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Soluble Polyimide-reinforced TGDDM and DGEBA Epoxy Composites

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Electronic Supplementary Information

Abstract Polyimide (PI) synthesized from aromatic diamine and dianhydrides via two-step poly-condensation method was highly soluble in TGDDM (MY-720) and DGEBA (E-51) at desirable temperature. TGDDM-PI (M-PI) and DGEBA-PI (E-PI) composites within 0.5%–3% PI loading could be prepared without organic solvent. On the cryogenically fractured surfaces of M-PI and E-PI composites, no obvious heterogeneous phase was observed by SEM. The mechanical properties were promoted significantly by PI, especially for impact strength. Adding 2% PI-2W into MY-720 and E-51 composites, the impact strength increased to 21 and 51 kJ/m², the tensile strength increased by 62% and 19%, and the flexural strength by 18% and 13%, respectively, with slight increases in tensile modulus. These results were related to the promotion in plasticity of composites and changes in fragile→ductile fracture mode. Moreover, T_g and thermal stability of M-PI and E-PI were increased effectively.

Keywords Polyimide; TGDDM and DGEBA epoxy resin; Impact strength; Toughness

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INTRODUCTION

Epoxy resins are widely used because of their outstanding mechanical, thermal, and electrical properties, as well as excellent chemical stability and resistance to moisture,^[1,2] which are really acceptable in many fields.^[3] However, the applications of epoxy resins are often limited due to their inherent brittleness, poor flexibility, low fracture toughness and fracture resistance resulting from high crosslinked structure,^[4] especially for tetra-functional epoxy systems.^[5] There have been many studies to overcome these drawbacks through adding modifiers into the epoxy matrix, including rubber,^[6] nanoparticles,^[7] diluents,^[8] and so on. Major toughening pathways were related to particle deboning/cavitation, such as plastic void growth and localized shear banding of matrix. However, a significant promotion of fracture toughness was followed probably by the degradation in thermal stability, and Young's modulus.^[9] And thermal mechanical properties such as storage modulus and glass transition temperature were often influenced to a significant extent.^[10] In the adhesive fields, the degradation in modulus and thermal resistance was undesirable. For the fiber-composites, the degradation caused unacceptable decreases in various properties. Recently, it was shown that the fracture

toughness of epoxy resin was improved by engineering thermoplastic polymers with a good combination of toughness, stiffness, and thermal-oxidative stability, such as polyethersulfone (PES),^[11] polyurethane,^[12] poly(ether imides),^[13] poly(propylene oxide) (PPO),^[14] polycarbonate,^[15] and polymethyl-methacrylate,^[16] etc. It often occurred that the formed homogeneous blends of toughening thermoplastic polymers and epoxy resin in the uncured state underwent phase separation during curing.^[17] As a result, toughness was increased effectively without significant decreases in mechanical and thermal properties. With the modification by hydroxyl terminated poly(ether ether ketone), the fracture toughness of EP/PES composites was promoted to 3.24 MPa·m^{1/2}.^[18] Using phenolic hydroxyl poly(ether sulfone) containing a side-chain as curing agent, the synthesized composites showed low thermal expansion coefficients and high T_g (275 °C). Moreover, the cured epoxy films were bendable and transparent.^[19] However, commercially available engineering thermoplastic polymers could be immiscible with uncured epoxy, and thus some undesirable conditions such as high temperature or organic solvent were used to incorporate modifiers into the epoxy.^[20]

As known, polyimide is an excellent engineering thermoplastic in the aspects of mechanical properties, chemical stability, electroluminescence, and so on.^[21] Que *et al.* synthesized several trifluoromethyl-containing polyimides and then incorporated them into E-51.^[22] The obtained composites showed high glass transition temperature and good fracture toughness. However, an organic solvent was necessary for in-

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incorporating the polyimide into epoxy matrix due to poor miscibility. Incomplete removal of organic solvents would degrade the performance of cured mixtures. In this work, the polyimide (PI) with various molecular weights, which is highly soluble in tetraglycidyl diaminodiphenyl methane (MY-720) and diglycidyl ether of bisphenol-A (E-51) at desirable temperature, was synthesized successfully by the reaction of aromatic diamine monomer containing *tert*-butyl groups with aromatic dianhydride. MY-720 and E-51 composites incorporated with various PI contents (M-PI and E-PI) were prepared without organic solvent, and investigated in terms of mechanical and thermal mechanical properties.

EXPERIMENTAL

Materials

MY-720 (Huntsman Chemical Trading (Shanghai) Co., Ltd.), E-51 (Shanghai Huayi Resin Co., Ltd), 4,4'-diamino-diphenyl sulfone (DDS, Sinopharm chemical reagent Co., Ltd.), 2-*tert*-butylaniline (Shanghai Naicheng Biotechnology Co., Ltd.), pyromellitic anhydride (PMDA) (J&K Scientific Co., Ltd.), paraformaldehyde (Shanghai Macklin Biochemical Technology Co., Ltd.), acetic anhydride (Aladdin Biochemical Technology Co., Ltd.), *N,N*-dimethylacetamide (DMAc, Shanghai Zhonghe Chemical Technology Co., Ltd.), montmorillonite (Fenghong New Material Co., Ltd.) were used, and 4,4'-methylenebis(2-*tert*-butylaniline) (MBTBA) was synthesized according to the procedure previously reported.^[23]

Preparation of Polyimide (PI)

MBTBA (7.5 mmol, 2.325 g) was dissolved 15 mL of DMAc in a three-necked flask with a magnetic stirrer. PMDA was added slowly during 10 min, placing the contents at 25 °C for 7 h, and then pyridine and acetic anhydride were added to the above-mentioned mixture (Fig. 1). In N₂ atmosphere, the mixture was heated slowly to 105 °C and maintained for 2.5 h for cyclodehydration. After the reaction, the mixture was cooled to room temperature, then washed by ethanol to obtain white fibrous precipitate, and finally dried in a vacuum oven at 40 °C for 24 h. The obtained material was PI. Changing various polymerization conditions (molar ratio, temperature, solid content etc.), the molecular weight of as-synthesized PI was 1.14×10^4 , 1.49×10^4 , 2.04×10^4 , and 2.76×10^4 g/mol (Fig. S1 in the electronic supplementary information, ESI). Moreover, the characterizations of PI with ¹H-NMR spectroscopy and FTIR are shown in Figs. S2 and S3 (in ESI).

Preparation of DDS-cured Resin Containing PI

As-synthesized PI was dissolved directly at various resin/PI weight ratios under stirring into MY-720 and E-51 at 130 and 70 °C, respectively, to obtain apparent blends. Then these blends added with DDS (external hardener) at epoxide/amino equivalent ratio were poured into the pre-heated molds, which were moved into ovens. The curing program for MY-720 was 150 °C for 3 h, 170 °C for 3 h, 200 °C for 2 h, and 240 °C for 2 h. The one for E-51 was 120 °C for 1 h, followed by 140 °C for 2 h, 160 °C for 4 h, 180 °C for 3 h, and 200 °C for 2 h. The as-synthesized composites are denoted as M/E-PI-x-y, of which M means MY-720, and E, E-51; x is 1W, 1.5W, and 2W, corresponding to molecular weights of 1.14×10^4 , 1.49×10^4 , and 2.04×10^4 g/mol, respectively; y is 0.5, 1, 2, and 3, PI loading. The synthesis pathways of M-PI and E-PI are shown in Fig. 2.

Characterization

The determination of weight-average (M_w) and number-average (M_n) molecular weights of as-synthesized PI, the analyses by TG-DTG, DMA, and SEM for thermal stability, thermal mechanical properties, and cryogenically fractured surfaces, and the determination of mechanical properties for composites were described in the previous work.^[23] The solubility of PI in MY-720 and E-51 was analyzed at room temperature with ultraviolet and visible spectrophotometer (UV752N, China) at 670 and 560 nm, respectively.

RESULTS AND DISCUSSION

Thermal Stability of PI

The thermal stability of PI with 1W–2.8W was evaluated by TG tests (Fig. S4 in ESI). Almost similar results of weight loss versus temperature are ascribed probably to a small difference in the molecular structure. The temperature corresponding to 5% weight loss is 485 °C, and the one to 27% decomposition is about 533 °C, due to the removal of *t*-butyl and carbonyl groups, which almost matches the theoretical weight ratio of *t*-butyl and carbonyl group to PI (Fig. S4 in ESI). Finally, the residue at 900 °C is 54%, indicating that PI possesses good char-forming ability. In fact, the section of benzene-1,2,4,5-tetra-carboxylic acid dehydrate can be degraded to carboxylic acid, which catalyzes the carbonation of PI.^[24]

PI Solubility in Epoxy Resin and Dispersion in Epoxy Composites

PI solubility in MY-720 and E-51 at room temperature was

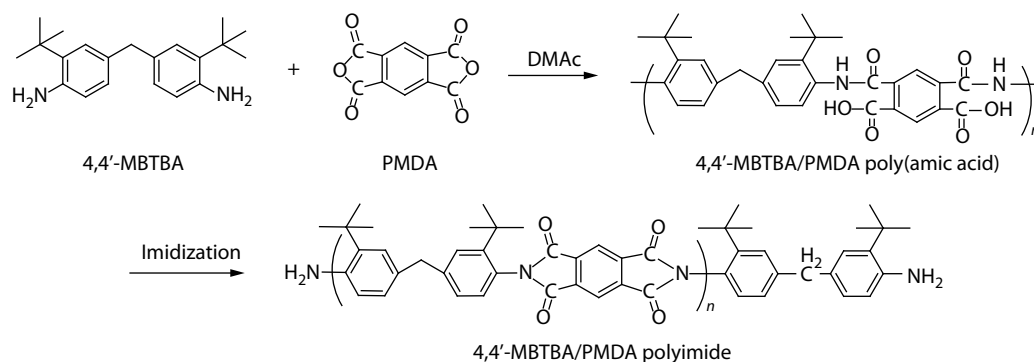


Fig. 1 The synthesis of PI.

investigated with UV-Vis spectrophotometry (Fig. 3). The absorbance of MY-720 containing PI at 670 nm is directly proportional to PI loading in a range of 0%–3%, with the slope of 0.2210, 0.2709, 0.2806, and 0.3121 for 1W, 1.5W, 2.0W, and 2.5W, respectively (Fig. 3a). The blends of PI and E-51 can absorb radiation at 560 nm, whose intensity linearly increases with PI loading in a range of 0%–15% (Fig. 3b). The slope for 1W, 1.5W, 2.0W, and 2.5W is 0.0505, 0.0622, 0.0820, and 0.1231, respectively. This phenomenon indicates that the absorbance of PI-containing MY-720 and E-51 blends follows Lambert-Beer law, that is, the blends of MY-720 or E-51 epoxy and PI are homogeneous, suggesting that defective formation during curing and plasticization of the cured polymer resulting from incomplete removal of solvents can be avoided. In another experiment, the solubility of as-synthesized PI in MY-720 or E-51

was further investigated using optical microscopy. The homogeneity of blends containing MY-720 or E-51 and 2% PI-2.0W is observed at 100 μm scale (Fig. S5 in ESI). On the other hand, all the PI samples show good solubility in nonpolar and polar solvents, except for ethanol and acetone (Table S1 in ESI).

The cryogenically fractured surfaces of M-PI and E-PI composites were observed at 1 μm scale by SEM. As shown in Fig. 4, E-PI surface presents homogenous phase, while for M-PI, there appear a small number of fine particles dispersed evenly in MY-720 matrix. In fact, before reaction, MY-720 and PI are miscible (Fig. 3a). The phase homogeneity of composites probably is dependent on the difference between two product structures. On the photos of FE-SEM at 100 nm scale, E-PI-1.5W-2 presents a homogeneous morphology, and M-PI-1.5W-2 presents almost similar morphology to neat MY-720

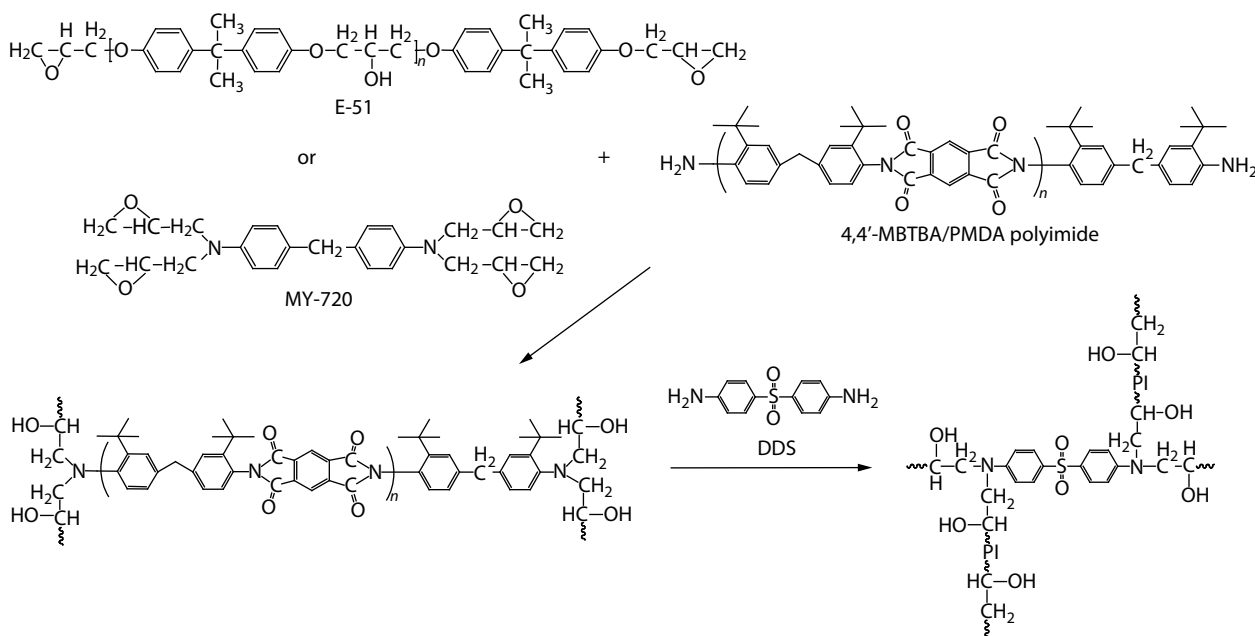


Fig. 2 The syntheses of M-PI and E-PI composites.

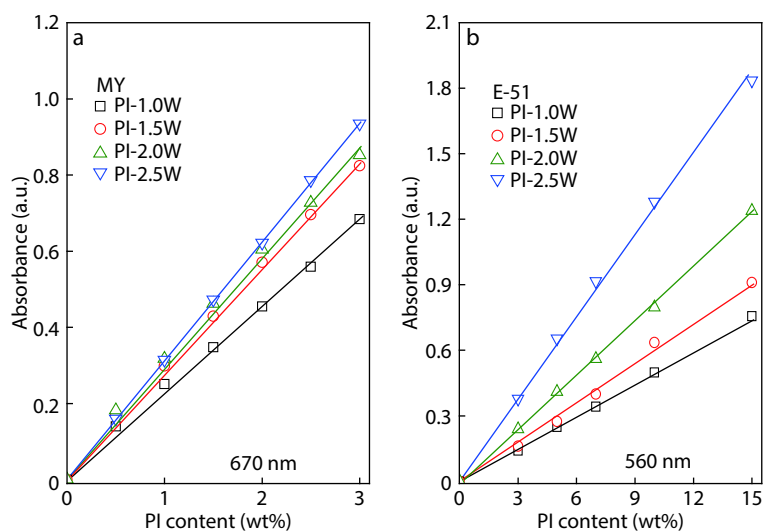


Fig. 3 UV-Vis absorbance at room temperature versus PI contents in MY-720 (a) and E-51 (b).

(Fig. 5). As reported, there often exists phase separation in the epoxy resins toughened with thermoplastic polymers.^[25,26] As generally considered, the miscibility between thermoplastic polymers and epoxy resins can be affected by the difference in surface free energy and the dimension of interaction. The terminal $-\text{NH}_2$ groups of PI play a significant role in the formation of covalent compounds (Fig. 2). PI addition into MY-720 may affect curing reaction, resulting in two or more structures (Fig. 2). Here, bulky tertiary butyl group at aromatic ring of PI can retard chain close-packing by enlarging free volume

of polymers, and the steric hindrance effect prevents molecular chains from getting close to each other, resulting in a significant decrease in the interaction between PI molecular chains. Thus, the miscibility increases due to high interaction between PI and epoxy matrix. Generally, the introduction of fluorine could promote PI solubility in organic solvents or PI miscibility with epoxy matrix.^[27] There is almost no literature about good miscibility between PI and tetra-functional epoxy systems. Thus, high solubility and miscibility of as-synthesized PI in epoxy resin are desirable for industrial applications.

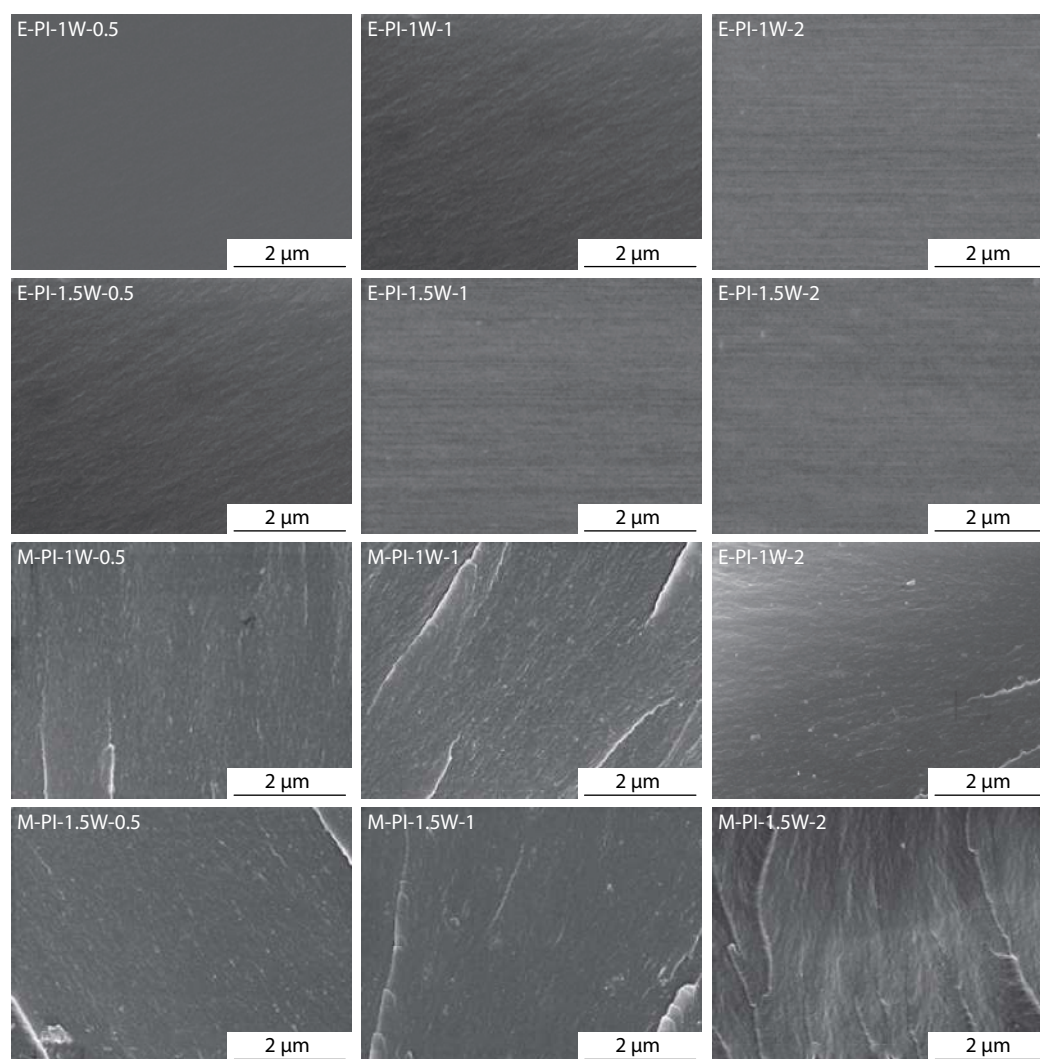


Fig. 4 SEM images of cryogenically fractured surfaces of E-PI and M-PI composites with various loadings of PI.

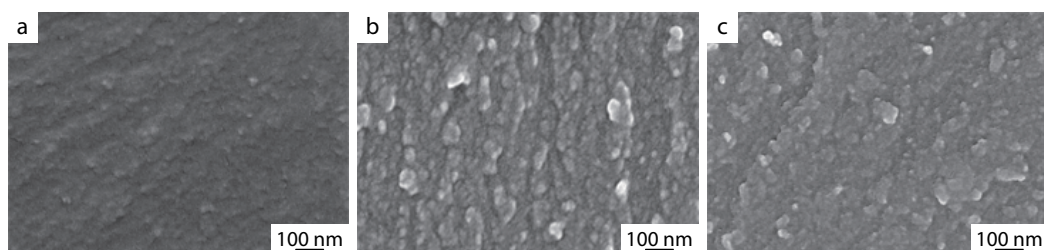


Fig. 5 FE-SEM images of cryogenically fractured surfaces of E-PI-1.5W-2 (a), M-PI-1.5W-2 (b) and MY-720 (c).

Mechanical Properties

Mechanical properties for M-PI and E-PI are shown in Fig. 6. The tensile strengths of MY-720 and E-51 are determined to be 39 ± 3.51 and 63 ± 1.91 MPa, respectively (Table 1), as reported previously.^[28,29] With the incorporation of PI into MY-720, the tensile strength (Fig. 6a) is $42 \pm 3.25 \sim 47 \pm 2.75$ MPa for PI-1W, $56 \pm 4.05 \sim 61 \pm 5.75$ MPa for PI-1.5W, and $57 \pm 3.12 \sim 63 \pm 2.24$ MPa for PI-2W (Table 1). Correspondingly, the tensile modulus increases with PI loading (Fig. 6b). M-PI-2W-2 presents the largest tensile strength (63 ± 2.24 MPa, increasing by 62%) and tensile modulus (3444 ± 59 MPa, increasing by 26%). This phenomenon can be attributed to a great increase in rigid chain structure through increasing density of aromatic rings. In this context, PI acts enhancing materials, as carbon nanotubes do.^[30] In the case of rubber acting as additives, the tensile strength of composites decreases with the reduction of crosslink density due to the low rigidity of rubber.^[31] Similarly, PI promotes the flexural strength of MY-720 to a significant extent (Fig. 6c). For

PI-1W, 1.5W, and 2W, the increase in flexural strength reaches 10.2%, 10.2%, and 17.7% at 2% loading, respectively. It is interesting to find that the impact strength of M-PI composites increases greatly from 8 ± 2.45 kJ/m² for MY-720 to $10 \pm 0.37 \sim 17 \pm 2.03$ kJ/m² for PI-1W, $11 \pm 3.68 \sim 20 \pm 2.62$ kJ/m² for PI-1.5W, and $12 \pm 2.77 \sim 21 \pm 1.85$ kJ/m² for PI-2W (Table 1). M-PI-2W-2 shows 163% increase compared with MY-720. Increasing in PI loading to 3%, the mechanical properties cannot be further promoted but show a decrease tendency, which is probably due to the effect of high PI loading on crosslink density to a significant extent. For the same reason, the mechanical properties of E-PI composites present a similar tendency (Figs. 6a–6d). E-PI containing 1.0% PI presents the highest tensile strength and modulus, while the composite containing 2.0% PI exhibits the highest flexural, strength and impact strength.

In our previous work, almost the same result was obtained on E-PI prepared using *m*-phenylenediamine as curing agent.^[23] In another experiment, 1% PI-1.5W modified naph-

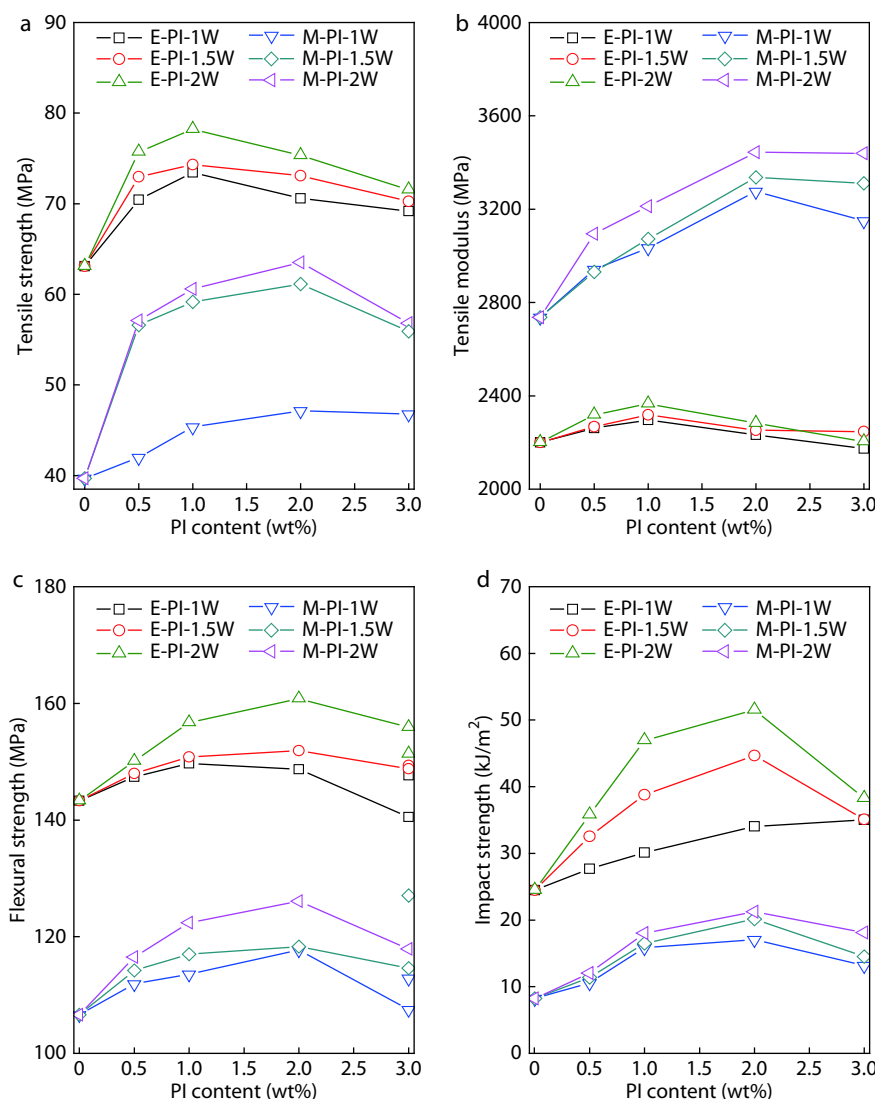


Fig. 6 Mechanical properties of M-PI and E-PI composites: tensile strength (a), tensile modulus (b), flexural strength (c), impact strength (d).

Table 1 Mechanical properties data of M-PI and E-PI composites.

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Impact strength (kJ/m ²)
MY	39 ± 3.51	2737 ± 43	107 ± 3.45	8 ± 2.45
M-PI-1W-0.5	42 ± 3.25	2941 ± 33	112 ± 2.11	10 ± 0.37
M-PI-1W-1	45 ± 2.18	3034 ± 65	114 ± 3.06	15 ± 1.94
M-PI-1W-2	47 ± 2.75	3276 ± 51	118 ± 2.55	17 ± 2.03
M-PI-1W-3	47 ± 4.26	3150 ± 43	108 ± 4.11	13 ± 2.96
M-PI-1.5W-0.5	56 ± 4.05	2931 ± 40	114 ± 4.21	11 ± 3.68
M-PI-1.5W-1	59 ± 5.48	3072 ± 58	117 ± 3.24	16 ± 3.78
M-PI-1.5W-2	61 ± 5.75	3336 ± 42	118 ± 2.90	20 ± 2.62
M-PI-1.5W-3	56 ± 6.22	3311 ± 62	115 ± 5.98	15 ± 1.56
M-PI-2W-0.5	57 ± 3.12	3094 ± 86	116 ± 3.10	12 ± 2.77
M-PI-2W-1	60 ± 2.08	3212 ± 45	122 ± 4.01	18 ± 3.02
M-PI-2W-2	63 ± 2.24	3444 ± 59	126 ± 3.77	21 ± 1.85
M-PI-2W-3	57 ± 3.45	3439 ± 41	118 ± 2.37	18 ± 2.33
E-51	63 ± 1.91	2200 ± 65	143 ± 3.24	24 ± 3.48
E-PI-1W-0.5	70 ± 3.99	2262 ± 97	147 ± 2.33	27 ± 4.82
E-PI-1W-1	73 ± 4.53	2296 ± 57	150 ± 4.22	29 ± 5.25
E-PI-1W-2	70 ± 4.21	2233 ± 46	149 ± 2.14	32 ± 3.21
E-PI-1W-3	69 ± 5.20	2174 ± 55	141 ± 3.36	35 ± 2.88
E-PI-1.5W-0.5	72 ± 2.13	2268 ± 69	148 ± 5.32	32 ± 5.21
E-PI-1.5W-1	74 ± 3.21	2319 ± 56	151 ± 4.36	38 ± 2.50
E-PI-1.5W-2	73 ± 4.32	2252 ± 67	152 ± 1.34	44 ± 5.20
E-PI-1.5W-3	70 ± 3.56	2247 ± 23	149 ± 3.71	35 ± 4.36
E-PI-2W-0.5	75 ± 2.29	2318 ± 96	150 ± 3.23	33 ± 3.45
E-PI-2W-1	78 ± 3.53	2366 ± 88	157 ± 1.56	39 ± 4.03
E-PI-2W-2	75 ± 4.74	2282 ± 52	161 ± 2.32	51 ± 3.54
E-PI-2W-3	72 ± 2.36	2204 ± 61	156 ± 2.28	38 ± 4.19

thallene epoxy resin presents the increase in impact strength from 6.4 kJ/m² to 9.7 kJ/m² (Fig. S6 in ESI). Obviously, the PI promotion results from the effective interaction between epoxy resin and PI, leading to homogeneous blending of PI and epoxy matrix, where PI is dispersed within the matrix network, decreasing the crosslink density of the matrix through the dilution effect of the uncrosslinked thermal plastic chains and enhancing the ability for the matrix to deform.^[32] Under strain, PI chains are plastically stretched in the epoxy matrix, which can produce ductile deformation, promote crack path deflection, pinning and bridging, and thus increase the impact strength of matrix.^[33] It should be pointed out that a bulky *t*-butyl group of PI interspersed within the matrix network retards the approaching of chain of epoxy, increases free volume of the network, and thus decreases the crosslink density. PI with the high molecular weight has longer chain, and thus may effectively modify inherent brittleness of the matrix network.

Fracture Surface

The toughening mechanisms need to be understood through the observation of fracture behaviors. The fracture surfaces of M-PI and E-PI after impact determination were observed by SEM (Fig. 7). MY-720 presents smooth and flat fracture surface without any hints for plastic deformations ahead the crack tip during fracture propagation, indicating its brittle nature of weak resistance to crack initiation and propagation (Fig. 7a1).^[34] On the fracture surface of M-PI-1W-0.5, the river-like lines, crack branching and pinning are observed. Increasing PI loading, the fracture surfaces of M-PI become rougher, on which bigger convex square ribs protruded (Figs. 7b1–7d1) and diverted to different directions under the impact, suggesting that a significant fracture energy is dissipated.^[35] Figs. 7(e1)–7(g1)

show the fracture surfaces of MY-720 epoxy loaded with various PI-1.5W loadings. There appear tougher fracture features on the surface of M-PI-1.5W. At 1% loading, the river-like lines are transformed into dendrite substructures and convex square ribs, and finally into some large pieces of resin ruptures during the impact. Further increasing PI-1.5W loading to 2%, these structures are further promoted. These phenomena are characteristics of plastic deformation of matrix, crack deflection, and ductile nature of crack faces. For E-PI composites (Figs. 7b2–7g2), the toughness of E-PI-1.5W is larger than that of E-PI-1W, and a similar change trend in surface structure to M-PI composites is observed. Combining the data of impact strength, these changes are believed to be the contributions to the improved impact resistance,^[36] confirming that PI can integrate into the network of epoxy matrix, improve the plasticity of epoxy resin, promote crack pinning and crack bridging, prevent crack generation and propagation, make the mode of fracture change from fragile to ductile, and absorb the excess energy during fracture of brittle materials, resulting in the increase in impact strength.

Dynamic Mechanical Properties

The dynamic mechanical analyses for M-PI and E-PI are performed during heating cycle to obtain the temperature dependent properties of materials, such as storage modulus and loss $\tan\delta$ (Fig. 8). For M-PI-1W-0.5, the storage modulus at 50 °C decreases slightly to 3.45 GPa from 3.73 GPa for MY-720 (Table 2), due to less regularity caused by PI incorporation. The increase in PI-1W to 1% and 2% seems favorable for storage modulus, probably due to the rigid compensation of PI-1W to some extent. With the increase in molecular weight of PI to 1.5×10^4 , the storage modulus can be compensated effectively probably through tangle of long PI chains, whose inherent

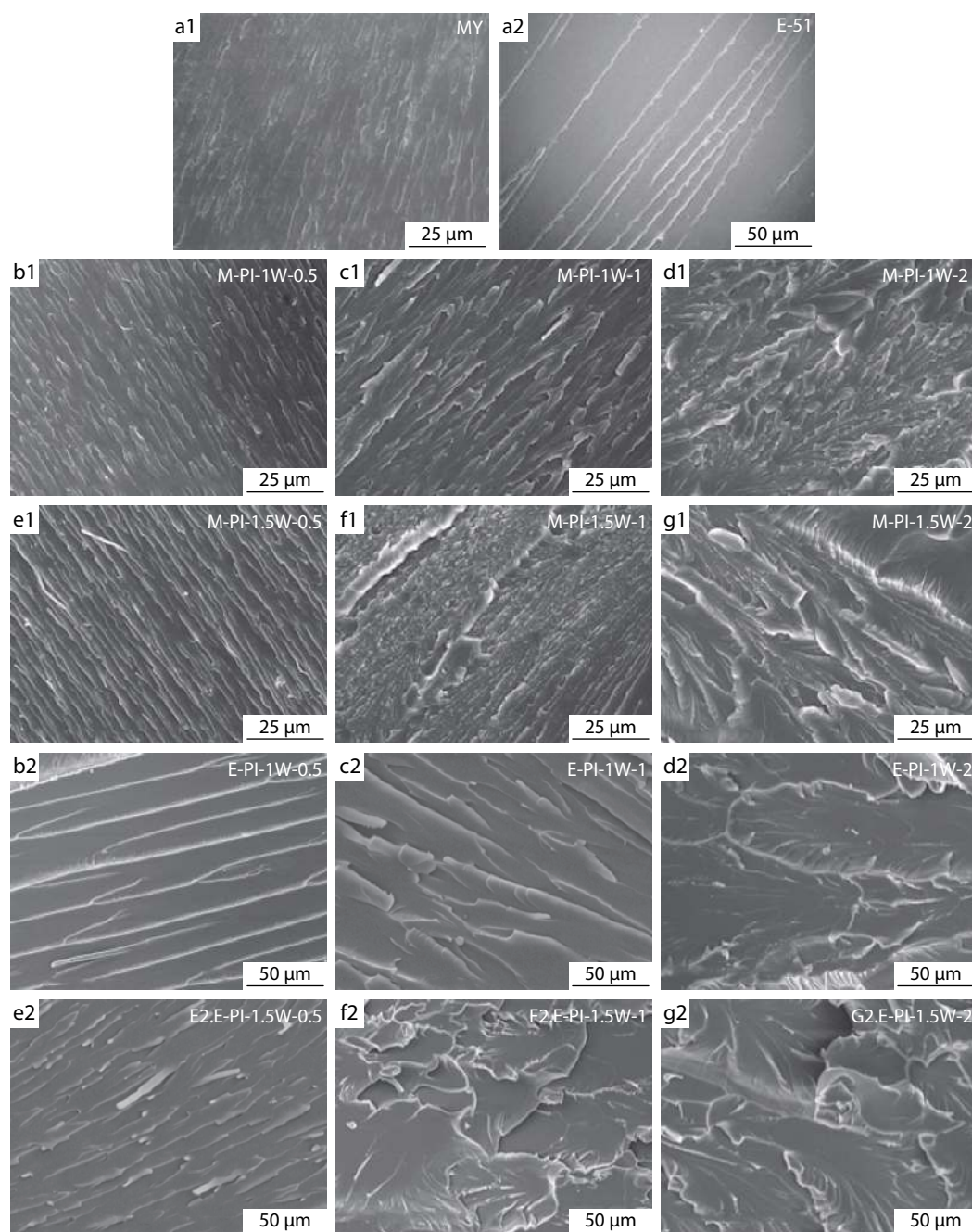


Fig. 7 SEM images of fracture surfaces of M-PI and E-PI composites: neat MY (a1) and E-51 (a2), M-PI-1W (b1–d1), M-PI-1.5W (e1–g1), E-PI-1W (b2–d2), E-PI-1.5W (e2–g2).

higher thermal mechanical properties can improve the elastic properties of the epoxy system. M-PI-1.5W composites present almost similar storage modulus to MY-720. It is interesting to find that the storage modulus for E-PI increases with the increase in either molecular weight or PI loading, which really can be ascribed to much higher rigidity of PI than E-51 matrix. E-PI-1.5W-2 presents the highest value of 3.1 GPa.

Fig. 8 and Table 2 show the loss $\tan\delta$ versus temperature for M-PI and E-PI composites during heating cycle. There is only one relaxation peak on the $\tan\delta$ curves, which confirms the homogeneity of M-PI and E-PI without a significant phase

separation, consistent with the results from the SEM photos of cryogenically fractured surfaces of M-PI and E-PI. The isolated particles observed on the cryogenically fractured surfaces of M-PI composites (Fig. 4) should exist as very small part, which cannot affect the continuity of phase. For all M-PI composites, T_g increases to a small extent, although T_g of PI with 1W–8W molecular weight is 210–217 °C,^[37] lower than that of MY-720. Here, the decrease in crosslink density may be replenished by the formation of both covalent bonds between PI and MY-720. For E-PI-1W-0.5 and E-PI-1W-2, T_g is 208 and 203 °C, respectively. For E-PI-1.5W, T_g is 200–203 °C,

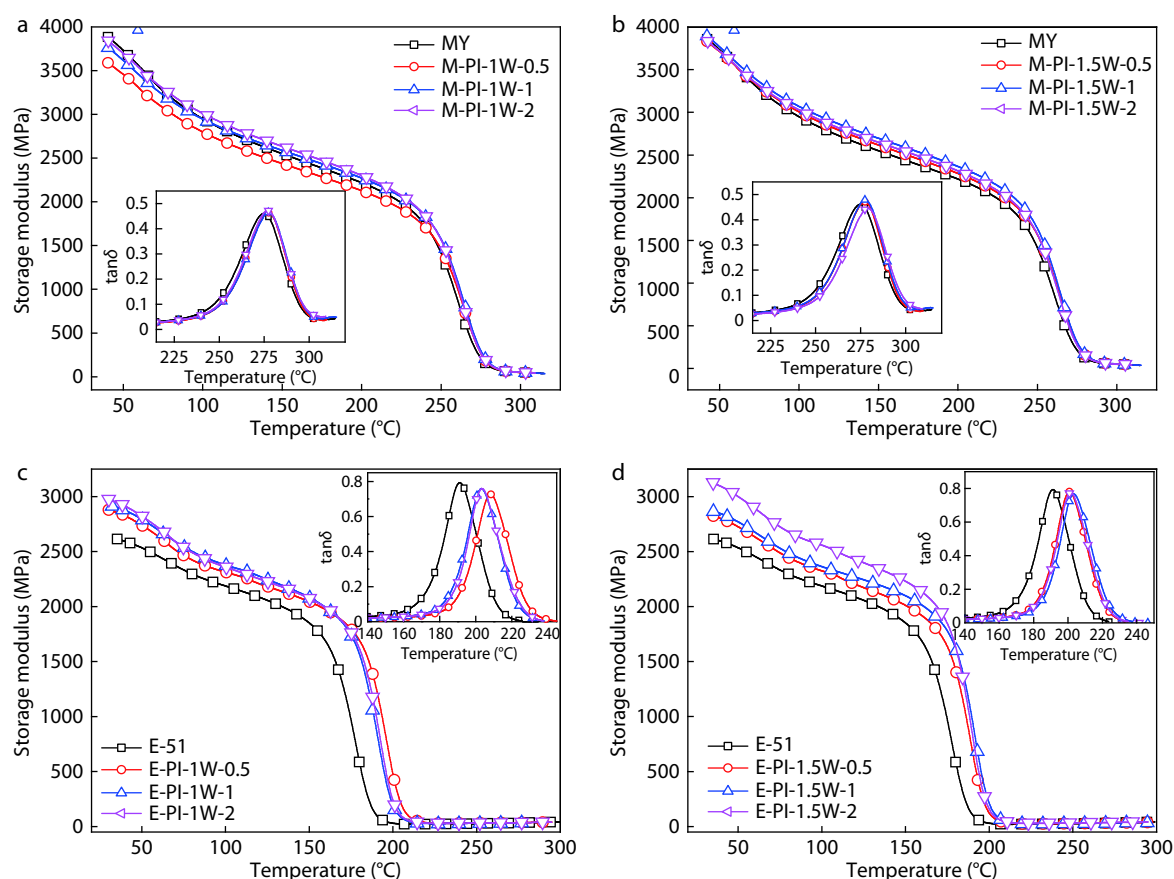


Fig. 8 Storage modulus and $\tan\delta$ versus temperature for M-PI and E-PI composites: M-PI-1W (a), M-PI-1.5W (b), E-PI-1W (c), E-PI-1.5W (d).

Table 2 TG and DMA data of M-PI and E-PI composites.

Sample	Temperature of weight loss (°C)			Residual weight at 700 °C (wt%)	T_g (°C)	G' (GPa)
	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$			
MY	359	381	411	23.1	275	3.73
M-PI-1W-0.5	361	383	415	24.3	277	3.45
M-PI-1W-1	360	382	411	25.7	277	3.62
M-PI-1W-2	359	382	415	26.7	276	3.70
M-PI-1.5W-0.5	365	378	412	26.8	277	3.72
M-PI-1.5W-1	368	379	413	26.9	278	3.78
M-PI-1.5W-2	370	381	414	27.1	279	3.72
E-51	381	396	428	13.5	191	2.50
E-PI-1W-0.5	374	396	428	14.2	208	2.73
E-PI-1W-1	378	396	428	14.8	203	2.79
E-PI-1W-2	382	398	429	16.5	203	2.82
E-PI-1.5W-0.5	384	398	427	15.1	200	2.72
E-PI-1.5W-1	384	399	428	15.6	203	2.77
E-PI-1.5W-2	375	395	435	17.5	201	3.10

suggesting that further increase in PI molecular weight is not favorable for crosslink. Additionally, it is found that the addition of 2% PI-1.5W into naphthalene epoxy resin increases T_g to 143.3 °C from 122.3 °C (Fig. S7 in ESI). Thus, the highly promoted impact strength of naphthalene epoxy resin should be related to a strong interaction between PI and epoxy matrix (Fig. S6 in ESI). The reactions of terminal $-\text{NH}_2$ groups of PI with epoxy matrix can promote the uniform penetration of PI into cross-linked network, and the restriction of a bulky *t*-butyl group in PI to the mobility of epoxy molecular chains. In

many cases of engineering thermoplastic as a toughener for epoxy resin, the impact strength was significantly improved at the cost of modulus and temperature resistance.^[10,20]

Thermal Stability

TG analyses for M-PI and E-PI composites are shown in Fig. 9. In N_2 atmosphere, PI addition increases the residual weight at 700 °C gradually from 23% to 27% for M-PI and from 13% to 17% for E-PI with the increase in both PI loading and molecular weight (Table 2). This phenomenon is related to the fact that

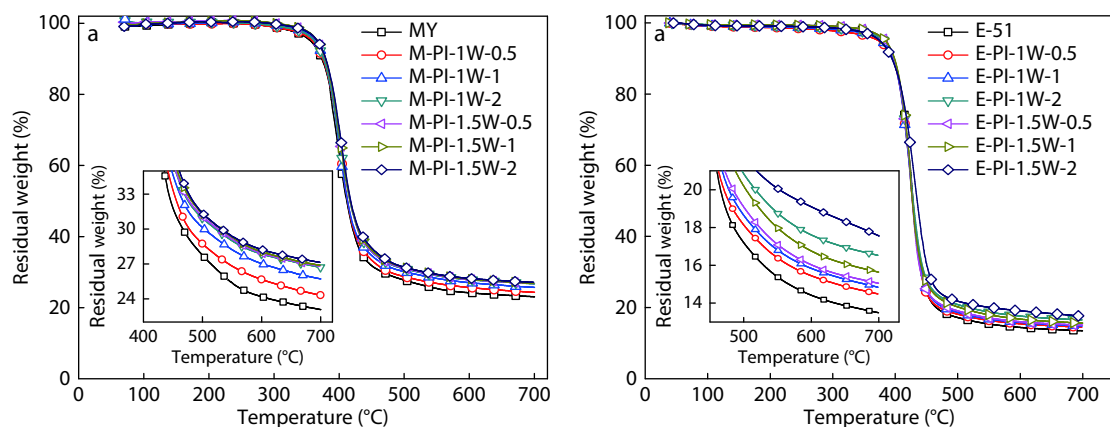


Fig. 9 TG curves of M-PI (a) and E-PI (b) composites.

the thermal stability of PI is higher than that of epoxy resin, because PI contains high density of benzene ring and hence enhances more char formation. Some recent studies have found that PI can be used as a flame-retardant.^[38,39] The benzene-1,2,4,5-tetra-carboxylic acid dehydrate section of as-synthesized PI can be decomposed into acid, which can catalyze the carbonation of PI and epoxy resin around acid.

CONCLUSIONS

PI was synthesized from aromatic diamine and aromatic dianhydrides *via* a two-step polycondensation method. As-synthesized PI with molecular weight of 1W–2.8W is highly soluble in MY-720 and E-51 at desirable temperature. M-PI and E-PI composites with various PI loadings can be processed through directly mixing resin and PI without the aid of organic solvent. No significant phase separation is observed on the cryogenically fractured surfaces of M-PI and E-PI composites by SEM. The mechanical properties of M-PI and E-PI composites are significantly enhanced with loading range of 0.5%–3% of PI, especially for the impact strength with the highest increases being 163% and 113% at 2% PI loading, respectively. SEM analyses for the fracture surface suggest that PI improves the plasticity of epoxy resin and changes the fracture mode from fragile to ductile. DMA measurement shows the increase in T_g of E-PI composites by 17 °C for PI-1.0W loading as low as 0.5% and the increase in the storage modulus from 2.5 GPa to 3.1 GPa. M-PI composites keep T_g and storage modulus being almost constant. Moreover, M-PI and E-PI composites can maintain the thermal stability of the matrix. Compared with the reported results about the composites modified with other polyimides, the as-synthesized PI in this work is more favorable for promotion of mechanical property and thermal mechanical property of MY-720 and E-51 composites (Table S2 in ESI).

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2395-9>.

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