

The Application of Highly Soluble Amine-terminated Aromatic Polyimides with Pendent *Tert*-butyl Groups as a Tougher for Epoxy Resin^{*}

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Abstract Polyimides (PIs) with various molecular weights synthesized *via* the reaction of aromatic diamine monomer containing *tert*-butyl groups with aromatic dianhydride were highly soluble in common organic solvents and some epoxy resins at room temperature. These PIs can be incorporated in the absence of organic solvent into epoxy resin E51 with the loading below 2 wt% forming EP-PI composites. No phase separation is observed by SEM on cryogenically fractured surfaces of EP-PI composites. The PI can improve mechanical properties, especially impact strength. Adding 2 wt% PI-1.5W, the impact strength reaches to 55 kJ/m² with the increase in tensile and flexural strengths by 14% and 3%, respectively. SEM analyses for the fracture surface suggest that PI reduces the crosslink density, improves the plasticity of epoxy resin and changes the mode of fracture from fragile to ductile. Moreover, the glass transition temperature of EP-PI composites was found to increase to a significant extent.

Keywords: Polyimide; Epoxy resin; Solubility; Impact strength.

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INTRODUCTION

Epoxy resins have been widely used from 1940 because of their excellent mechanical, thermal and electrical properties, outstanding chemical and moisture resistance^[1]. These superior performance characteristics have gained a wide acceptance for epoxy resins as high-performance resins for advanced applications in the electronic, structural, protective coating and aerospace industries^[2]. Unfortunately, the usefulness of epoxy resins for many applications is often limited due to their inherent brittleness, poor flexibility, low fracture toughness and fracture resistance arising from their high crosslinked structure^[3].

Many studies have been conducted to remedy these shortcomings by incorporating modifiers into the epoxy, such as diluents^[4], liquid rubber^[5], organic or inorganic nanoparticles^[6] and so on. Major toughening mechanisms involve particle deboning/cavitation, inducing plastic void growth and localized shear banding of matrix. However, a remarkable improvement in fracture toughness was often accompanied by the decreases both in thermal stability and in the elastic modulus of material^[7]. Other desirable properties (*e.g.* thermal mechanical properties) may also be affected^[8]. For adhesive applications, the decreases in modulus and temperature

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resistance are usually of no significance. In matrices of fiber-composites, these effects can lead to unacceptable decreases in the properties.

In order to obtain an improvement in fracture toughness, high-performance engineering thermo-plastic polymers which have a relatively good thermal stability and low water uptake, such as poly(ether ether ketone) (PEEK)^[9], poly(ether sulfone) (PES)^[10], polyimide^[11] and polymethyl-methacrylate^[12], have been incorporated into epoxy resins. Alessi *et al.*^[13] prepared EP/PES composites with 20% commercial PES, and found that the fracture toughness increased from 0.6 to 1.5 MPa·m^{1/2}. Lin *et al.*^[14] prepared a side-chain phenol-functionalized PES which was served as a curing agent for epoxy. The obtained materials presented a low thermal expansion coefficient with T_g of 241 °C. However, due to high molecular weight and inherent properties of the thermoplastic, the blends are often immiscible in the uncured epoxy state, and high melting temperature or organic solvent was often required during the incorporation of modifiers into the epoxy.

Aromatic polyimides have been used for a variety of applications that require high thermal stability, excellent mechanical properties and high chemical resistance^[15, 16]. Han *et al.*^[17] employed fluorinated polyimide to investigate reaction-induced phase separation of epoxy/polyimide blends. Takeichi *et al.*^[18] synthesized a reactive polyimide containing hydroxyl functionalities and then added it into epoxy forming polyimide-epoxy composites. They found that the synthesized material presented high thermal stability and good mechanical properties. However, because of the immiscibility of polyimide in epoxy resin, organic solvents were needed to reach the incorporation of polyimide into epoxy matrix. In such situations, an incomplete removal of solvent from the blends will degrade the performance of the cured blend. The functional groups can improve the initial miscibility before curing without organic solvents. As reported, a miscible system was formed at the initial step for amine-terminated PEEK and epoxy^[19], which can be improved with polymers with reactive functional groups. Moreover, lowering molecular weight of additive polymers and introducing big groups into the molecular chain of polymers have been found to be favorable for initial miscibility^[20]. In this work, we used an industrially desirable method to synthesize amine-terminated aromatic polyimides (PI) with two pendent *tert*-butyl groups. The as-synthesized PIs with various molecular weights are highly soluble at low temperatures either in common organic solvents or some epoxy resins such as E51 and MY720. The effects of as-synthesized PIs on the structure, toughness strength, thermal stability and thermal mechanical properties of epoxy-PI composites were investigated.

EXPERIMENTAL

Materials

2-*Tert*-butylaniline (Changzhou Yonghe Fine Chemical Co., Ltd), polyform-aldehyde (Shanghai Civi Chemical Technology Co., Ltd.), benzene-1,2,4,5-tetra-carboxylic acid dehydrate (Shanghai Civi Chemical Technology Co., Ltd.), *N,N*-dimethyl-acetamide (Shanghai Lingfeng united Chemical Co Ltd China), acetic anhydride (Shanghai Lingfeng united Chemical Co., Ltd. China), montmorillonite (Zhejiang SanDing technology co., Ltd.), epoxy resin (E51) (Shanghai resin factory Co., Ltd), *m*-phenylenedi- amine (Aladdin reagent (Shanghai) Co., Ltd).

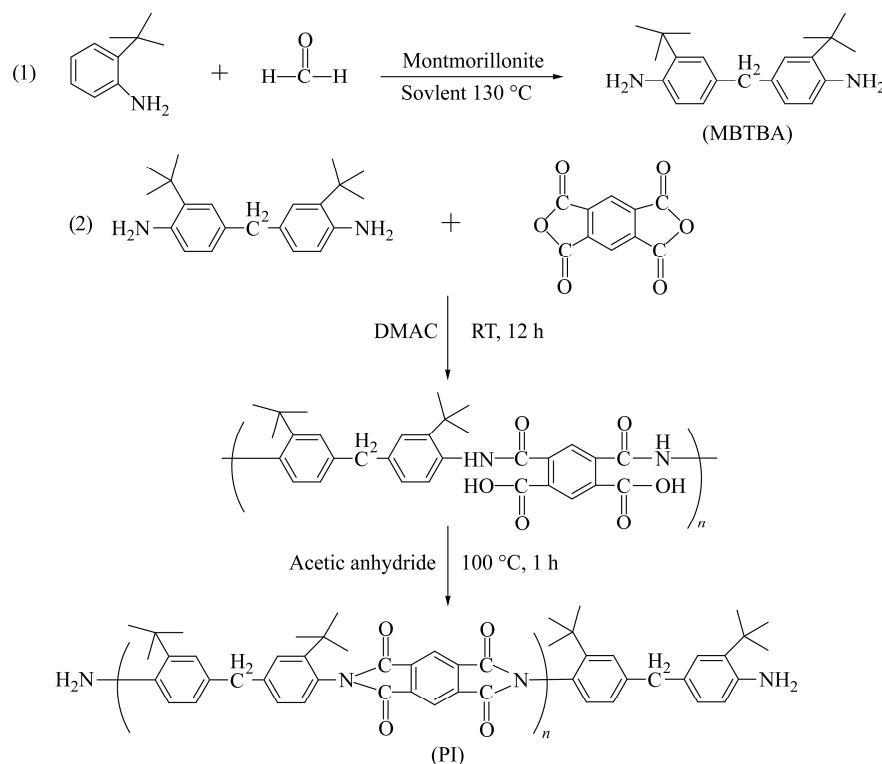
Preparation of 4,4'-Methylenebis (2-*tert*butylaniline) (MBTBA)

A round-bottom flask with a magnetic stirrer was charged with 0.894 g (0.006 mol) 2-*tert*-butyl-aniline, 0.075 g (0.0015 mol) polyformaldehyde, 0.18 g montmorillonite and an appropriate amount of ethyl acetate. The contents were heated to 130 °C for 12 h and then treated at room temperature through washing, vacuum filtering and recrystallization. Finally MBTBA was obtained. The structure of MBTBA was confirmed by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (IR).

Preparation of the Soluble PIs

0.4 mol (0.124 g) MBTBA was dissolved in 1.6 mL of *N,N*-dimethylacetamide in a round-bottomed flask with a magnetic stirrer. Benzene-1,2,4,5-tetracarboxylic (0.4 mol (0.08 g)) was added slowly over a period of 10 min, keeping the contents at room temperature for 12 h, and then acetic anhydride and sulfasalazine were added to the

mixture, after which the cyclodehydration reaction was heated to 100 °C and kept for 2 h. The reaction mixture was then cooled to room temperature and poured into ethanol under vigorous stirring. White fibrous precipitate formed was filtered and dried, and finally PI with molecular weight of 20043 g/mol was obtained. Changing the ratio of MBTBA to PMDA and the reaction time (Table S1), PIs with various molecular weights, such as 9660, 15069 and 58905 g/mol, were prepared. The whole process was described in Scheme 1. NMR and FTIR confirmed that the as-synthesized solid was PIs, and the molecular weights of PIs were measured by gel permeation chromatography (GPC).



Scheme 1 Synthesis of MBTBA and PIs

Preparation of Cured Resin Samples with Polyimide

Commercial epoxy resin and as-synthesized PIs were mixed together in various weight ratios in the absence of solvent. The mixture was stirred at 70 °C for 45 min (forming apparent fluid), and then added with *m*-phenylenediamine as external hardener in an epoxide/amino equivalent ratio of 1/1. The resulted new mixture was poured into a mold and placed in an oven for curing. The curing schedule was 80 °C for 2 h, followed by 150 °C for 165 min. The obtained EP-PI composites were noted as EP-PI-X-Y%, of which X is 1, 1.5 and 2, meaning molecular weights of 9660, 15069 and 20043 g/mol, respectively, and Y is 0.5, 1 and 2, meaning loading percentage.

Characterization

A Fourier transform infrared (FTIR) spectrometer (Nicolet Magna IR550, USA) was used to identify the structure of the monomer and polymers. Solid samples were coated on KBr disks. ¹H-NMR analysis was conducted on an Avance500 spectrometer at 400 MHz. CDCl₃ was used as solvent and tetramethylsilane as internal reference. Weight average (*M_w*) and number average (*M_n*) molecular weights were determined by gel permeation chromatography (GPC). Waters (Ultrastaygel) columns 1515 was used for GPC analysis with tetrahydrofuran (THF, 1 mL/min) as the eluate and polystyrene as reference standard. Elemental analysis was carried out on an Element-VARIOEL to determine the content of C, N and H in polyimide. Solubility was

determined qualitatively by placing 10 mg of polymer into 1 mL solvent at room temperature for 24 h. Thermo-gravimetric analysis (TGA) of the polyimide and EP/PI composites were performed under nitrogen atmosphere from room temperature to 800 °C at a heating rate of 20 K/min using a Perkin-Elmer Pyris Diamond TG/DTG thermo-gravimetric analyzer. Differential scanning calorimetry (DSC) thermo-grams were recorded with a Perkin-Elmer Pyris-7 (TA Instruments, USA) at a heating rate of 5, 10, 15 and 20 K/min under a nitrogen atmosphere. The samples sealed in hermetic cups were placed in the DSC cell and then dynamic scans were recorded. A dynamic mechanical thermal analyzer (DMA TA Q800) was used to study the storage modulus and damping factor of the cured polymers under an air atmosphere in the tensile mode, at a frequency of 1 Hz and a heating rate of 5 K/min from room temperature to 240 °C. The tensile and flexural strength were performed on an electronic universal testing machine (model CMT5205, Shenzhen Sun Think Science and Technology Development Co., LTD.) according to ASTM D638 and ASTM D790, with the crosshead spread of 5 and 2 mm/min, respectively. The presented results were the averages on five parallel experiments. The notched Izod impact strength was measured on an Izod impact strength tester at the temperature of (23 ± 1) °C, according to ASTM D256 with the sample dimensions of 80 mm $\times$ 10 mm $\times$ 4 mm; the presented results were the averages of five parallel experiments.

RESULTS AND DISCUSSION

Synthesis and Characterization of MBTBA and PIs

The structures of as-synthesized MBTBA and PIs were confirmed by ^1H -NMR spectroscopy. The complete assignment of proton signals is shown in Fig. 1. Figure 1(A) presents the ^1H -NMR spectrum of diamine monomer MBTBA in CDCl_3 . Signals in a δ range of 6.54–7.07 are ascribed to the protons of aromatic rings and a signal at $\delta = 3.68$, to the protons of $-\text{NH}_2$ group. Characteristic peaks of $-\text{CH}_3$ and $-\text{CH}_2$ appear at $\delta = 1.39$ and 3.78. On ^1H -NMR spectrum of PI-2W (Fig. 1B), $-\text{NH}_2$ signal shifts to $\delta = 3.98$, and almost completely disappears, ascribed to the protons of terminal amine group of PI, while a new peak appear at $\delta = 8.51$, attributed to the aromatic protons of dianhydride monomer. The peaks at $\delta = 6.97$, 7.16 and 7.51 are attributed to the aromatic protons of MBTBA grafted in PI-2W. Characteristic peaks of $-\text{CH}_3$ appear at $\delta = 1.32$, while the peak at $\delta = 4.14$ is assigned to the protons of $-\text{CH}_2$. FTIR absorption spectra of MBTBA and PI-2W are shown in Fig. 2. For MBTBA (Fig. 2a), the peaks appearing at 2968, 2909 and 2868 cm^{-1} are ascribed to C–H bonds;

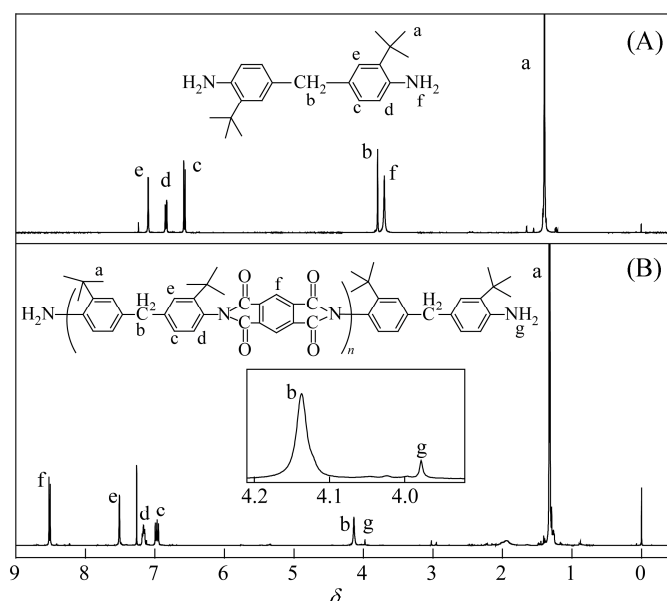


Fig. 1 NMR spectra of (A) MBTBA and (B) PI-2W; insert, the enlarging spectrum in a range of $\delta = 3.9$ –4.2

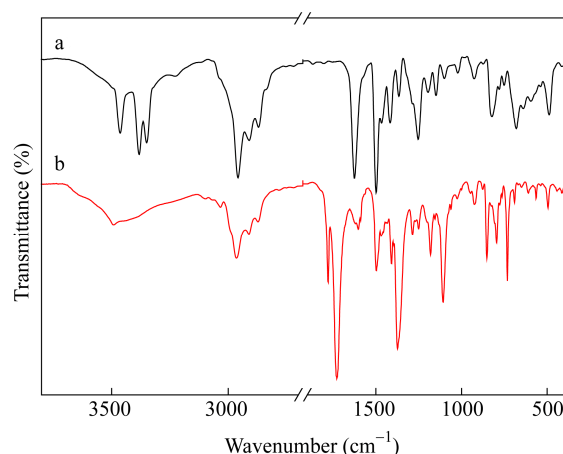


Fig. 2 FTIR spectra of (a) MBTBA and (b) PI-2W

a strong peak at 3463 cm^{-1} , to OH groups; two peaks at 3344 and 3381 cm^{-1} , to —N—H stretch from the —NH_2 group. Compared with the spectrum of MBTBA, it can be found that the peaks at 3344 and 3381 cm^{-1} disappear in the spectrum of PI-2W (Fig. 2b), implying that the terminal —NH_2 group of MBTBA reacts with PMDA to form PI. Additionally, some new peaks appear at 1778 cm^{-1} (C=O asymmetrical stretching), 1728 cm^{-1} (C=O symmetrical stretching), 1371 cm^{-1} (C—N—C stretching), 732 cm^{-1} (C—N bending vibration) and 1250 cm^{-1} (imide C—N), indicative of imide formation. PI with other molecular weights present similar $^1\text{H-NMR}$ and FTIR spectra to those of PI-2W. The molecular weight distribution of PIs was determined by GPC (Fig. S1). Changing reaction conditions (as shown in Experimental), PI samples with molecular weight of 9660, 15069, 20043 and 58905 g/mol, noted as PI-1W, PI-1.5W, PI-2W and PI-6W respectively, can be obtained with the corresponding molecular weight distribution of 1.74, 1.84, 1.70 and 1.72, respectively (Table S1). The results of elemental analyses also illustrate the formation of PIs (Table S2).

Solubility Test

The solubility characteristics of PIs with various molecular weights in a range of 1 W–6 W were investigated in common organic solvents (Table 1). All PIs show good solubility in nonpolar and polar solvents, except for ethanol and propanone. Meanwhile, it is interesting to find that PIs also present good solubility in some epoxy resins such as E51 and MY-720 at low temperatures. Francis *et al.*^[9, 21] reported that the fracture toughness of DGEBA epoxy resin was enhanced by blending with hydroxyl-terminated PEEK with either pendent *tert*-butyl (PEEKTOH) or methyl groups (PEEKMOH), and the soluble temperature of PEEK in epoxy resin was $180\text{ }^\circ\text{C}$ when using the pendent *tert*butyl, while $120\text{ }^\circ\text{C}$ for methyl groups. Bulky tertiary butyl at benzene ring of PI may

Table 1. Solubility of PIs in organic solvent and epoxy monomer

	DMF	DMAC	EAC	THF	CHCl_2	CHCl_3	Dioxane	NMP
PI-1W	+	+	+	+	+	+	+	+
PI-1.5W	+	+	+	+	+	+	+	+
PI-2W	+	+	+	+	+	+	+	+
PI-6W	+	+	+	+	+	+	+	+

	Cyclohexanone	Pyridine	Ethanol	Methanol	acetone	MY-720	E51
PI-1W	+	+	—	—	—	+	+
PI-1.5W	+	+	—	—	—	+	+
PI-2W	+	+	—	—	—	+	+
PI-6W	+	+	—	—	—	+	+

Note: “—” and “+” denote “insoluble” and “soluble”, respectively.

prevent close packing of polymer chains by increasing free volume of polymer and thus reduce effectively the interaction between the molecular chains of PI. As a result, the PI-solvent and PI-epoxy matrix interaction can be enhanced, leading to the improvement in solubility^[20]. This result suggests that during the preparation of EP/PI composites, no organic solvent is required, avoiding defective formation during cure and plasticization of the cured polymer resulting from incomplete removal of solvents. That is, the performance degradation caused by the introduction of solvent molecules will be avoided.

Curing Behavior Analysis

The effects of PIs on curing reaction were investigated by DSC. The peak temperatures of curing exotherm (T_p) are summarized in Table 2. For each composite, T_p shifts towards higher temperature with increasing heating rate (β). Incorporation of PIs can not substantially change T_p s, compared with neat EP. DSC is extensively used to characterize curing behavior of resin system in dynamic or isothermal modes. Activation energy of curing reaction can be estimated by Kissinger^[22] and Ozawa^[23]:

$$-\ln(\beta/T_p^2)/d(1/T_p) = E_{a1}/R \quad (\text{Kissinger equation})$$

$$\ln\beta = A' - 1.052E_{a2}/(RT_p) \quad (\text{Ozawa equation})$$

where β is the heating rate; T_p , the peak temperature of the cure exotherm; R , the ideal gas constant, equal to $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; E_{a1} and E_{a2} are activation energy, which can be calculated from the slope of $\ln(\beta/T_p^2)$ against $1/T_p$ plot and $\ln\beta$ against $1/T_p$ plot, respectively.

Curing reaction order can be determined by crane^[24]:

$$d(\ln\beta)/(1/T_p) = -(E_a/(nR) + 2T_p) \quad (\text{Crane equation})$$

where R is the ideal gas constant. T_p , β and n are peak temperature of curing exotherm, DSC heating rates and the curing reaction order, respectively. In this equation, $E_a/(nR) \gg 2T_p$, so the equation can be simplified and the curing reaction order could be obtained in the following:

$$d(\ln\beta)/(1/T_p) = -E_a/(nR)$$

where E_a is the activation energy calculated by Kissinger's and Ozawa's methods.

On the basis of the experimental results from the dynamic DSC study, the isoconversional plots are obtained by Kissinger and Ozawa modes (Fig. 3). E_a , A and n of neat EP and EP-PI composites are obtained using equations mentioned above. As shown in Table 2, E_{a1} and E_{a2} obtained using Kissinger and Ozawa methods for neat EP were 53.8 and 57.9 kJ/mol, respectively. Whereas E_{a1} and E_{a2} for EP-PI composites decrease significantly and the lowest values obtained for EP-PI-1.5W-0.5% composites is 45.3 and 49.8 kJ/mol. This phenomenon can be explained by the fact that the terminal amine group of PI increases the reactive points of system, and the crosslinking reaction occurs more easily. However, E_{a1} and E_{a2} increase with increase in the content of PIs to some extent, indicating that the addition of PIs increases system viscosity and decreases the effective collision between epoxy and curing agent.

Table 2. Curing kinetics parameters for EP and EP-PI composites derived from the multi-temperature scan methods

Samples	T_p				Kissinger method		Ozawa method		n
	5 (K/min)	10 (K/min)	15 (K/min)	20 (K/min)	E_{a1} (kJ/mol)	A_1 $\times 10^6$	E_{a2} (kJ/mol)	A_2 $\times 10^6$	
EP	409	426	436	444	53.8	1.44	57.9	4.84	0.95
EP-PI-1W-0.5%	409	428	437	444	51.6	1.01	55.7	2.46	0.95
EP-PI-1W-1%	407	423	434	441	52.8	1.15	56.8	3.93	0.95
EP-PI-1.5W-0.5%	407	428	439	447	45.3	0.10	49.8	0.21	0.95
EP-PI-1.5W-1%	406	426	436	443	49.4	1.00	53.7	0.75	0.95
EP-PI-1.5W-2%	409	427	435	444	52.5	0.97	56.7	1.73	0.95
EP-PI-2W-0.5%	409	428	438	443	51.7	0.73	55.8	1.36	0.95
EP-PI-2W-1%	409	428	436	444	53.3	1.34	57.4	2.07	0.95

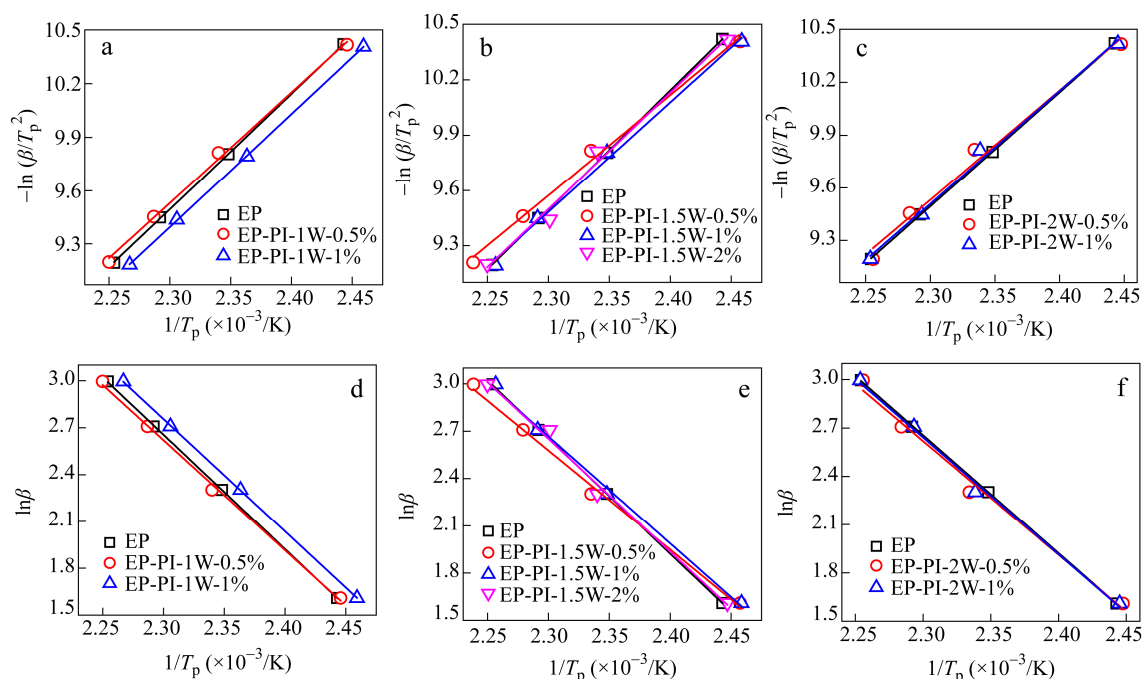


Fig. 3 Plots for determination of E and A by Kissinger (a, b and c) and Ozawa methods (d, e and f) in curing reactions

Dispersion of PI in Epoxy

EP-PI compositions with 0.5 wt%–2 wt% loadings of PIs of various molecular weights were prepared in the absence of solvent. No phase separation can be observed on the photos of the cryogenically fractured surfaces of EP-PI compositions by SEM (Fig. 4), and particularly, on the magnified photo of EP-PI-2W-2% composite (Fig. S2), indicating that all EP-PI compositions are composed probably of a continuous phase, due to excellent miscibility between PIs and epoxy (Table 1). PIs have a relatively equal surface free energy compared to the epoxy matrix and hence can readily permeate into epoxy or adhere well to epoxy. These results are really different from those reported in which phase-separation was observed often in the epoxy resins toughened with other thermoplastic polymers^[2].

Mechanical Properties

Mechanical tests were performed to evaluate the effect of PIs on the mechanical properties of E51 epoxy resin. Tensile strength, flexural strength and impact strength of neat epoxy resin were determined to be 134 MPa, 80 MPa and 18 kJ/m³ (Table 3), respectively, similar to the values reported previously^[25]. As shown in Fig. 5(a), adding PIs into EP within 0.5 wt%–1.0 wt%, the flexural strength of EP-PI compositions increases by 2%–9%, depending on the molecular weight of PIs. The highest effective promotion in flexural strength (increase by 10%) is obtained for EP-PI-2W-2% (Table 3). Further increase in the loading of PIs is not favorable for EP-PI containing 1W and 1.5W PI. The tensile strength of composites shows a similar trend and increases by 13%–23% within a loading range of 0.5 wt%–2.0 wt% (Fig. 5b), compared with that of neat epoxy. As reported, styrene/butadiene/methacrylate (SBM) triblock copolymer was used as a soft toughening agent, and the tensile strength decreased from 77.2 MPa for neat EP to 60 MPa for EP-SBM composites^[7]. Generally, polyimide materials possess excellent mechanical properties. Cheng *et al.* found that the tensile strength of bis-ADA-DCB was 121 MPa^[26]. Verker *et al.* reported that the tensile strength of PMDA-ODA presented a higher value (140 MPa)^[27]. The structure of PMDA-ODA is similar to PI in this work. Additionally, PIs are much more rigid than epoxy due to their much higher density of benzene ring^[28], and the storage modulus of PIs were 3.5–4.0 GPa^[29]. PI can contribute to improvement of tensile and flexural strengths of composites, although the incorporation of PI into the epoxy network can reduce crosslink density to some extent. Probably, in this context,

PI acts as an enhancing material, as carbon nanotubes do. In the case of rubber acting as additives, the tensile and flexural strengths of composites decrease with the reduction of crosslink density, due to rubber's very low rigidity.

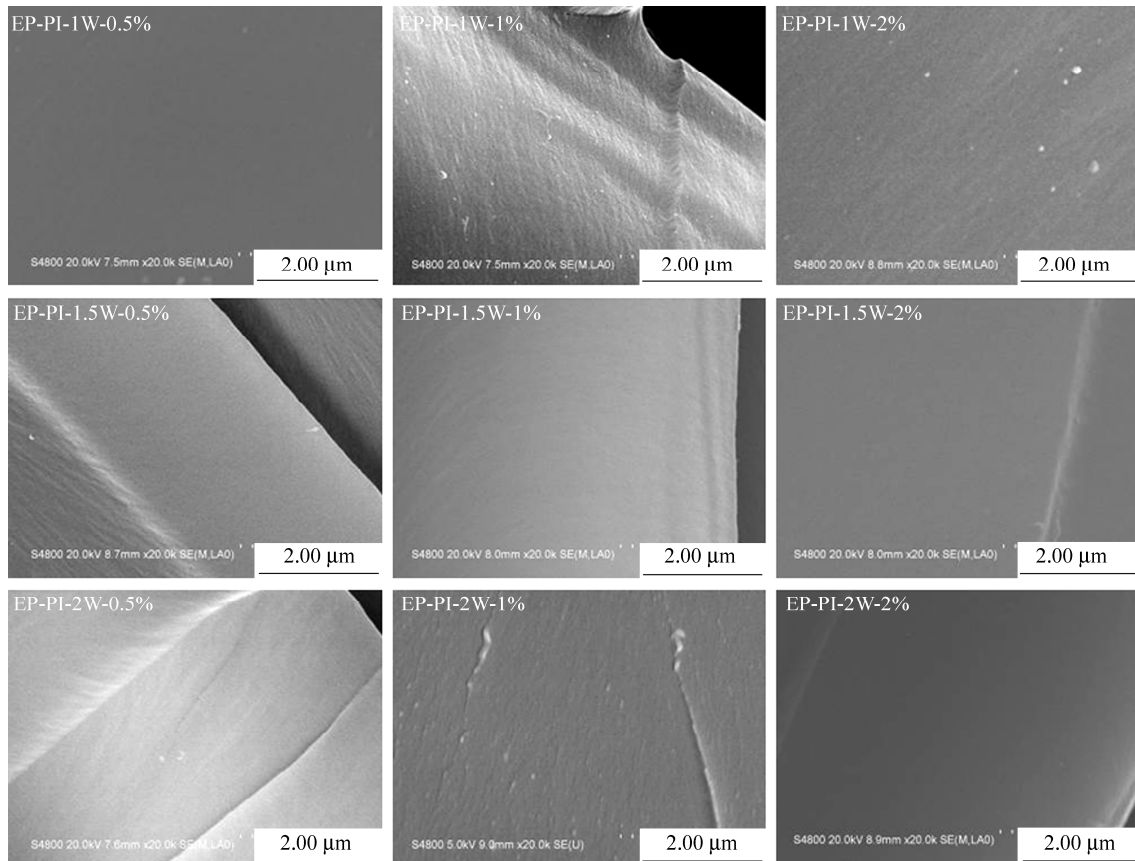


Fig. 4 The cryogenically fracture surfaces of EP-PI composites with various loadings of PIs

Table 3. Mechanical property data of EP-PI composites

Samples	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (MPa)	Elongation (%)	T_g (°C)	G' (GPa)	$\rho \times 10^{-3}$ (mol/cm ³)
EP	134.66 ± 2.22	79.91 ± 4.89	17.50 ± 4.75	13.25 ± 2.07	164	2.89	7.95
EP-PI-1W-0.5%	136.36 ± 3.23	93.73 ± 6.99	28.92 ± 4.84	16.86 ± 1.31	171	2.50	6.98
EP-PI-1W-1%	137.42 ± 3.72	95.08 ± 5.53	31.15 ± 5.05	17.52 ± 0.44	171	2.55	6.32
EP-PI-1W-2%	134.74 ± 4.34	90.42 ± 3.75	32.13 ± 5.33	17.23 ± 1.19	171	2.65	7.36
EP-PI-1.5W-0.5%	137.93 ± 3.73	93.31 ± 3.48	44.68 ± 5.22	19.31 ± 0.67	171	2.51	6.96
EP-PI-1.5W-1%	140.29 ± 2.40	95.36 ± 6.86	50.38 ± 3.69	18.38 ± 0.98	172	2.68	7.51
EP-PI-1.5W-2%	138.17 ± 1.45	91.45 ± 4.60	54.65 ± 3.76	18.22 ± 0.78	171	2.70	7.10
EP-PI-2W-0.5%	142.58 ± 3.16	98.65 ± 4.89	42.14 ± 4.24	17.12 ± 0.51	173	2.71	7.47
EP-PI-2W-1%	145.75 ± 2.83	96.24 ± 3.78	44.52 ± 4.09	16.59 ± 1.30	173	2.81	6.96
EP-PI-2W-2%	147.11 ± 3.17	94.39 ± 4.05	44.74 ± 3.72	16.17 ± 2.72	173	2.55	5.90

It is interesting to find that EP-PI composites show great improvement in toughness property. As shown in Fig. 5(c), the increase in toughness by PIs follows 1.5W > 2W (> 6W) > 1W. Main increase occurs at 0.5 wt% loading at which the impact strength is 29, 42 and 45 kJ/m² for EP-PI-1W, -2W and -1.5W, respectively. For EP-PI-1W and -2W, further increase in PI loading up to 2.0 wt% can almost not change significantly the impact strength (or 6W, Table S3), indicating that there seems a factor which limits the amount of PIs interpenetrating

or integrating network. However, the impact strength of EP-PI-1.5W composites presents a further increase trend, and the highest value reaches 55 kJ/m² (Table 3, the corresponding increase is 214%), implying that suitable chain length is important for PIs to interpenetrate network of epoxy matrix. Thus significant enhancement in toughness can be attributed to the strong interaction between PIs and epoxy resin, due to the reaction of terminal amine group of PI with the epoxy group, which makes PIs blend homogeneously with the epoxy matrix, and integrate into epoxy matrix network, which reduce crosslink density of epoxy matrix as a result of the dilution effect of the uncross-linked thermal plastic chains and increasing the ability of the materials to deform^[30]. Under strain, PIs are plastically stretched in the epoxy matrix, resulting in ductile deformation, crack path deflection, crack pinning and crack bridging, and hence the increased toughness of epoxy.

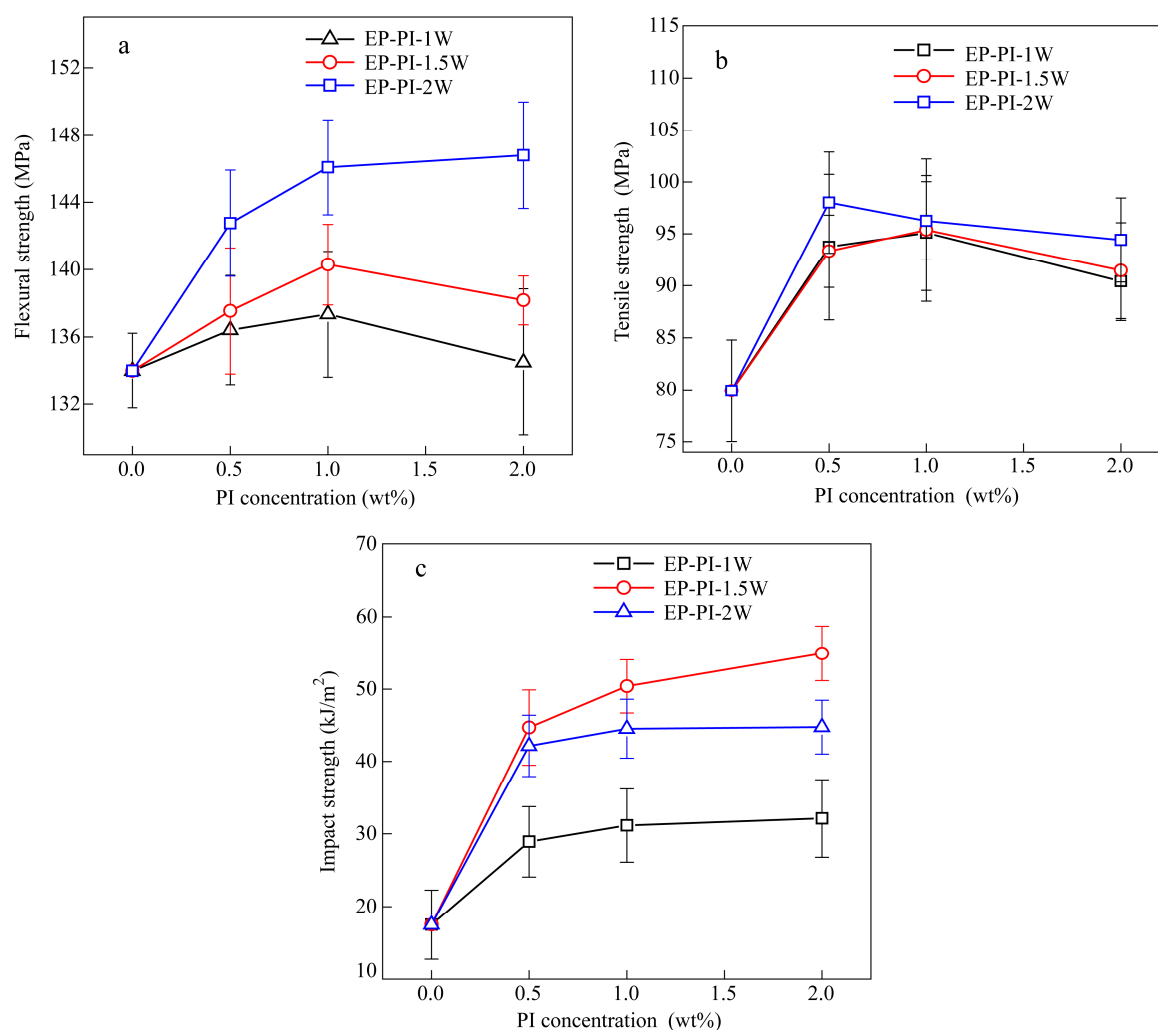


Fig. 5 Mechanical properties of EP-PI composites with various loadings of PIs

Fracture Surface Observation and Discussion

In order to further inform the fracture behaviors and toughening mechanisms, fracture surfaces of EP-PI composites were observed using SEM (Fig. 6). The fracture surface of neat epoxy is rather flat and smooth except for several river-like lines without any hints for significant plastic deformation (Fig. 6a), revealing its brittle nature of weak resistance to crack initiation and propagation. These observations agree well with a low measured toughness of the materials^[31]. The increases in river-like lines, crack branching and pinning, indicative of a ductile manner of fracture which might increase the fracture toughness^[32], were observed on the fractured

surfaces of EP-PI-1W-0.5% (Fig. 6b). With the increase in PI, EP-PIs composites exhibit rougher fracture surface (Figs. 6c and 6d). For EP-PI-1W-2% (Fig. 6d), the river-like lines turn into dendrite substructure, and thus much fracture energy is likely dissipated. By comparison, EP-PI-1.5W composites with 0.5 wt%, 1 wt% and 2 wt% loading (Figs. 6e, 6f and 6g) display the fracture surfaces of tough fracture features. For 0.5 wt% addition (Fig. 6e), the fractured surface exhibits rougher fracture surface with more convex square ribs which are kicked up under the impact. As the addition of PI increases, the fracture surfaces become rougher and diverted to different directions, just like the turbulent seas with heavy waves characterize the frigid waters, and large pieces of resin ruptures happen under the impact (Fig. 6g). These convex square ribs and waves are formed when the cracks move in different planes coalesce which are believed to contribute to the improved impact resistance^[33]. Figures 6(h)–6(j) show the fractured surfaces of epoxy blend with 0.5 wt%, 1 wt% and 2.0 wt% of PI-2W, respectively. It can clearly be seen that the fracture of EP-PI-2W-0.5% composites are rough and river marks form with hackles and ribbons on the surfaces, which are evidence for the plastic deformation of matrix, crack deflection and ductile nature of crack faces, characteristic of tougher fracture^[34]. In a word, compared with the fracture surface of neat epoxy, the fracture surfaces of EP-PI composites represent rougher fracture surface

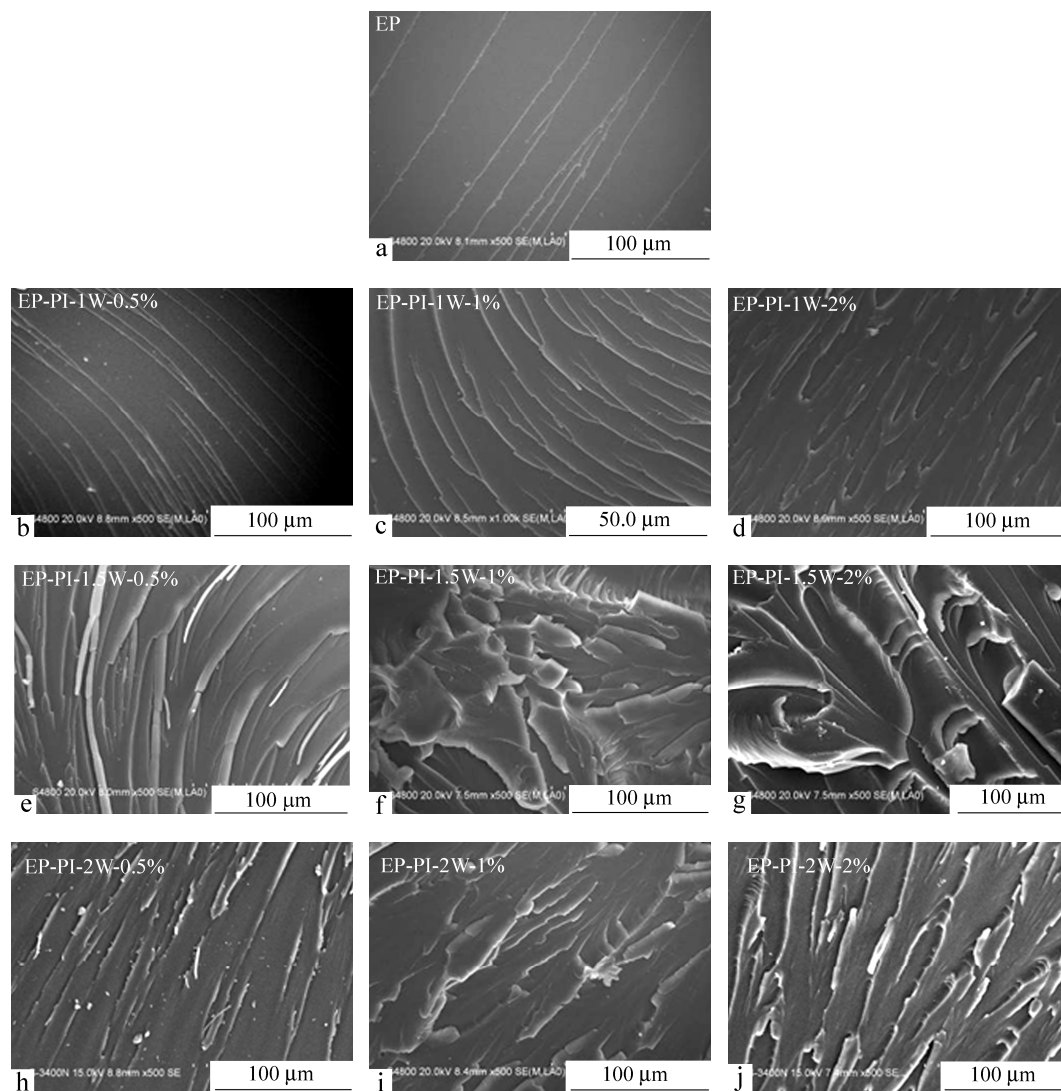


Fig. 6 SEM images of the fracture surface of EP and EP-PI composites with various loadings of PIs

with more river-like lines, crack branching, convex square ribs or heavy waves. These results unambiguously confirm that the addition of PI integrated into the network of epoxy matrix improves the plasticity of epoxy resin, prevents crack generation and propagation, makes the mode of fracture change from fragile to ductile and absorbs the excess energy during fracture of brittle materials, resulting in the increase in toughness.

Dynamic Mechanical Properties

The dynamic mechanical analyses were performed to obtain the temperature dependent properties of materials, such as storage modulus, loss modulus, and loss $\tan\delta$. These dynamic properties reflect the amount of energy stored in the composites as elastic energy and dissipated during mechanical strain, which are highly affected by the existence of additives^[35]. Figure 7 and Figure S3 show the storage modulus and loss $\tan\delta$ versus temperature for EP-PI composites during heating cycle. The addition of PIs with various molecular weights into epoxy resins results in slight reductions of the storage modulus at 40 °C of epoxy resin from 2.9 GPa for neat EP to 2.5–2.8 GPa for EP-PI composites with a loading of 0.5 wt%–2 wt% (Figs. 7a, 7c and 7e), dependent on the molecular weight. For example, the storage modulus was 2.7, 2.7 and 2.8 GPa for EP-PI-1W-2%, EP-PI-1.5W-2% and EP-PI-2W-1% composites, consistent with the tendency of T_g changes. The decrease in storage modulus could be related to the reduced crosslink density and increase in the flexibility of composites^[36]. If it is assumed that addition of PIs is decreasing the crosslink density, the value can be calculated using $\rho = G'/3RT$ ^[37], where, ρ is the crosslink density, R is the universal gas constant and T is the absolute temperature ($T_g + 40$ °C). Affine behavior is characterized by network chains and crosslinks that move proportionately to the macroscopic deformation of the system, and the calculated crosslink densities are presented in Table 3. It can be seen that the crosslink density of epoxy resin was 7.8 mol/ cm³, with addition of PIs 0.5 wt%–2 wt%, the crosslink density decreased to 5.9–7.5 mol/cm³, indicating that the linear molecular chains of PIs integrate into the network of epoxy matrix and dilute the crosslink density.

On $\tan\delta$ curves, only one relaxation peak is observed for EP-PI composites (Figs. 7b, 7d and 7f, curves of $\tan\delta$ at low temperature range for EP-PI and EP are shown in Fig. S3), further confirming that phase-separation does not occur, that is consistent with the results of the cryogenically fracture surfaces of EP-PI compositions. T_g of neat epoxy resin was 164 °C, while T_g of EP-PI composites rose up to a range of 171–173 °C (Table 3) dependent on the molecular weight of PIs which significantly affected T_g of polyimides, and in turn, T_g of EP-PI composites. A slight increase in the breadth of peaks is also observed, suggesting that the distribution of relaxation times is broader. Good compatibility between PI and epoxy matrix is confirmed through complete solution of PI in epoxy, and the reactions of terminal $-\text{NH}_2$ groups with epoxy promote the uniform penetration of PI into cross-linked network of epoxy matrix and the formation of interpenetrating polymer networks. The big tertiary butyl group in PI molecular chains restricts the mobility of epoxy molecular chains strongly interacted with PI^[38]. Moreover, EP-PI composites exhibit more elastic behavior than neat epoxy during tests, and the height of relaxation peaks decreases to 0.58 from 0.78 for neat epoxy resin.

Thermal Stability Analysis

Figure 8 shows TG curves of EP-PI composites. In nitrogen atmosphere, the decomposition of neat EP starts at about 364 °C (Table S4), 10% and 50% weight losses occur at 372 °C and 394 °C, and the residual is only 4.5% after thermal analysis to 600 °C. However, for EP-PI composites, the onset degradation temperature increases to about 379 °C, and the temperature of 10% and 50% weight loss increases to some extent. The residual at 600 °C is in a range of 13.3%–20.8%. It should be noted that the residual of EP-PI composites is much higher than the PI loadings of all samples under study. As known, PIs can be used as flame-retardant. Therefore, this phenomenon is related to the fact that the benzene-1,2,4,5- tetra-carboxylic acid dehydrate section of PIs can be decomposed into acid which can catalyze the carbonation of PI and EP around it, as shown in the action of acid in flame-retardant.

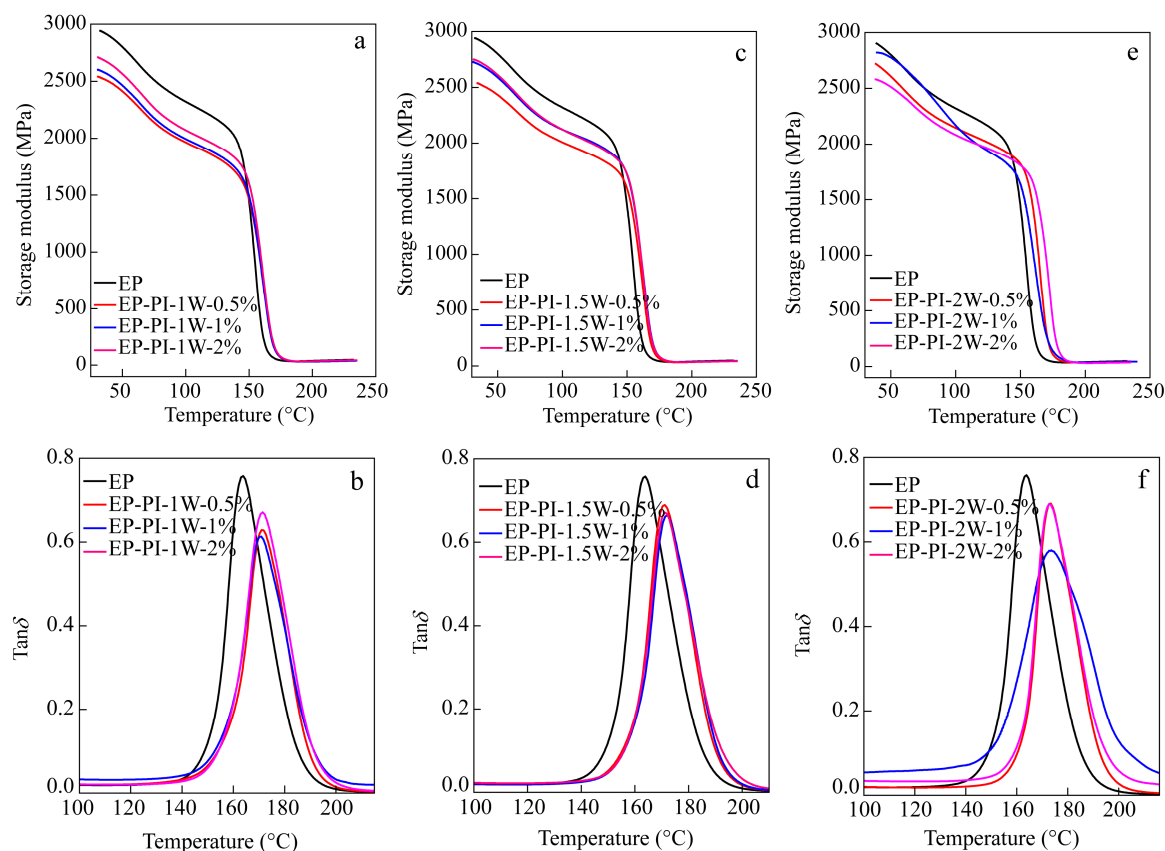


Fig. 7 Storage modulus and loss factor versus temperature for EP and EP-PI composites with various loadings of PIs

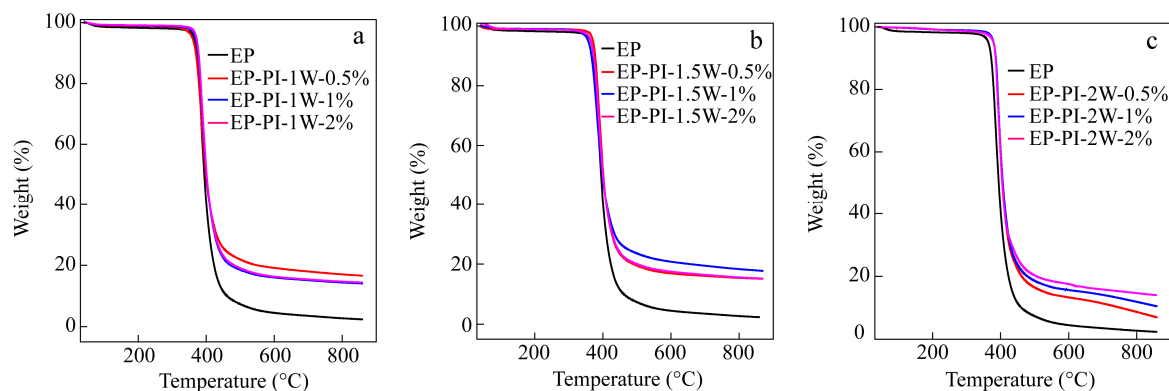


Fig. 8 TG curves of EP and EP-PI composites with various loadings of PIs

CONCLUSIONS

PIs with high solubility at low temperatures were synthesized through the reaction between aromatic diamine monomer containing *tert*-butyl groups and aromatic dianhydride, and characterized by NMR, FTIR and GPC. The experimental results provide an evidence for the successful synthesis of PI with the molecular weight of 9660, 15069, 20043 and 58905 g/mol and the corresponding molecular weight distribution of 1.74, 1.84, 1.70 and 1.72, respectively. Solubility test shows that PIs under study have good solubility in most nonpolar and polar solvents, except ethanol and propanone, and in some epoxy resins such as E51 and MY-720 at low temperatures.

EP-PI composites were processed readily without any organic solvent. SEM revealed that no phase

separation occurs. A significant increase of mechanical properties of EP-PI composites, including the tensile, flexural and impact strengths, was observed, especially for impact strength (65%–214%). The highest improvement was obtained for PI-1.5W-2% with impact strength of 55 kJ/m². DMA measurements showed that the storage modulus of EP-PI composites slightly decreased, but T_g increases by 7–9 K. It can be observed on SEM photos that the EP-PI composites show rough fracture surface with more river-like lines, crack branching and convex square ribs or heavy waves, which suggests that the addition of PIs results in ductile deformation, promotes crack path deflection, crack pinning and crack bridging, improves the plasticity of epoxy resin, and changes fragile fracture mode of EP into ductile one.

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