

Thermal and Mechanical Properties of Epoxy Resin Modified with N-(4-hydroxyphenyl)terahydrophthalic Anhydrideimide

XU Renxin, CHENG Shixin, ZHOU Jing, SHEN Jie, LI Zheng, TAN Xing

(School of Materials Science & Engineering, Wuhan University of Technology, Wuhan 430070, China)

Abstract: A novel epoxy-imide resin based on diglycidyl ether of bisphenol-A and N-(4-hydroxyphenyl)terahydrophthalic anhydrideimide (HTAM) was synthesized. The structural characterization of the epoxy-imide resin was conducted by FT-IR spectra. 4,4'-diaminodiphenylmethane (DDM) was used as a curing agent for the epoxy-imide resin. The thermal properties of the cured resin were evaluated with dynamic mechanical analyses (DMA) and thermogravimetric analysis (TGA). The results showed that the cured resin exhibited a high glass transition temperature (T_g) of 186 °C when the molar amount of HTAM was 0.04 mol in the resin. The yields of the cured resin at 800 °C raised from 16.45% to 19.41%. The flexural properties were also measured, the flexural strength raised from 79.4 to 95.7 MPa, and the flexural modulus exhibited from 2.6 to 3.0 GPa.

Key words: epoxy-imide resin; glass transition temperature; char yield; flexural properties

1 Introduction

Epoxy resins, a kind of important thermosetting resins, are widely applied in circuit package, laminating, adhesive, coating and aerospace owing to their many outstanding performances, such as low shrinkage in cure, excellent electrical insulating property, desirable chemical and solvent resistance, and great mechanical strength^[1-5]. However, with the development of the application of composites, more stringent requirements have been put forward on the flame retardancy, moisture resistance and heat resistance of epoxy resin. Especially in the field of aerospace, epoxy resin as the most widely used matrix resin of the composites, was required a higher glass transition temperature and char yield.

The properties of the cured resin mainly depend on the chemical structure of epoxy resin and its curing agent^[6,7]. For the past few years, considerable studies have been reported to combine the versatility of epoxy resins with the high-temperature properties of imide group^[8,9]. Most of the reported papers paid attention

to mixing epoxy resins with thermoplastic polyimides or polybismaleimides^[10], and curing epoxy resins with agents containing imide group^[11-15]. The lap shear strength of the epoxy resins (GY-250) cured with bis(carboxyphthalimide)s retained 75% (138 kg/cm²) at 175 °C, and the T_g was 114 °C in this cured systems^[16]. A series of novel curing agents containing imide group were synthesized, which showed higher activation energy than aromatic amines and better thermal stability^[17]. However, one of the main disadvantages of the two methods was the imperfect miscibility between epoxy resin and imide compounds, bringing about poor processibility and limits on resin application. What's more, few reports were found on modifying the chemical structure of epoxy resin with imide group^[18]. The imide-modified epoxy resin cured with siloxane-containing dianhydride showed higher yield and glass transition temperature ($T_g=173$ °C)^[19]. And some epoxy resins modified with imide group and cured with 4,4'-diaminodiphenylsulfone, exhibited a better thermal stability and higher glass transition temperature^[20,21].

As a probable approach to advanced thermosetting resins, studies aimed to prepare a novel imide modified epoxy resin. In this paper, a novel imide named N-(4-hydroxyphenyl)terahydrophthalic anhydrideimide (HTAM) was synthesized and then epoxy-imide resins (EPIM) were prepared through the chemical method, using the novel imide, diglycidyl ether of bisphenol-A (E-53) and triphenylphosphine (TPP). EPIM was cured with 4,4'-diaminodiphenylmethane (DDM).

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XU Renxin(徐任信): Assoc. Prof.; Ph D; E-mail: xurenxin@whut.edu.cn

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The thermal stabilities and mechanical properties were enhanced by the introduction of imide group into the backbone of epoxy resin.

2 Experimental

2.1 Materials

Tetrahydrophthalic anhydride, 4-aminophenol, DDM, TPP and acetic acid were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. E-53 with an epoxide equivalent weight (EEW) of about 188 g/equiv from Yueyang Baling Huaxing Petrochemical Co., Ltd was used.

2.2 Synthesis of N-(4-hydroxyphenyl) tetrahydrophthalic anhydrideimide^[22]

66.95 g (0.44 mol) tetrahydrophthalic anhydride was dissolved in 400 mL acetic acid, then 43.65 g (0.4 mol) 4-aminophenol was added in this solution. The solution was stirred for 4 h at room temperature, and then at refluxing temperature for 6 h in an inert atmosphere. After cooling to room temperature, the solution was poured into a large amount of deionized water, the precipitate was collected by filtration and washed with 5% aqueous NaHCO₃ solution, and then washed with deionized water until the filtrate was neutral, and dried at 70 °C under vacuum to get a white powder product (HTAM).

2.3 Synthesis of epoxy-imide resin^[23]

EPIM was prepared by reacting E-53 and HTAM with various feeding ratios. E-53 and HTAM were charged into a 250 mL, 3-necked round-bottom flask, equipped with a heating oil bath, reflux condenser and inlet atmosphere. The amount of materials listed in Table 1. TPP (0.4 g) was added into the mixture as a reaction evaporator. The mixture was then heated to 130 °C for 4 h, and then cooled to room temperature. A faint yellow liquid product (EPIM) was obtained.

Table 1 Amount of raw materials and catalyst for the preparation of EPIM

No.	Feeding ratio		
	Liquid E-53/g	^a HTAM/mol	TPP/g
EPIM-1	100	0.02 (4.87 g)	0.4
EPIM-2	100	0.04 (9.73 g)	0.4
EPIM-3	100	0.06 (14.60 g)	0.4
EPIM-4	100	0.08 (19.46 g)	0.4

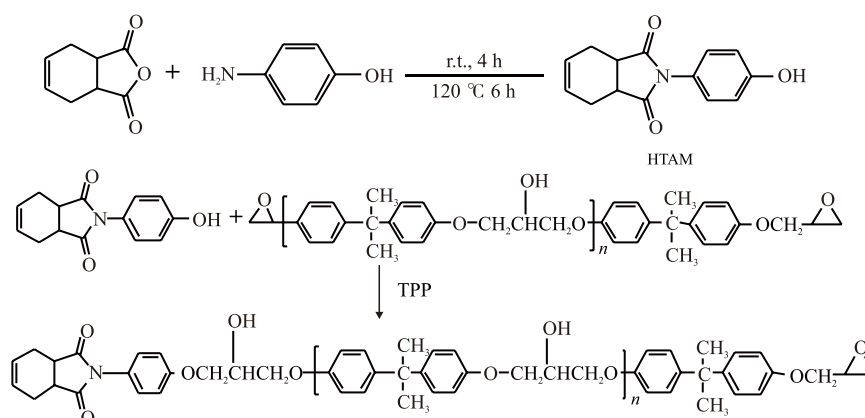
^a The molar amount of HTAM was added in 100 g E-53

2.4 Preparation of cured epoxy resins

The cured epoxy resins were obtained from curing EPIM with DDM as a curing agent. Certain amounts of the epoxy resins and the curing agent DDM were mixed in acetone at room temperature. After evaporating the solvent, the mixture was heated in an oven, and cured at 120 °C for 2 h, 140 °C for 2 h, and 160 °C for 4 h, continuously.

2.5 Measurements

Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet 6700 infrared spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets. ¹H NMR spectra were obtained on a Bruker AV400 NMR spectrometer using DMSO-d₆ as the solvent. Differential scanning calorimetry (DSC) thermograms were recorded with PerkinElmer DSC 4000 at a heating rate of 10 °C/min in nitrogen atmosphere. Dynamic mechanical thermal analysis (DMA) was carried out with a PerkinElmer Diamond instrument using 50 mm×10 mm×2 mm rectangular samples at a programmed heating rate of 10 °C/min from 30 to 280 °C at a frequency of 1 Hz in air atmosphere. Thermogravimetric analysis (TGA) was performed using NETZSCH STA449F3 at a heating rate of 10 °C/min in nitrogen atmosphere from 40 to 800 °C. Flexural properties was tested by three-point bending using MTS 810100KN according to ASTM D790-03.



Scheme 1 Preparation of HTAM and EPIM

3 Results and discussion

3.1 Synthesis of N-(4-hydroxyphenyl) tetrahydrophthalic anhydrideimide

HTAM was synthesized through the condensation reaction between the tetrahydrophthalic anhydride and 4-aminophenol (Scheme 1). Fig.1 shows the FT-IR spectrum of HTAM, in which the absorption around $3\ 334\ \text{cm}^{-1}$ attributed to the vibration of Ph-OH stretching can be found. The absorption peaks at $1\ 773\ \text{cm}^{-1}$ and $1\ 693\ \text{cm}^{-1}$ are on behalf of the asymmetrical and symmetrical stretching of C=O, respectively. The absorption for benzene ring can be detected at $1\ 517\ \text{cm}^{-1}$. ^1H NMR spectrum of the HTAM (Fig.2) also confirms the chemical structure of the synthesized product. The peaks are observed at 9.72 (1H, -OH), 6.85-6.97 (4H, Ar-H), 5.94 (2H, CH=CH), 3.25 (2H, -CH-), 2.27-2.47 (4H, -CH₂-). Fig.3 shows a melt point of $176\ ^\circ\text{C}$ observed with DSC.

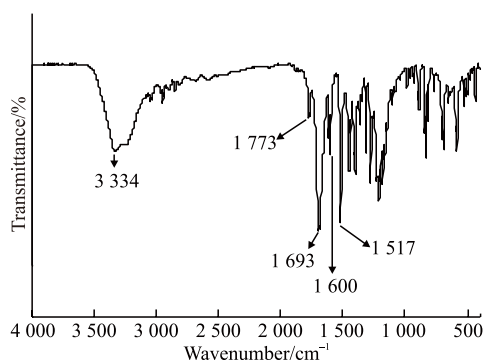


Fig.1 FT-IR spectrum of HTAM

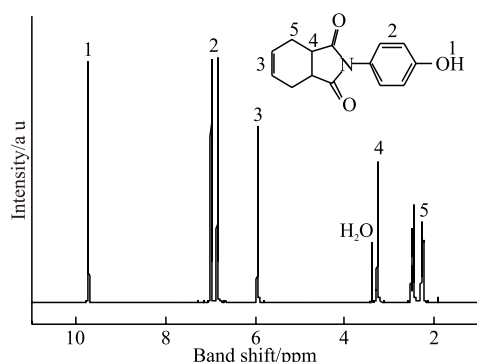


Fig.2 ^1H NMR spectra of the HTAM

3.2 Preparation of epoxy-imide resin

The preparation of EPIM was performed by reacting E-53 and HTAM via condensation reactions between the phenol group and the oxirane group (Scheme 1). The occurrence of the reaction between the group of phenol and oxirane was monitored by FT-IR (Fig.4). It can be observed that the intensity

of the absorption peak of the oxirane ring decreases at $913\ \text{cm}^{-1}$, which reveals the reaction between the oxirane ring and phenol group. The structure of the resulting resin compounds is also demonstrated with the absorption peaks at $1\ 385\ (\text{C-N})$ and $1\ 700, 1\ 778\ \text{cm}^{-1}\ (\text{C=O})$, which are the characteristic peaks of imide.

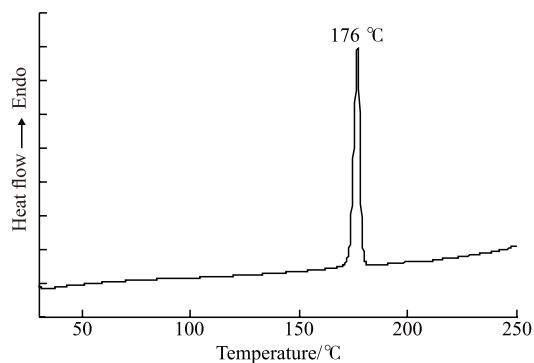


Fig.3 DSC curves of HTAM

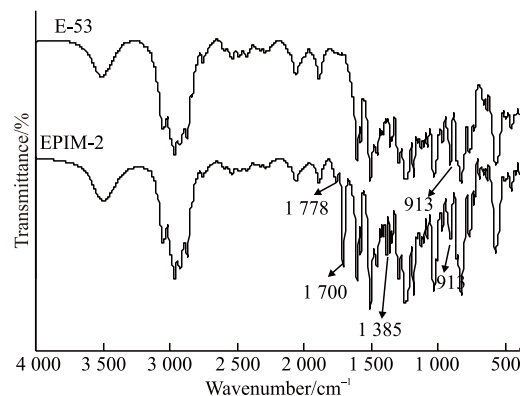


Fig.4 FT-IR spectra of epoxy resin before (E-53) and after (EPIM-2) reacting with HTAM

3.3 Thermal resistance properties of the cured resin

3.3.1 Dynamic mechanical thermal analyses of the cured resin

Dynamic mechanical observations are performed to analyze the $\tan\delta$ of the epoxy/DDM cured product. Fig.5 shows the DMA scans of the cured resin, and the peak temperature of the $\tan\delta$ curves is the glass transition temperature (T_g)^[24] of the polymer listed in Table 2. The T_g of the pure epoxy/DDM cured resin (E-53/DDM) is $160\ ^\circ\text{C}$. The sample is EPIM-2/DDM with the maximum value of glass transition temperature ($T_g=186\ ^\circ\text{C}$). With increasing content of imide group, the rigid segment increases the rotational barrier of the polymer chains, which leads to an increase of T_g for the polymer. With more than a certain amount, the decrease of crosslink density leads to the enhancement of the mobility of the polymer chain, which leads to a decrease of T_g of the cured materials.

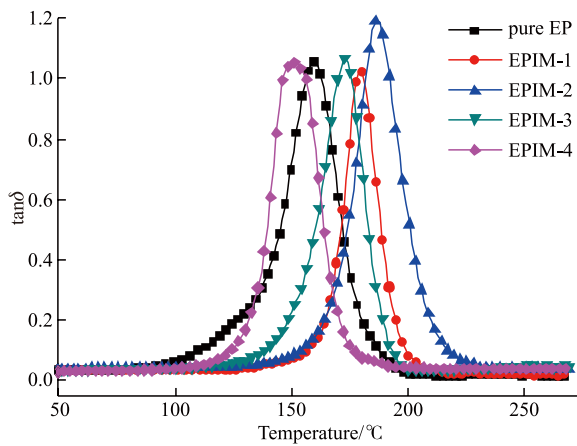


Fig.5 Loss factor curves of cured polymer composites varying with temperature

3.3.2 Thermogravimetric analyses of the cured resin

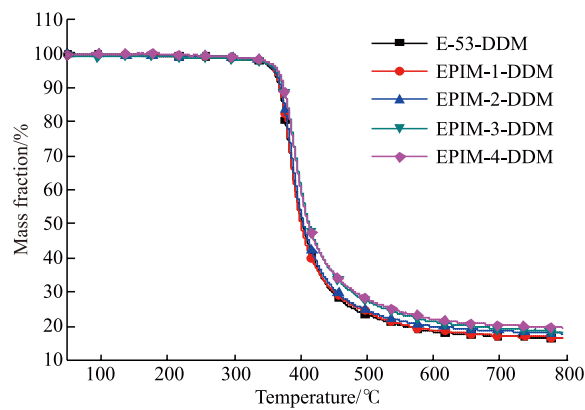


Fig.6 TGA curves of EPIM/DDM

Table 2 TGA analysis data and T_g of the cured epoxy resin.

Sample	T_g /°C	$T_{5\%}$ /°C	T_{max} /°C	Char yields at 800 °C /%
E-53/DDM	160	358	384	16.45
IMEP-1/DDM	179	359	389	16.67
IMEP-2/DDM	186	361	386	17.95
IMEP-3/DDM	172	363	395	18.30
IMEP-4/DDM	151	365	400	19.41

The thermal stability and degradation behaviors of the cured resin were investigated by TGA. Fig.6 and Fig.7 are the TGA and DTG curves of the epoxy resins/DDM cured resin in nitrogen atmosphere, respectively. Thermal decomposition characteristic data are presented in Table 2. From these data, it is clearly observed that the thermal stability of the cured resin is

improved slightly with the imide group in the chemical structure. When the molar amount of HTAM increases from 0 to 0.08 mol, the 5 % weight loss temperature ($T_{5\%}$) is raised from 358 to about 359-365 °C, and the char yields at 800 °C of the cured resin are also raised from 16.45 % to about 16.67%-19.41 %. With increasing imide group content, the effect of increasing imide group on the thermal stability of epoxy resin is thus demonstrated.

3.4 Flexural properties of the cured epoxy resin

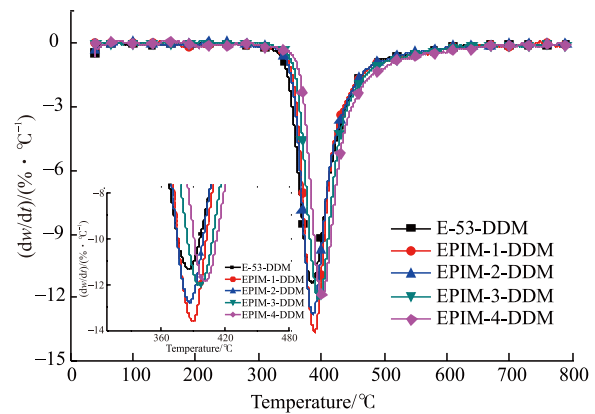


Fig.7 DTG curves of EPIM/DDM

The flexural properties were determined by the three point bending test, and the test results are shown in Table 3. Flexural strength of the cured resin is influenced by the chemical group, glass transition temperature, network structure and others. In the research system, the glass transition temperature and the network structure are changed by adding imide group into the structure of epoxy resin. As shown in Fig.7, with increasing content of imide group, the flexural strength firstly increases and then decreases and the flexural modulus shows a similar trend. When the content of imide group is less than 0.04 mol, the rigid segment leads to an increase of the flexural strength, and the decrease of crosslink network leads to a decrease of the flexural strength when the content is more than 0.04 mol.

4 Conclusions

The imide product of HTAM was synthesized, and the imide group was incorporated into epoxy

Table 3 Flexural properties data of the cured epoxy resin

Flexural properties	Sample				
	E-53- DDM	EPIM-1-DDM	EPIM-2-DDM	EPIM-3-DDM	EPIM-4- DDM
Flexural strength/MPa	79.4	90.8	95.7	89.6	85.2
Flexural modulus/GPa	2.6	2.9	3.0	2.8	2.7

resin by the reaction between the oxirane group and phenol group. The thermal and mechanical properties of epoxy-imide resin were investigated for different compositions of imide group. Epoxy-imide/DDM cured resin had high glass temperatures and desirable thermal properties. The cured resin achieved a high glass transition temperature of 186 °C with EPIM-2/DDM sample and it was higher than the T_g of the pure epoxy resin which is 160 °C. The yields at 800 °C raised from 16.45% to about 16.67 %-19.41% with increasing HTAM content from 0 to 0.08 mol. With measuring the cured resin's flexural strength and flexural modulus, the epoxy-imide resins also showed favorable mechanical properties. The flexural strength was up to 95.7 MPa at EPIM-2/DDM and decreased to 85.2 MPa at EPIM-4/DDM. Also, the flexural modulus increased to 3.0 GPa and then fell to 2.7 GPa. In conclusion, the resulted resins have outstanding properties so that it can be potentially applied in aerospace composite materials.

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