal cure period. In the *FT*-i.r. spectrum, those peak absorptions identified as 1780 and 1850 cm^{-1} are the stretch absorption of C=O in anhydride (PA); 1710–1715 cm^{-1} is the stretch absorption of C=O in carboxylic acid (DIDA); 906–915 cm^{-1} is the stretch absorption of C–O in epoxide group; and 1508–1511 cm^{-1} is the C=C absorption of aromatic rings. Since aromatic rings did not change during the cure reaction, their absorption peak (A_{ref}) could be used as an internal standard. Each absorption peak of characterized group (A_n) would be then normalized first by dividing it by the absorption peak of aromatic rings as follows. Normalized absorption:

$$A_n(t)* = A_n(t)/A_{ref}(t).$$

The reactivities of PA and DIDA with epoxide during the curing process could be viewed from the normalized absorption changes of characterized groups with time. The ratios of normalized absorption peaks of PA, DIDA, and epoxy, at various times during the cure period of 125°C/30 min, are listed in *Table 4*. During the first period of curing at 125°C,

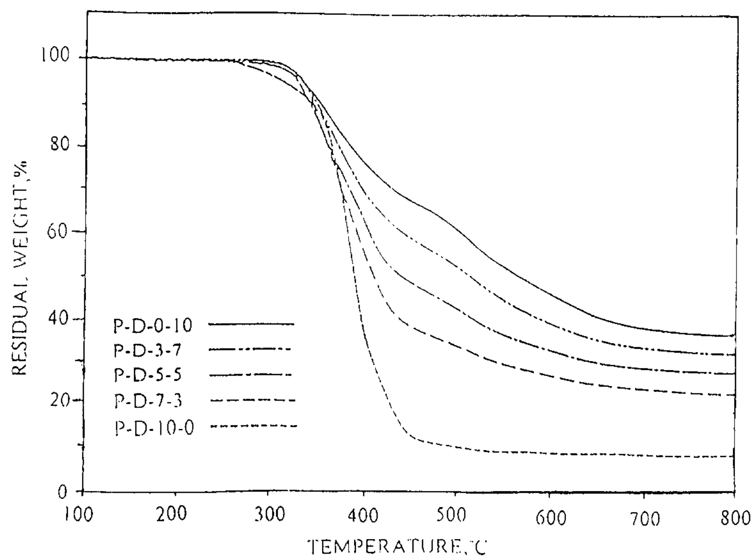


Figure 6 T.g.a. thermograms of cured Epon 828/PA-DIDA polymers in nitrogen. The heating rate is 10°C/min

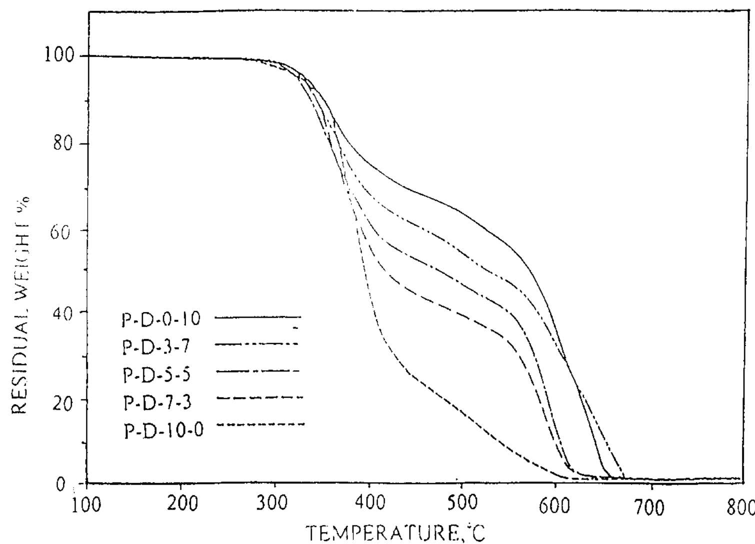


Figure 7 T.g.a. thermograms of cured Epon 828/PA-DIDA polymers in air. The heating rate is 10°C/min

the DIDA had little or no reaction with the epoxy. The major reaction occurred between the epoxide and anhydride. Therefore, the characterized absorption ratio of PA dropped very fast, whereas the characterized absorption ratio of DIDA remained relatively unchanged. After the PA completely reacted, the curing temperature was then increased to 185°C. During this period of curing, the reaction between epoxy and DIDA progressed.

Thermal properties of Epon 828/PA-DIDA system

Damping behaviours of cured samples were studied using a Rheometrics Dynamic Spectrometer (RDS) and the result is shown in *Figure 5*. The damping peak is associated with the partial loosening of the polymer structure so that groups and small chain segments can move. This occurs near T_g at low frequency[14]. *Table 5* lists the tan δ peak temperature of the cured Epon 828/PA-DIDA system. Nielsen stated that the tan δ peak at a frequency of 1 Hz was at a temperature 5–15°C above the T_g, as measured by differential thermal analysis[14]. In our case, the tan δ peak of Epon 828 cured with DIDA (P-D-0-10) is at a temperature 10°C above the T_g of the same system, as measured by d.s.c. Using PA as the solo curing agent, the cured polymer exhibits a damping peak at a temperature of 133°C, which is about 50°C below the one cured with DIDA. So, introducing imide groups into the polymer structure can significantly increase the rigidity of polymer chain as well as the glass transition temperature. When binary curing agents of PA and DIDA were used in the formulation, it is noteworthy that two types of damping behaviour were observed. In the P-D-7-3 system, a major damping peak with a shoulder peak was observed in the

Table 5 The tan δ peak temperature of cured Epon 828/PA-DIDA polymer

Code	Peak temp. (°C)
P-D-0-10	185
P-D-3-7	170
P-D-5-5	154
P-D-7-3	130,190
P-D-10-0	133

Table 6 T.g.a. data of cured Epon 828/PA–DIDA polymer in nitrogen and air environment[a]

	Code	T^b_{max} (°C)	Temperature at characteristic weight loss (%)					Residue (%)		
			5%	10%	20%	30%	50%	300°C	400°C	500°C
N_2	P-D-10-0	398	353	369	399	443	580	99.6	79.8	62.9
	P-D-3-7	382	356	367	385	408	525	99.7	73.2	54.1
	P-D-5-5	373	343	357	375	393	448	98.6	66.9	43.6
	P-D-7-3	374	348	359	373	385	413	99.3	59.0	29.7
	P-D-10-0	394	329	360	378	387	397	97.7	44.9	9.9
Air	P-D-10-0	376	345	367	392	450	582	98.2	77.9	65.1
	P-D-3-7	385	341	357	381	406	538	98.0	71.8	56.3
	P-D-5-5	368	335	351	371	390	482	97.9	65.5	47.6
	P-D-7-3	379	341	358	373	385	425	98.1	60.9	39.7
	P-D-10-0	401	338	365	381	390	404	98.0	56.0	19.9

[a]The heating rate is 10°C/min
[b]T_{max}, maximum decomposition rate temperature

RDS result. The major damping peak reflected the relaxation behaviour of the crosslinked structure of epoxy and PA, and the shoulder peak was the relaxation of the crosslinked structure of epoxy and DIDA. This may mean that the crosslinking reaction of epoxy with DIDA results in a microgel structure imbedded in and crosslinked to the .crosslinked structure of epoxy with PA. However, in the P-D-3-7 and P-D-5-5 systems, only one damping peak was observed and the peak temperature of tan δ was gradually decreased as the content of PA in the formulation increased. This infers that the crosslinked structure is mixed chains of epoxy reacted with PA and epoxy reacted with DIDA. *Figures 6 and 7* show the TGA thermograms of cured epoxy polymer in nitrogen and air environments, respectively. Summaries of the TGA results, the thermal resistance and the residue weight content of cured Epon 828/PA-DIDA system, at various temperatures, are listed in *Table 6*. The cured epoxy polymer can sustain a temperature up to 340°C without significant weight loss. When the thermal decomposition was started, the PA-cured epoxy polymer had a faster decomposition rate than that of the DIDA-cured epoxy polymer. Therefore, the higher the DIDA content in the formulation, the better the thermal resistance in the cured epoxy polymer was observed. Using both PA and DIDA as curing agents overcome the disadvantages encountered (difficulty in processing and a high curing temperature of 180–200°C) in using DIDA alone as the curing agent in the formulation. The result is to sacrifice a certain degree of thermal resistance of the cured epoxy polymer.

CONCLUSIONS

The diimide–diacid compound was synthesized and used as a curing agent for epoxy. The glass transition temperature and thermal resistance of cured epoxy polymer were improved through the introduction of imide group into the structure. In order to improve the processing ability, a binary curing agent of diimide–diacid and phthalic anhydride was then used in the formulation. If PA was the major curing agent, two phase structures appeared as a microgel structure of epoxy reacted with DIDA imbedded in and crosslinked to the crosslinked structure of epoxy with PA. If DIDA was the major curing agent, the crosslinked structure is mixed chains of epoxy reacted with PA and epoxy reacted with DIDA. The thermal resistance depended on the relative content of PA and DIDA in the formulation.

REFERENCES

1. Chin, W. K. and Shau, M. D., Epoxy-imide, phosphorylated epoxy-imide polymers, in *The Polymeric Materials Encyclopedia*, ed. J. C. Salamone, CRC Press, Vol. 3, D–E, 1996, pp. 2210.
2. Martinez, P. A., Cádiz, V., Mantecón, A. and Serra, A., *Angew. Makromol. Chem.*, 1985, **133**, 97.
3. Serra, a., Cádiz, V., Mantecón, A. and Martinez, P. A., *Tetrahedron*, 1985, **41**, 763.
4. Serra, A., Cádiz, V., Martinez, P. A. and Mantecón, A., *Angew. Makromol. Chem.*, 1986, **140**, 113.
5. Martinez, P. A., Cádiz, V., Serra, A. and Mantecón, A., *Angew. Makromol. Chem.*, 1985, **136**, 159.
6. Serra, A., Cádiz, V., Martinez, P. A. and Mantecón, A., *Angew. Makromol. Chem.*, 1986, **138**, 185.
7. Serra, A., Cádiz, V., Martinez, P. A. and Mantecón, A., *Makromol. Chem.*, 1986, **187**, 197.
8. Mantecón, A., Cádiz, V., Serra, A. and Martinez, P. A., *Eur. Polym. J.*, 1987, **23**, 481.
9. Hau, M. D. and Chin, W. K., *J. Polym. Sci. Part A: Polym. Chem.*, 1993, **31**, 1653.
10. Ichino, T. and Hasuda, Y., *J. Appl. Polym. Sci.*, 1987, **34**, 1667.
11. Sasaki, S. and Hasuda, Y., *J. Polym. Sci. Part C: Polym. Lett.*, 1987, **25**, 377.
12. Serra, A., Cádiz, V. and Mantecón, A., *Angew. Makromol. Chem.*, 1987, **155**, 93.
13. Adhinarayanan, K., Packirisamy, S., George, R. S., Lakshmana Rao, V. and Ramaswamy, R., *J. Appl. Polym. Sci.*, 1991, **43**, 783.
14. Nielsen, L. E., *Mechanical Properties of Polymers and Composites*, Vol. 1, Marcel Dekker, NY, 1974.