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Novel Thermoplastic Polyimide Composite Materials

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1. Introduction

Novel thermoplastic polyimide (TPI) offer several potential advantages over thermoset polyimides. First, TPI has an indefinite shelf life, low moisture absorption, excellent thermal stability and chemical resistance, high toughness and damage tolerance, short and simple processing cycles and potential for significant reductions in manufacturing costs. Second, they have the ability to be re-melt and re-processed, thus the damaged structures can be repaired by the applying heat and pressure. Thirdly, TPI offer advantages in the environmental concerns. Usually, TPI has very low toxicity since it is the completely imidized polymer, does not contain any reactive chemicals. Due to the re-melt possibility by heating and re-dissolvability in solvents, TPI could be recycled or combined with other recycled materials in the market to make new products [1-3].

For injection or extrusion moldings, conventional polyimides do not have enough flow properties, therefore, only limited fabrication processes such as compression, transfer or sintering molding could be applied. Significant efforts have been devoted to develop melt processable polyimides. Most of the efforts have been focused on exploiting of the correlation between chemical structures and polymer properties, such as Tg and melting ability etc. to improve TPI's melt processability, thus resulted in some commercial TPI materials such as amorphous LARC-TPI resin (Tg ~ 250 °C), ULTEM® resin (Tg ~ 217 °C) and semi-crystalline Aurum® resins (Tg ~ 250 °C and Tm ~ 380 °C). Bell and St. Chair investigated the effect of diamine structure on the thermal properties of polyimides and such studies led to the invention of LARC-TPI [4-7]. The characteristic structure of LARC-TPI, meta-substituted diamine and the flexible linkage between the benzene rings enhanced the thermoplasticity. To make the polyimides more processable, there have been reports of several modification of polymer structure [8, 9]. In recent years, a new developed TPI was commercialized as EXTEM® XH and UH resins by SABIC Innovative Plastics. With its high temperature capability (Tg ~ 267 °C and 311°C) and high melt flow ability, EXTEM resin differentiates its position within TPIs as well as other high performance polymers [10, 11].

In this paper, a series of novel TPI composites have been prepared and their thermal, rheological and mechanical properties were characterized. The TPI resins have excellent

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melt flow capability, which can be fiber-reinforced or filler-modified to give high quality a series of TPI composites. Moreover, very thin-walled complex parts can be injection molded at elevated temperatures.

2. Experimental

2.1 Materials

1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) was synthesized in this laboratory according to the reported methods^[12, 13]. 4,4-Oxydiphthalic anhydride (ODPA) was purchased from Shanghai Research Institute of Synthetic Resins, China and dried in a vacuum oven at 180 °C for 12 h prior to use. Phthalic anhydride (PA) was commercially purchased and sublimed prior to use. *N*-methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation over P₂O₅ prior to use. Toluene (Beijing Beihua Fine Chemicals Co., China) was used as received without further purification. Carbon fiber (T800) was purchased from Toray and used as received. Glass fiber was purchased from Beijing Xingwang Glass Fiber Ltd. Corp. and used as received. Graphite, poly(tetrafluoroethylene) (PTFE) and molybdenum disulfide (MoS₂) were afforded by Beijing POME Corp. and used as received.

2.2 Measurements

Differential scanning calorimetry (DSC) was performed on a TA Q100 thermal analysis system in nitrogen atmosphere at a flow rate of 50 cm³/min and the scanning range was from 50 to 350 °C. The glass transition temperature (T_g) was determined by the inflection point of the heat flow versus temperature curve. Complex viscosity (η^*) were measured on a TA AR2000 rheometer. A TPI resin disk with 25 mm in diameter and ~1.5 mm in thickness was prepared by press-molding the resin powder at room temperature, which was then loaded in the rheometer fixture equipped with 25 mm diameter parallel plates. Measurements were performed using the flow mode with a constant stress (104 Pa) and about 5 N normal forces. In the temperature ramp procedure, an initial temperature of 200 °C was set and then the parallel plates with testing sample were equilibrated at this temperature for 10 min. The complex viscosity (η^*) as a function of the scanning temperature (T) were measured by scanning the temperature from 200 °C to 400 °C at a rate of 3 °C / min.

Thermal gravimetric analysis (TGA) and the coefficients of thermal expansion (CTE) were performed on a Perkin-Elmer 7 Series thermal analysis system at a heating rate of 20 °C /min in nitrogen atmosphere at a flow rate of 30 cm³/min. Dynamic mechanical analysis (DMA) was performed on a Perkin-Elmer 7 Series thermal analysis system, and the scanning temperature range was from 50 °C to 320 °C at a heating rate of 5 °C/min and at a frequency of 1 Hz. A three-point bending mode was employed and the specimen size was 15.0 × 3.0 × 1.2 mm³. The storage modulus (G'), loss modulus (G'') and tangent of loss angle (tan δ) were obtained as the function of scanning temperature. Melt flow index (MFI) were measured in according with GB/T3680-2000 at elevated temperature.

The mechanical properties were measured on an Instron-5567 universal tester at different temperature. The tensile strength, modulus, and elongation at break were measured in according with GB/T16421-1996 at a strain rate of 2 mm/min. The flexural strength and modulus were measured in according with GB/T5270-1996 at a strain rate of 2 mm/min.

The compressive strength and modulus were measured in according with GB/T2569-1997 at a strain rate of 2 mm/min. Izod impact (unnotched) were measured in according with GB/T16420-1996.

2.3 Preparation of the TPI resins

TPI with controlled molecular weights was prepared by the reaction of ODP A with 6FAPB in the presence of PA as endcapping agent in NMP at elevated temperatures (scheme 1) [14-17]. 6FAPB (2161.65 g, 5.047 mol) and NMP (21 L) were placed into a 50 L agitated reactor equipped with a mechanical stirrer, a thermometer, nitrogen inlet/outlet and a condenser. The mixture was stirred at ambient temperature for ~1 h until the aromatic diamine was completely dissolved to give a homogeneous solution. ODP A (1508.00 g, 4.859 mol) and PA (41.62 g, 0.281 mol) were then added. An additional 0.6 L of NMP was used to rinse all of the anhydrides, resulting in a mixture with 15% solid content (w/w). After the mixture was stirred in nitrogen at 75 °C for 4 h, 2 L of toluene and a few drops of isoquinoline as a catalyst were added. The obtained solution was gradually heated to 180 °C and held for 10 h with stirring. The water evolved during the thermal imidization was removed simultaneously by azeotropic distillation. After the thermal imidization reaction was completed, the reaction solution was cooled down to room temperature and then poured into excess of ethanol with vigorous stirring to precipitate the polyimide resin. The solid resin was then isolated by filtration, thoroughly washed with warm ethanol and dried at 100 °C overnight to remove most of the ethanol. The polyimide resin was fully dried at 205 °C in a vacuum oven for ~24 h to give 3420 g (97%) of TPI.

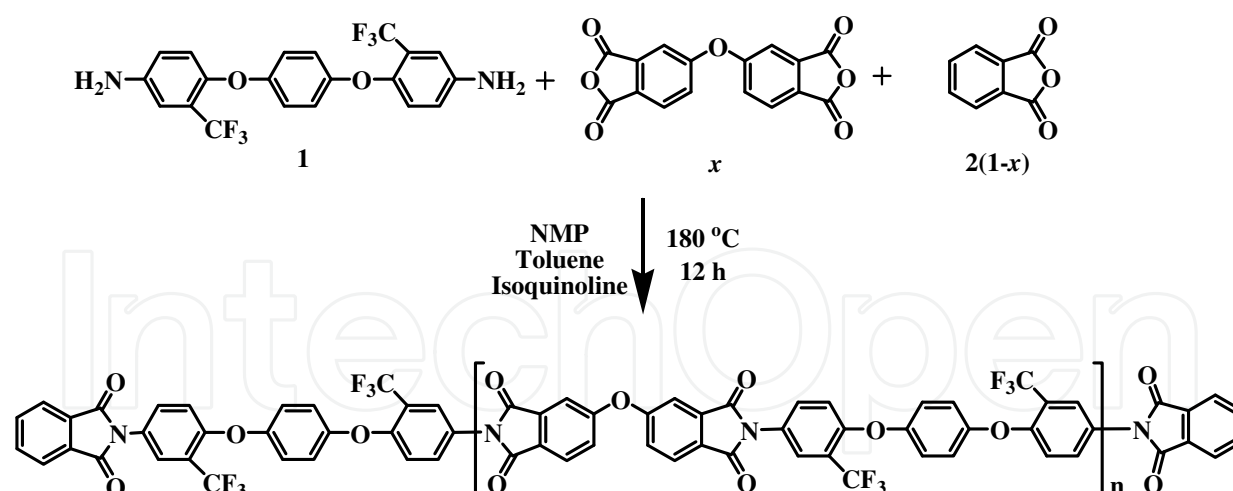
2.4 Preparation of TPI composites

The pure TPI resin powder was dried at 205°C for 6 h in a vacuum dryer, and then extruded at elevated temperature with carbon fiber, glass fiber, graphite, poly(tetrafluoroethylene) (PTFE) or molybdenum disulfide (MoS₂) to give composite molding particulates, which were abbreviated as CF-TPI, GF-TPI, Gr-TPI, PTFE-TPI and MoS₂-TPI, respectively, as shown in Table 1. The composite molding particulates could be injection-molded at elevated temperature to give the TPI composites. The test composites samples were injected on a standard 120-ton injection molding machine equipped with a general purpose screw in accordance to the guidelines presented in Table 2.

3. Results and discussion

3.1 Preparation of TPI resins and TPI composites

The TPI resin with designed polymer backbones and controlled molecular weights were prepared by a one-step thermal polycondensation procedure as shown in Scheme 1. The offset of the aromatic dianhydride (ODP A) to the aromatic diamine (6FAPB) and endcapping agent (PA) was used to control the polymer molecular weights. The water evolved during the thermal imidization was removed simultaneously from the reaction system by azeotropic distillation. The TPI resin showed several characteristic absorption in FT-IR spectra, including the absorptions at 1780 and 1720 cm⁻¹ attributed to the asymmetrical and symmetrical stretching vibrations of the imide groups, the band at 1380 cm⁻¹ assigned as the C-N stretching vibration, and the absorptions at 1100 and 725 cm⁻¹ due to the imide ring deformation, etc.



Scheme 1. Synthesis of thermoplastic polyimide resin

The chemical compositions of the TPI composites were listed in Table 1. Firstly, the pure TPI resin powder was dried at $205\text{ }^\circ\text{C}$ for 6h in a vacuum dryer to completely remove the moisture in the resin, which was then extruded at elevated temperatures with carbon fiber, glass fiber, MoS_2 or PTFE to afford the TPI molding particulates. The processing parameters for the injection of the TPI molding particulates were shown in Table 2, in which the melt temperature was settled at $350 - 370\text{ }^\circ\text{C}$ and the molding temperature at $150 - 160\text{ }^\circ\text{C}$.

	TPI	Carbon Fiber	Glass Fiber	Graphite	MoS_2	PTFE
TPI	100	-	-	-	-	-
CF-TPI-10	90	10	-	-	-	-
CF-TPI-20	80	20	-	-	-	-
CF-TPI-30	70	30	-	-	-	-
GF-TPI-15	85	-	15	-	-	-
GF-TPI-30	70	-	30	-	-	-
GF-TPI-45	55	-	45	-	-	-
Gr- TPI-15	85	-	-	15	-	-
Gr- TPI-40	60	-	-	40	-	-
MoS_2 -TPI-15	85	-	-	-	15	-
MoS_2 -TPI-30	70	-	-	-	30	-
PTFE-TPI-20	80	-	-	-	-	20

Table 1. Chemical compositions of the TPI composites

Processing Conditions	Unit	Parameter
Drying Conditions	$^\circ\text{C}/\text{hr}$	160/4~6
Moisture Content (max.)	%	0.02
Melt Temperature	$^\circ\text{C}$	350~370
Mold Temperature	$^\circ\text{C}$	150~160
Back Pressure	MPa	0.3~0.5
Screw Speed	RPM	40~80

Table 2. Injection molding conditions of the molding particulates

3.2 Rheological properties of the TPI molding particulates

Dynamical rheology was employed to investigate the melt properties of the molding particulates. Figure 1 compares the melt viscosities of carbon fiber-filled TPI resins with different loadings at different temperature and the dates are summarized in Table 3. It can be seen that the molten viscosities of molding particulates decreased gradually with increasing the temperature scanned at 200-400°C, primarily attributed to the melting of TPI resin in the molding particulates. The minimum melt viscosities of the molding particulates increased with increasing of the carbon fiber loadings. For instance, the minimum melt viscosity of CF-TPI-10 was 1.8×10^3 Pa·s at 400 °C, lower than that of CF-TPI-30 (6.7×10^3 Pa·s at 400 °C). Meanwhile, the melt viscosity at the processing temperature (360 °C) was increased from 4.7×10^3 Pa·s for CF-TPI-10 to 9.4×10^3 Pa·s for CF-TPI-30, indicating that the addition of carbon fiber in TPI resins increased the melt viscosities of the molding particulate, thus lowering their melt processabilities. The melt viscosities of other TPI composites filled with glass fiber, graphite, molybdenum disulfide (MoS_2) and poly(tetrafluoroethylene) (PTFE) are also shown in Table 3. It can be seen that the molding particulates (Gr-TPI, MoS_2 -TPI and PTFE-TPI) showed good melt processabilities with complex melt viscosities of 3.6×10^3 Pa·s (Gr-TPI-15) at 360 °C, 4.1×10^3 Pa·s (MoS_2 -TPI-15) at 360 °C, and 4.5×10^3 Pa·s (PTFE-TPI-20) at 360 °C, respectively. It should be noted that glass fiber-filled TPI molding particulates showed much higher complex melt viscosities than the pure TPI resin. For instance, GF-TPI-30 has a complex melt viscosity of 4.5×10^4 Pa·s at 360 °C, 4.7 times higher than CF-TPI-30 (9.4×10^3 Pa·s at 360 °C).

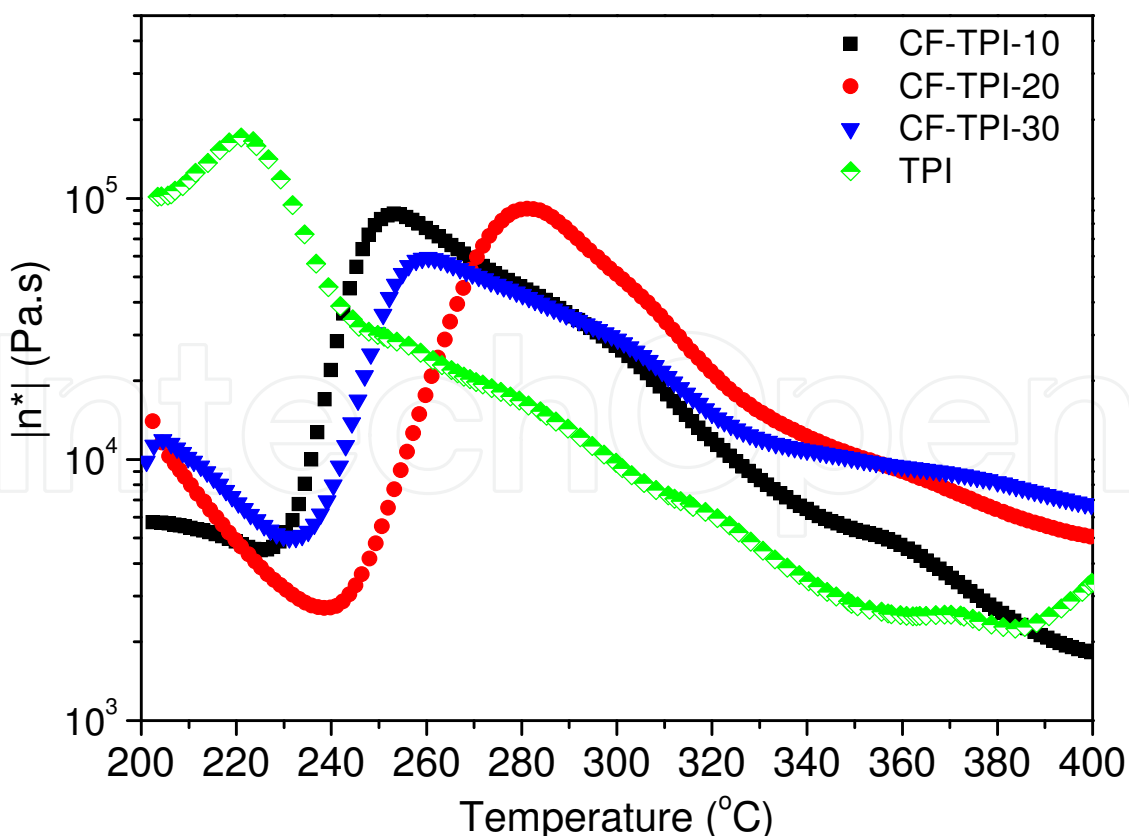


Fig. 1. Dynamic rheological behaviors of the carbon fiber-filled TPI molding particulates

	Minimum melt viscosities (Pa.s)	Complex melt viscosities (Pa.s) at 360 °C
TPI	2.5×10 ³ at 360 °C	2.3×10 ³
CF-TPI-10	1.8×10 ³ at 400 °C	4.7×10 ³
CF-TPI-20	5.1×10 ³ at 400 °C	9.1×10 ³
CF-TPI-30	6.7×10 ³ at 400 °C	9.4×10 ³
GF-TPI-15	8.7×10 ³ at 340 °C	3.4×10 ⁴
GF-TPI-30	1.5×10 ⁴ at 300 °C	4.5×10 ⁴
Gr-TPI-15	2.4×10 ³ at 280 °C	3.6×10 ³
Gr-TPI-40	4.4×10 ³ at 330 °C	6.3×10 ³
MoS ₂ -TPI-15	3.0×10 ³ at 400 °C	4.1×10 ³
MoS ₂ -TPI-30	4.0×10 ³ at 290 °C	4.9×10 ³
PTFE-TPI-20	3.4×10 ³ at 280 °C	4.5×10 ³

Table 3. Melt Viscosities of TPI and TPI-c molding particulates at Elevated Temperature

Melt flow index of the molding particulates was shown in Table 4. The pure TPI resin showed highest melt flow index of 10.1 g/10 min at 360 °C under a pressure of 10 kg, which could be employed to inject very thin-walled complex parts due to its excellent melt flow ability. Figure 2 shows a representative thin-walled complex part which has a wall thickness of 0.2mm. In general, the TPI resins filled with different fillers such as graphite, molybdenum disulfide and poly(tetrafluoroethylene) etc. all showed good melt flow properties with melt flow index of > 2.0 g/10min. In comparison, the carbon fiber-filled TPI molding particulates showed better melt flow properties than the Glass fiber-filled ones. For instance, CF-TPI-30 has a melt flow index of 2.4 g/min at 360 °C under 10 kg, compared with GF-TPI-30 (0.5 g/min at 360 °C under 21.6 kg. Meanwhile, the filler loadings also have obvious effect on lowering the melt flow index. For instance, MoS₂-TPI-30 has a melt flow index of 0.8g/10 min at 360 °C under 10 kg, much lower than MoS₂-TPI-15(3.2 g/10 min at 360 °C under 10 kg).



Outer diameter: 1.5mm; Inner diameter : 1.1mm

Fig. 2. The Injection molded TPI thin-walled parts

	Temperature/ °C	M/kg	t/s	g/10min
TPI	360	10	10	10.1
CF-TPI-10	360	10	30	3.8
CF-TPI-20	360	10	30	2.5
CF-TPI-30	360	10	30	2.4
GF-TPI-15	360	21.6	60	0.9
GF-TPI-30	360	21.6	60	0.5
Gr-TPI-15	360	10	10	8.9
Gr-TPI-40	360	10	30	6.0
MoS ₂ -TPI-15	360	10	30	3.2
MoS ₂ -TPI-30	360	10	60	0.8
PTFE-TPI-20	360	10	60	2.4

Table 4. Melt Flow Index at 360 °C of the Molding Particulates

3.3 Thermal properties of the TPI molded composites

Figure 3 compares DSC curves of the injection-molded TPI composites with different carbon fiber loadings. It can be seen that molded composites showed glass transition temperature (T_g) in the range of 215-216 °C, which was not obviously changed by the carbon fiber loadings. Figure 4 shows the DMA curves of a representative molded composite (CF-TPI-20), in which the peak temperature in the Tan δ curve was at 211 °C. The storage modulus curve did not turn down until the temperature was scanned up to 201 °C, demonstrating that the carbon fiber-filled TPI molded composites have outstanding thermo-mechanical properties. Figure 5 depicts the thermal stabilities of carbon fiber-filled TPI molded composites. The temperatures at 5% and 10% of original weight losses were measured at 550 °C and 580 °C, respectively. The initial decomposition temperatures were determined at 550 °C and the char yields at 750 °C was > 60%.

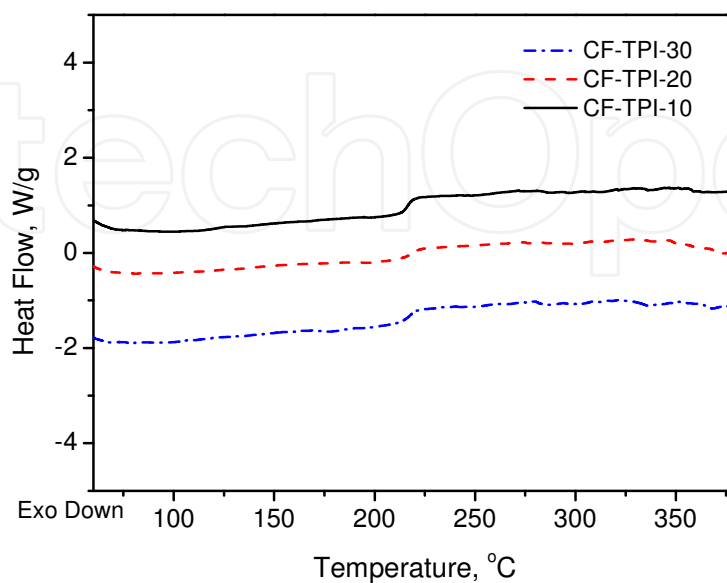


Fig. 3. DSC curves of carbon fiber-filled TPI molded composites

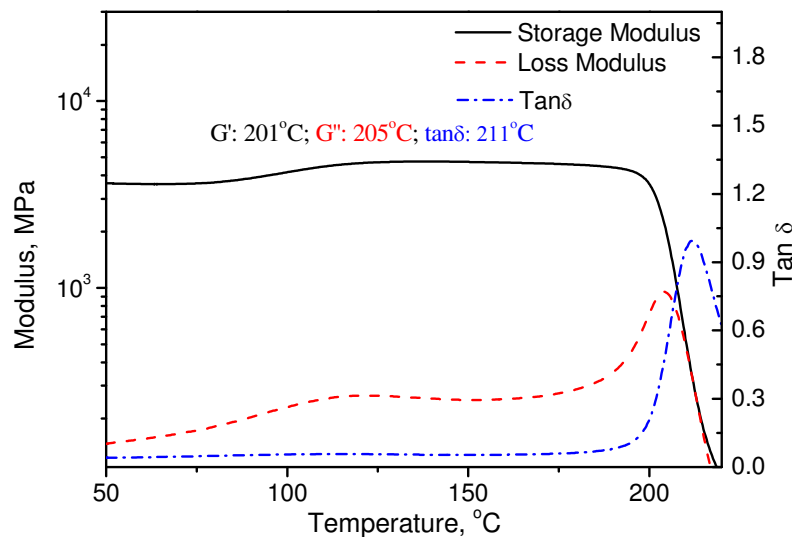


Fig. 4. DMA curves of CF-TPI-20 molded composite

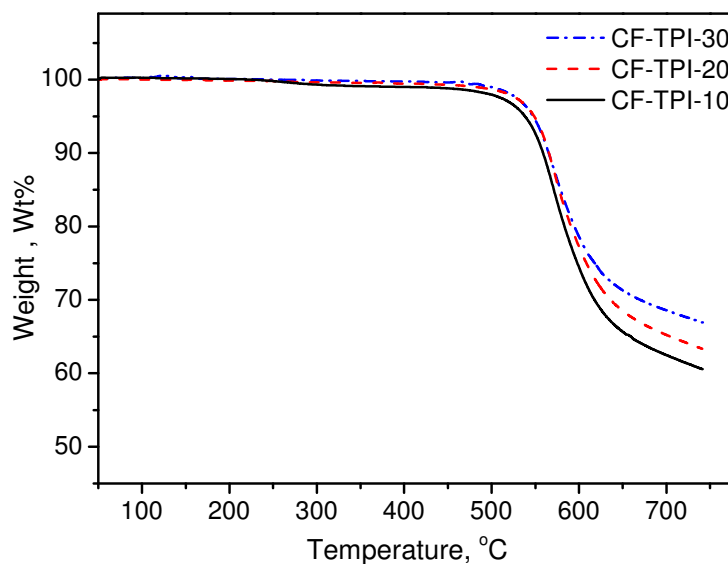


Fig. 5. TGA curves of carbon fiber-filled TPI molded composites

3.4 Mechanical properties of the molded composites

Table 5 compares the mechanical properties of the injection molded TPI composites. The pure TPI resin exhibited good combined mechanical properties with tensile strength of 100 MPa, tensile modulus of 5.6 GPa, elongation at break of 57.6%, flexural strength of 154 MPa, flexural modulus of 3.8 GPa, and izod impact (un-notched) of 156 kJ/m². The carbon fiber-filled TPI molded composites possess mechanical properties better than the pure TPI resin with tensile strength of 177-219 MPa, tensile modulus of 7.3-12.4 GPa, flexural strength of 241-327 MPa and Izod impact of 20.8-24.4 kJ/m², demonstrating that carbon fiber have significant reinforcing effect. The glass fiber-filled TPI molded composites also showed good mechanical strength, but lower modulus than the carbon fiber-filled ones. For instance, GF-TPI-30 has a modulus of 7.5 GPa, only 60% of CF-TPI-30 (12.4 GPa). The other TPI molded composites filled with graphite, molybdenum disulfide and poly(tetrafluoroethylene) all

showed good combined mechanical properties, demonstrating that the addition of filler did not deteriorate the TPI mechanical properties.

	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at breakage (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Compressive strength (MPa)	Compressive modulus (GPa)	Izod impact (unnotched) (KJ/m ²)
TPI	100	5.6	57.6	154	3.8	159	3.6	156
CF-TPI-10	177	7.3	3.40	241	8.8	168	5.4	20.8
CF-TPI-20	177	10.1	2.14	278	13.5	215	7.6	20.8
CF-TPI-30	219	12.4	2.34	327	17.8	205	7.2	24.4
GF-TPI-15	121	4.8	3.42	191	5.7	145	3.7	20.4
GF-TPI-30	137	7.5	2.20	211	9.2	182	5.3	23.1
GF-TPI-45	106	8.8	1.62	242	14.6	207	7.0	16.6
Gr-TPI-15	94	4.4	4.37	150	5.9	106	2.7	15.4
Gr-TPI-40	64	8.2	1.71	114	11.2	86	3.9	6.7
MoS ₂ -TPI-15	102	8.9	13.8	148	3.8	116	2.7	23.7
MoS ₂ -TPI-30	83	4.1	3.36	145	5.6	115	2.9	13.1
PTFE-TPI-20	98	3.0	6.64	156	4.3	99	2.8	26.9

Table 5. Mechanical properties of the TPI molded composites

4. Conclusions

Novel thermoplastic polyimide (TPI) resins with designed polymer backbones and controlled molecular weights have been synthesized by thermal polycondensation of aromatic dianhydrides and aromatic diamines in presence of endcapping agent. The TPI resins were reinforced with carbon fiber, glass fiber, or modified by adding of solid lubricants such as graphite, poly(tetrafluoroethylene) (PTFE) or molybdenum disulfide (MoS₂) to give TPI molding particulates, which could be injection-molded at elevated temperature to give the TPI molded composites. Thus, thin-walled molded parts could be fabricated. The TPI molding particulates showed excellent melt processibility to produce high quality TPI molded composites with excellent combination of thermal and mechanical properties.

6. Acknowledgements

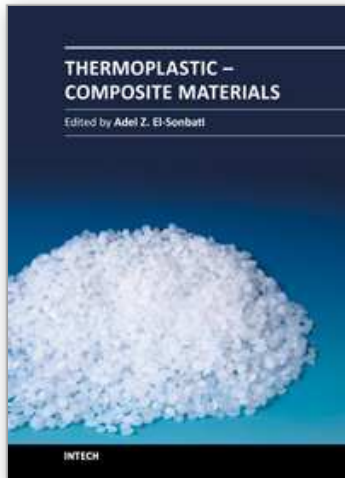
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Composite materials often demand a unique combination of properties, including high thermal and oxidative stability, toughness, solvent resistance and low dielectric constant. This book, "Thermoplastic - Composite Materials", is comprised of seven excellent chapters, written for all specialized scientists and engineers dealing with characterization, thermal, mechanical and technical properties, rheological, morphological and microstructure properties and processing design of composite materials.

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