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Preparations and Properties of a High Performance Semicrystalline Copolyimide and Composites Reinforced with Glass Fiber

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ABSTRACT: A semicrystalline copolyimide derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (*s*-BPDA), 1,3-bis-(4-aminophenoxy) benzene (TPER), and 4,4′-oxydianiline (4,4′-ODA), end capped with phthalic anhydride (PA), was synthesized. Glass fiber reinforced composite was also prepared by impregnating powdery glass fiber with poly(amic acid) followed by solution imidization techniques. This copolyimide displayed a glass transition temperature of 202°C and a melting temperature of 373°C by differential scanning colorimeter (DSC). Crystallization and melting behaviors were investigated under nonisothermal and isothermal crystallization conditions. Double exothermic peaks were found by DSC when the copolyimide was cooled from the melt and multiple melting behaviors can be observed after the coployimide had been isothermally crystallized at different temperatures. Mechanical properties were investigated by dynamical mechanical analysis (DMA) and tensile experiments. The samples were cured at different temperatures and then tested at different temperatures. Results indicated that the copolyimide and the composite showed excellent mechanical properties. Additionally, this copolyimide also showed lower melt viscosity by rheological analysis. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40345.

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INTRODUCTION

Since semicrystalline polyimides offer further advantages of increased solvent resistance and retention of mechanical properties above the glass transition temperature (T_g), these features have made semicrystalline polyimides the focus of considerable research over these years.[1–4] One of the typical examples is based on 1, 3-bis (4-aminophenoxy) benzene (TPER) and 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (*s*-BPDA), it displays excellent thermal properties, chemical resistance, and electric properties.[5–8] Furthermore, the outstanding crystallization capacity enables the final products to be used at 350°C for a long time. However, the high melting temperature (T_m) has led to difficulties in melt processing, because the processing temperature must be around 420°C. In addition, since TPER/*s*-BPDA displayed extremely fast crystallization rate when being cooled from the melt, the melt viscosity increased evidently as soon as the crystallization started.[9] Moreover, products finally obtained are mostly highly crystallized, applications are therefore greatly restricted.

Previously, we have introduced 4, 4′-oxydianiline (4, 4′-ODA) to react with *s*-BPDA/ TPER to solve above problems, and basic properties of the copolyimides were studied.[10] The copolyimide with 90% content of TPER caught us attention because of its excellent crystallizability and lower T_m. Isothermal melt crystallization kinetics of the copolyimide and *s*-BPDA/TPER had also been investigated.[11] Results demonstrated that the copolyimide exhibited lower crystallization rate than *s*-BPDA/TPER during isothermal crystallization process, indicating it will be easier to obtain products with different crystallinity by controlling crystallization progress.

In this article, detailed analysis on thermal properties, mechanical properties, and melt viscosity of this copolyimide were carried out. In addition, powdery glass fiber reinforced composite was also prepared. The powdery fiber was expected to flow easily with the molten matrix resins in the thermal curing process.[12] All the results demonstrate that this copolyimide is a high performance resin with excellent crystallizability, it will attract much interest in industrial fields in the future.

EXPERIMENTAL

Materials

4,4′-Oxydianiline (4,4′-ODA) was supplied by Sinopharm Chemical Reagent 1,3-Bis(4-aminophenoxy)benzene (TPER) was supplied by Shijiazhuang Haili Fine Chemical Liability 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (*s*-BPDA) was also obtained from Shijiazhuang Haili Fine Chemical Liability and was dried at 120°C prior to use. Phthalic anhydride (referred to as PA) was obtained from Shanghai shanpu Chemical *N*, *N*-dimethylacetamide (DMAc), which was used as a solvent for polymerization, was obtained from Tianjin TianTai Fine Chemicals and vacuum distilled before used. Xylene was supplied by Beijing Chemical Works. Glass fiber was from Nanjing Fiberglass R&D Institute, the density was 2.54 g cm^{-3}, diameter of the grains was about 8–13 μm, length: 5–50 μm and the length to diameter (l/d) is in the range of 1–5.

Polyimide Synthesis

Preparation of Poly(amic acid)s. Copolyimide capped with nonreactive PA end groups was synthesized with calculated number average molecular weight (M_w) of 32,000.[5] A 500 mL three-neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet and a drying tube, was used as the reaction vessel. To the reaction vessel was added 13.1549 g (0.045 mol) of TPER and 1.0012 g (0.005 mol) of 4, 4′-ODA, which were then dissolved in dry DMAc. Totally, 14.4658 g (0.049 mol) of *s*-BPDA was added. This solution was stirred and allowed to react under a nitrogen atmosphere for 8 h, and then 0.2469 g (0.0017 mol) of PA was added to the solution. Upon dissolution of the PA, enough DMAc was added to achieve a 10% solids concentration. This solution was stirred and allowed to react under a nitrogen atmosphere for another 8 h to afford the poly (amic acid) (PAA).

Preparation of Molding Powders. The PAA was converted to the respective polyimide using solution imidization techniques.[13] In this case, the drying tube used in the apparatus above was replaced with a reverse Dean Stark trap. 65 mL of xylene was added as an azeotroping liquid to the solution so as to achieve an 80/20 ratio of DMAc to xylene (for the composite material, glass fiber was first added into PAA before xylene, weight fraction was 20%). The solution was heated to about 150°C and allowed to stir. After about 2 h, partially imidized yellow particulates precipitated from the solution, and then the resulting slurry was poured into ethanol with stirring. The resulting powder was filtered, washed with ethanol, and dried in a vacuum oven at 250°C for 1 h to ensure complete imidization. Referenced homopolyimide based on *s*-BPDA and TPER ($M_w = 32{,}000$) was also synthesized in the same way as described above.

Preparations of Films and Compositls. The polyimides and composites were used in the form of powder and film in this study. The films were molded using a hot-Press. Quenched films were prepared by heating powders at 410°C for 20 min under 20 MPa load followed by quenching to cold water. Annealed films were prepared in two ways: (1) powders was heated in a hot-press at 410°C for 20 min under 20 MPa load followed by slowly cooling to room temperature at about 3°C min^{-1}; (2) the quenched films were isothermally crystallized at different temperatures for 60 min followed by quenching to cold water.

Characterization and Measurements

The inherent viscosity (η_{inh}) of the poly(amic acid) was determined using an Ubbelohde viscometer at a concentration of 0.5 g dL^{-1} in DMAc at 25°C.

Thermogravimetric analysis (TGA) was performed using a TA 2050 thermogravimetric analyzer, samples were heated at 5°C min^{-1} in nitrogen and air atmosphere.

Differential scanning calorimeter (DSC) measurement was conducted on a TA DSC Q100 analysis system on 4–5 mg of sample at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. DSC cooling scans at various rates were conducted: the samples were first heated at 20°C min^{-1} to 20°C higher than T_m and held for 5 min, then cooled to room temperature at different cooling rates, reheated at a rate of 10°C min^{-1}. DSC measurement for the polyimide isothermally annealed at various temperatures was also carried out. The samples were heated at 20°C min^{-1} to 20°C higher than T_m and held for 5 min. The powder samples were then cooled at 200°C min^{-1} to various temperatures and held for 60 min, and then cooled at a rate of 200°C min^{-1} to ambient temperatures. Then the samples were reheated at a rate of 10°C min^{-1}.

Dynamic mechanical analysis (DMA) was performed on a TA Q800 at a heating rate of 5°C min^{-1} and at a load frequency of 1 Hz in an air atmosphere.

Tensile properties were measured on a SHIMADZU AG-I tensile apparatus. Sample size was $4 \times 0.3 \times 0.005$ cm^3, strain rate was 8 mm s^{-1}, testing temperatures were 25°C, 220°C, 250°C, 280°C.

The morphology of the composite was observed by the Shimadzu SSX-550 scanning electron microscope (SEM) with an accelerating voltage of 15 kV.

Rheological experiments were carried out on a TA R2000 with a 25 mm diameter parallel plate fixture. Nitrogen was used for temperature control. Dynamic oscillatory viscosity data were collected at a frequency of 1 Hz and a strain of 1%.

RESULTS AND DISCUSSION

All the polyimides were synthesized according to the method described in the experimental section, and PA was used as an end capper which would maximize the thermal stability of the polymers. The composite comprising the copolyimide resin and powdery glass fibers was also prepared, and the weight fraction of glass fibers was 20%. In this study, the homopolyimide based on TPER and *s*-BPDA was abbreviated as TPER PI, and the copolyimide synthesized from 4, 4′ -ODA, TPER, and *s*-BPDA was abbreviated as co-PI A. Inherent viscosities of poly(amic acid)s are summarized in Table I.

Thermal Properties

Thermal Stability. Thermal stability of the polyimides and composites were evaluated by TGA in N_2 and air atmosphere. As is shown in Figure 1, all the materials exhibited excellent thermal stability. Temperatures of 5% weight loss in N_2 were all above 560°C as listed in Table I. The char yield of the composite at 800°C in air was about 20%, indicating the weight fraction of the glass fiber was 20%. Since degradation reactions such as cross-linking or chain extension could occur with a small accompanying weight loss, the TGA technique by itself is inadequate for reflecting the thermal stability of polymers.[4] As is known, the melt viscosity is critically dependent on molecular

Table I. Inherent Viscosity of PAAs and Thermal Properties

Sample code	Diamine composition	η_{inh}[a] (dL g^{-1})	T_g[b] (°C)	T_m[b] (°C)	T_d[c] (°C) N$_2$	T_d[c] (°C) air
co-PI A	TPER/4,4′-ODA(9/1)	1.30	202	373	563	523
TPER PI	TPER	1.05	201	384	565	527
Composite material	TPER/4,4′-ODA(9/1)	1.30	202	373	564	522

[a] Inherent viscosity measured by using Ubbelohde viscometer at a concentration of 0.5 g dL^{-1} at 25°C in DMAc.
[b] Determined by DSC from quenched films at a heating rate of 10°C min^{-1}.
[c] Temperatures for 5% weight loss at a heating rate of 5°C min^{-1} in nitrogen and air by TGA.

weights, which will increase remarkably when cross-linking or chain extension occurs. So, rheological analysis by testing the change of melt viscosity is another effective way to evaluate the thermal stability of polymers. In this article, rheological analysis was also carried out and the results will be discussed later.

Thermal Properties. Since the influence of residual water or solvent, DSC curves of as made powders are not given here. DSC heating scans for quenched films and annealed films are shown in Figure 2. It is interesting to note that neither of the polyimides could be quenched into a pure amorphous state after first heating, implying very fast crystallization kinetics. The quenched TPER PI displayed a T_g of 201°C and a T_m of 384°C. Co-PI A displayed a T_g of 202°C and a T_m of 373°C, and the crystallization peak appeared at 255°C, which was about 20°C higher than that of TPER PI. This should be attributed to the more rigid structure of 4, 4′-ODA in comparison with TPER. As the introductions of 4, 4′-ODA, the mobility of molecular chains decreased, so it would take molecular chains more time and more energy to rearrange, the crystallization therefore started at higher temperatures during heating scans. After slowly cooling from the melt, co-PI A exhibited a T_m of 373°C as is shown in Figure 2. For TPER PI, a weak endothermic peak, which can be attributed to the melting of less perfect crystal, appeared as a shoulder at 373°C, and a primary endothermic peak was observed at 384°C. X-ray diffraction (XRD) experiments had also been conducted, however, positions of the primary diffraction peaks of TPER PI and co-PI A were found to be same, indicating the crystal structures of the two polyimides should be same.

Multiple Melting Behaviors. Figure 3 shows the melting endotherms of co-PI A isothermally crystallized at various temperatures after a melt treatment in DSC. Multiple endothermic peaks were as evident as TPER PI.[5] Multiple melting behaviors is a very common observation in thermal studies of semicrystalline polyimides; however, the reasons for this are still not clear.[14–16] Hsiao found that positions of diffraction peaks of TPER PI were independent of crystallization temperatures, so he thought the triple-melting behavior of TPER PI should not be due to the polymorphism.[9] We have also conducted XRD experiments on TPER PI and co-PI A after they had been crystallized at different temperatures. Although positions of the diffraction peaks of two polyimides were also found to be independent of crystallization temperatures, positions of some diffraction peaks changed regularly during reheating process, indicating the crystal structures had changed during melting–recrystallization–melting process. Especially, a new diffraction peak appeared when co-PI A, which had been isothermally crystallized at 360°C for 1 h, was reheated. So polymorphism should be one reason for multiple melting behaviors of these two polyimides. Detailed analysis on crystal structures will be discussed in a future article. We have also done some other research on multiple melting behaviors, and all the results indicate that peak I at $T_c + 10$°C arises as a result of the melting of thinner lamellae that formed as a result of secondary

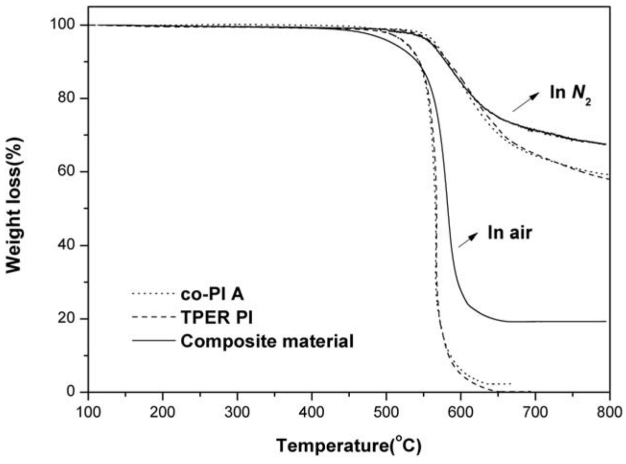

Figure 1. TGA curves in air and N$_2$ atmosphere.

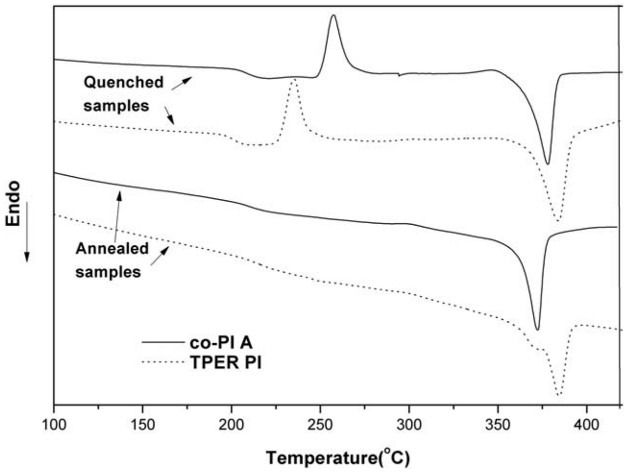

Figure 2. DSC curves of the quenched and the annealed samples.

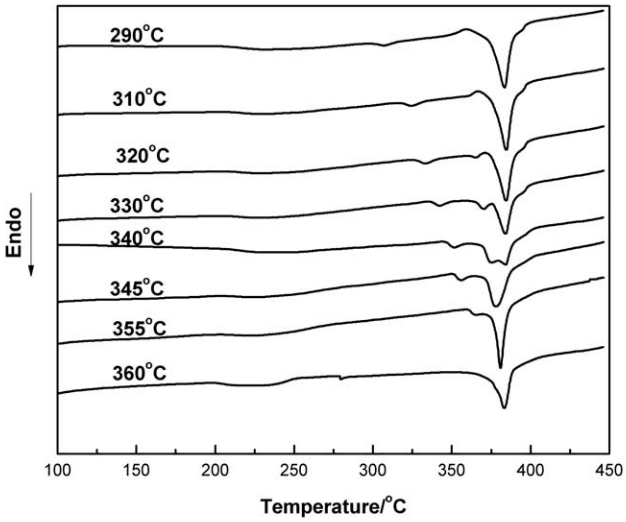

Figure 3. DSC heating scans for co-PI A after isothermally crystallizing at various temperatures.

crystallization at the crystallization temperature. Peak II is the melt of the dominant crystals formed during the isothermal crystallization progress. And Peak III is not only due to melting–recrystallization–melting process, the perfect crystals already exited during heating scans. Hoffman-Weeks plot had also been constructed to estimate the equilibrium melting temperature ($T_m°$) of co-PI A, and the value was found to be 410°C, which was as same as that of TPER PI.[17]

Double Crystallization Behaviors. Figure 4 shows the DSC cooling scans of co-PI A and TPER PI at various cooling rates from the melt. In general, when the cooling rate is lower, molecular chains have sufficient time to arrange orderly, the crystallization always starts and finishes at higher temperatures. When the cooling rate is higher, it is too late to form nuclei at higher temperatures, so nucleation usually arises at lower temperatures. The crystallization peaks therefore become broader and shift to lower temperatures. However, TPER PI is very special as is shown in Figure 4(a), onset temperatures of the crystallization peaks are almost same in despite of different cooling rates, indicating the fast nucleation. Nonisothermal crystallization kinetics of TPER PI had been studied, and the crystallization activation energy (ΔE) was found to be -936 kJ mol^{-1} by Kissinger method, this value also proved fast nucleation rate of this system.[18] When TPER PI was cooled from melt at 2°C min^{-1}, only a singular exothermic peak was observed at 350°C, which moved towards to lower temperatures very slowly with the increase of the cooling rates. When the cooling rate was higher than 20°C min^{-1}, the exothermic peak at 350°C appeared as a shoulder of the primary exothermic peak. The reason for double crystallization behaviors of TPER PI had also been investigated via the study of the nonisothermal crystallization kinetics, the apparent Avrami exponent n obtained by the Jeziorny method changed from 2.4 to 3.5, indicating the mechanism of nucleation had changed.[18]

For co-PI A, double crystallization behaviors was observed in despite of different cooling rates as is shown in Figure 4(b). Positions of the first exothermic peaks at 358°C were found to be independent of cooling rates and the primary exothermic peaks moved towards to lower temperatures quickly with the increasing cooling rates, indicating that co-PI A exhibited lower crystallization rate than TPER PI when being cooled from the melt. It is well known that the properties of crystalline polymers are strongly dependent on the crystal structures formed during processing. To obtain products with better properties, it is significant to search for the optimum processing conditions in an industrial process. Since TPER PI exhibits extremely fast crystallization rate from the melt, crystallization progress of co-PI A is obviously much easier to be controlled.

Mechanical Properties

Since glass fibers can greatly improve the mechanical properties of composites, they have always been used to reinforce polyimide resins. However, the key feature for preparing fiber reinforced polyimide composites is to impregnate matrix resin on the surface of fiber uniformly, fiber aggregation, or cluster due to the different gravities of fibers and matrix resin solution should be avoided in the impregnation process.[19] So short glass fibers reinforced polyimide composites are always prepared by

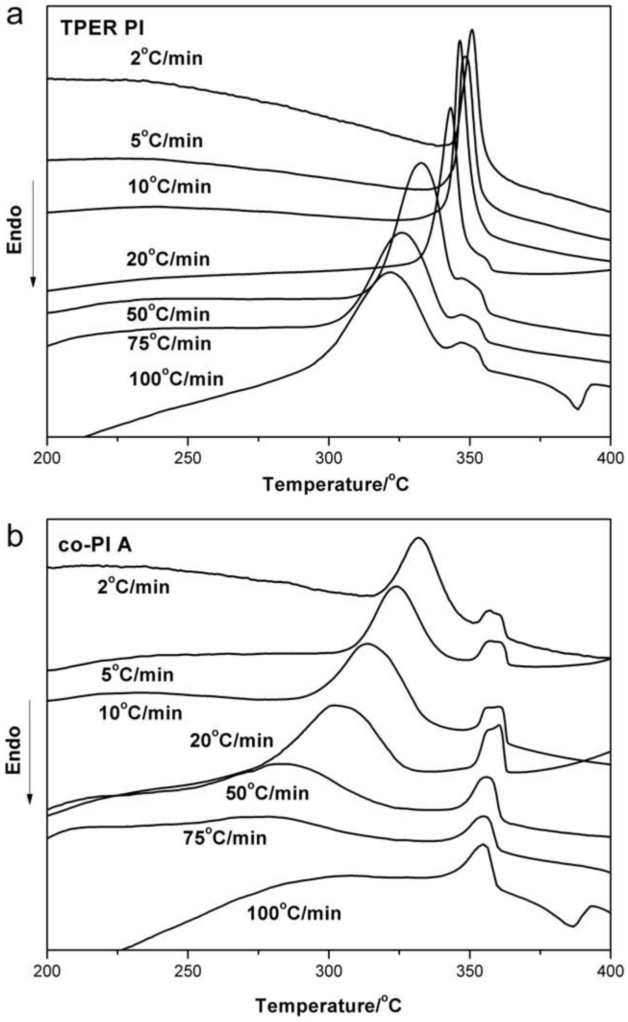

Figure 4. DSC cooling scans for TPER PI (a) and co-PI A (b) subjected to various cooling rates from the melt.

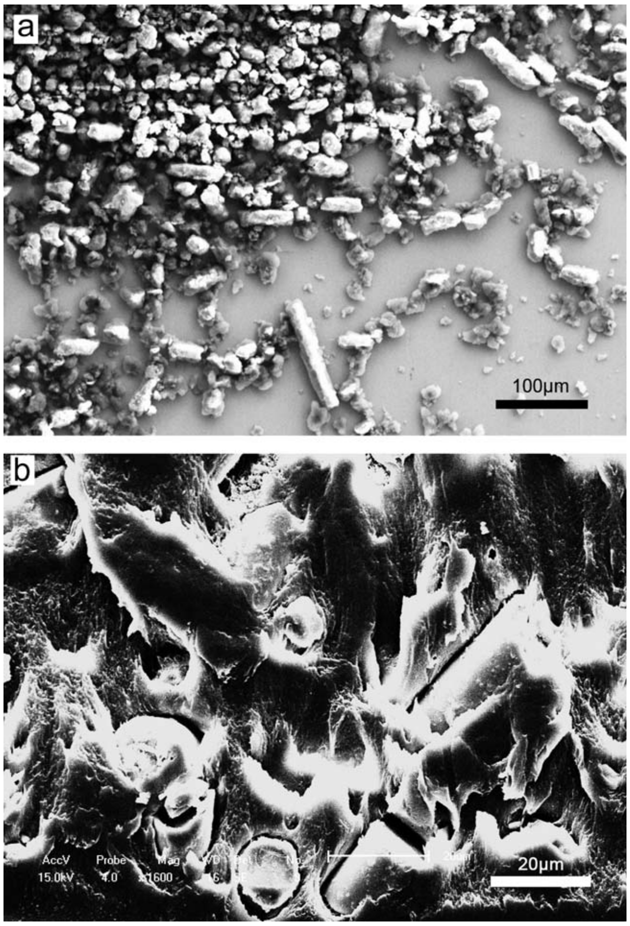

Figure 5. SEM photograph of the molding powder (a) and the composite (b) prepared from co-PI A and glass fibers.

wet impregnating chopped short fibers with PAA solution under strong stirring for a long time followed by evaporating the solvent. It is not only a waste of time and solvent, but also inappropriate for industry production. So the powdery glass fiber (5–50 μm of the length and 8–13 μm of the diameter) is adopted in this study. Although the mechanical properties of composites are supposed to be partially sacrificed, preparations of the molding powders would be much easier. They can be synthesized just by adding powdery glass fiber to poly(amic acid)s followed by solution imidization techniques.[13] In addition, powdery fibers were also expected to flow easily with the molten matrix resins in the thermal curing process so that the extrusion techniques or injection techniques would be suitable for fabricating some small and complicated parts. Figure 5(a) shows an SEM photograph of the molding powder. It can be seen that the particulates of glass fibers dispersed uniformly in the polyimide powders and no fiber clusters or aggregation was observed. Figure 5(b) shows an SEM figure of the fracture surface of the composite, which had been fractured in liquid nitrogen. It can be seen that the fibers were wrapped in a continuous polyimide resin phase and no voids or holes were detected.

Dynamical Mechanical Properties. As mentioned above, crystalline polyimides are supposed to exhibit better mechanical properties above glass transition temperatures, so they can be used at higher temperatures. Dynamical mechanical properties of the annealed films and the quenched films were therefore studied by DMA in this paper. In Figure 6(a), storage modulus of the quenched films decreased markedly when the temperature reached T_g, and then increased gradually as a result of cold crystallization. Storage modulus of TPER PI reached maximum at about 250°C, and the value was about 200 MPa. As the introductions of 4, 4′-ODA, co-PI A showed weaker crystallization capacity in comparison with TPER PI. Storage modulus of co-PI A reached maximum at about 260°C, and the value was only 100 MPa. The quenched composite behaved as same as TPER PI, it also started to crystallize earlier than co-PI A resin, indicating the existence of glass fibers had affected the crystallization progress. DMA curves of the annealed films are shown in Figure 6(b). Since there was sufficient time for nuclei formation and crystal growth when the films were cooled very slowly from the melt, all the polyimides displayed excellent retention of mechanical properties above T_g. Although co-PI A showed slightly lower storage modulus than TPER PI, it is still suitable for high temperature applications. In addition, storage modulus of co-PI A decreased earlier than TPER PI around melting temperatures, indicating the processing temperature of co-PI A should be lower. The composite displayed higher storage

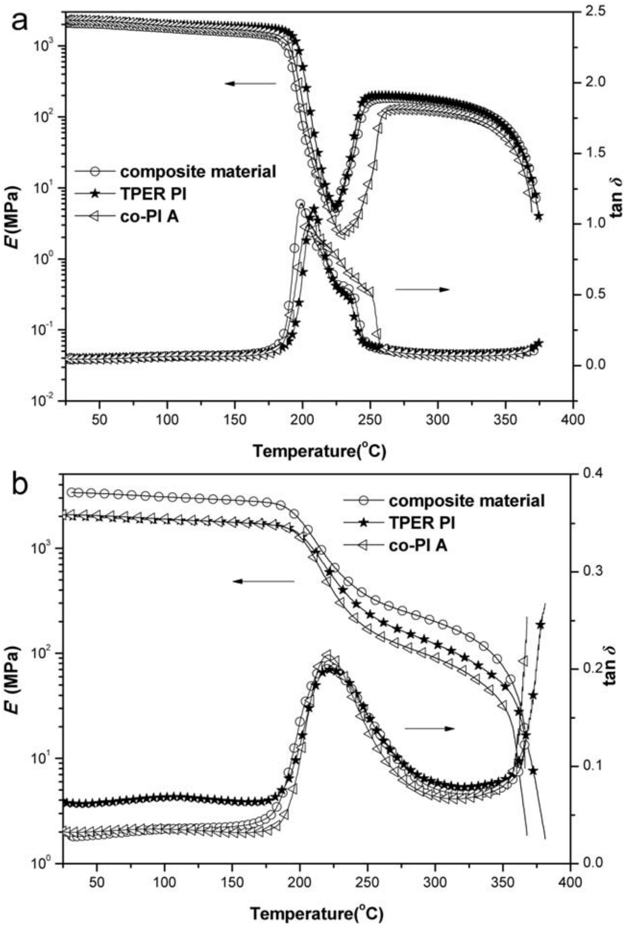

Figure 6. DMA curves of quenched films (a) and annealed films (b).

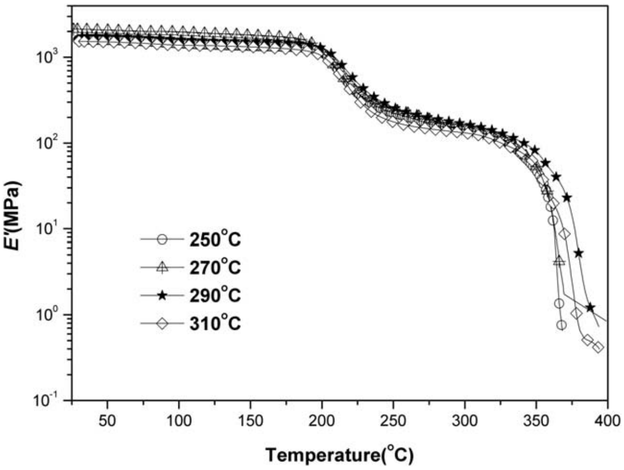

Figure 7. DMA curves of co-PI A after isothermally crystallizing at different temperatures.

modulus than neat resin, so they could be used at higher temperatures.[20]

Figure 7 shows the DMA curves of co-PI A after it was isothermally crystallized at different temperatures. Like in Figure 6(b), storage modulus above T_g maintained very well until the temperature reached T_m, and they showed slightly different after crystallized at different temperatures. Results indicated that crystal structures formed during isothermal crystallization process should be more perfect than those formed during cooling process. Storage modulus kept above 100 MPa even at 350°C.

Tensile Experiments. Tensile experiments were tested on film samples, including the quenched films and the isothermally annealed films. Testing temperatures were 25°C, 220°C, 250°C, and 280°C. Mechanical property of the composite was also tested. Table II summarizes the mechanical properties of the quenched samples when being tested at different temperatures. Co-PI A and TPER PI both exhibited more than 2000 MPa of modulus at 25°C, and about 1000 MPa of modulus at 220°C. When the testing temperatures were 250°C and 280°C, modulus of both polyimides decreased dramatically to only 1–2 MPa, indicating the quenched samples could be only used below glass transition temperatures. The composite exhibited higher modulus than the neat resin to a certain extent, but not very evidently. This should be attributed to the fillers, as is mentioned above. In comparison with chopped short glass fibers, although powdery glass fibers could benefit the preparation of molding powders, mechanical properties of composites would be partial sacrificed. Interestingly, the powdery glass fiber greatly increased the toughness of the composite at 220°C, as evidenced by 700% of the elongation and only 100 MPa of modulus. So the glass fiber here could be regard as a plasticizing agent.[21]

To investigate the mechanical properties of the crystalline samples, the quenched films were isothermally cold-crystallized at different temperatures and then were tested. Mechanical properties of the samples which have been crystallized at 250°C for 1 h can be seen in Table III. When being tested at 25°C and 220°C, they displayed a little higher modulus than quenched samples. When the testing temperature was 250°C, crystalline samples maintained the excellent mechanical properties, and the storage modulus reached 200 MPa, which were about 10^3 times higher than that of the quenched samples. With the increase of testing temperatures, max strength decreased, whereas the elongations increased markedly. In comparison with the neat resin, the composite always exhibited higher modulus, but lower max strength at 25°C and lower elongations at higher temperatures. Table IV summarizes the mechanical properties of co-PI A and the composite after they had been crystallized at 280°C for 1 h. The neat resin and the composite both displayed excellent mechanical properties at 280°C, as evidenced by more than 200 MPa of the storage modulus. The neat resin also displayed lower max strength and higher elongations with the increase of testing temperatures. As is shown in Figure 2, co-PI A started to crystallize at 250°C and finished at 280°C, so the crystal structure formed at 280°C should be more perfect than that formed at 250°C, and this had already been proved by XRD experiments. So when co-PI A crystallized at 250°C was tested at 220°C and 250°C, molecular chains could move freely and continued to arrange orderly, elongations therefore increased. However, since co-PI A crystallized at 280°C had been almost

Table II. Mechanical Properties of Quenched Films When Being Tested at Different Temperatures

Samples	Testing temperature (°C)	Modulus (MPa)	Max strength (MPa)	Elongation (%)
Co-PI A	25	$(2.1 \pm 0.2) \times 10^3$	87 ± 2	64 ± 10
	220	$(1.1 \pm 0.1) \times 10^3$	15 ± 2	260 ± 40
	250	1.4 ± 0.2	1.2 ± 0.1	650 ± 100
	280	0.2 ± 0.1	0.3 ± 0.1	400 ± 100
TPER PI	25	$(2.1 \pm 0.2)\times 10^3$	74 ± 6	30 ± 10
	220	$(0.9 \pm 0.1)\times 10^3$	11 ± 1	260 ± 40
	250	1.4 ± 0.5	1.1 ± 0.1	500 ± 100
	280	2 ± 0.3	2 ± 1	200 ± 20
Composite materials	25	$(2.6 \pm 0.2)\times 10^3$	78 ± 3	5 ± 0.5
	220	$(0.1 \pm 0.03)\times 10^3$	7 ± 2	700 ± 100
	250	60 ± 10	4 ± 1	300 ± 100
	280	200 ± 20	6 ± 1	60 ± 20

Table III. Mechanical Properties of Films Cold-Crystallized at 250°C for 1 h When Being Tested at Different Temperatures

Samples	Testing temperature (°C)	Modulus (MPa)	Max Strength (MPa)	Elongation (%)
Co-PI A	25	$(2.2 \pm 0.2)\times10^3$	90 ± 5	9 ± 1
	220	$(1.2 \pm 0.1)\times10^3$	20 ± 2	120 ± 20
	250	$(0.2 \pm 0.02)\times10^3$	10 ± 2	450 ± 30
TPER PI	25	$(2 \pm 0.2)\times10^3$	65 ± 5	7 ± 2
	220	$(1.2 \pm 0.1)\times10^3$	22 ± 2	40 ± 10
	250	$(0.2 \pm 0.02)\times10^3$	10 ± 2	400 ± 40
Composite materials	25	$(3.1 \pm 0.2)\times10^3$	50 ± 10	2 ± 1
	220	$(1.8 \pm 0.1)\times10^3$	30 ± 4	12 ± 4
	250	$(0.3 \pm 0.05)\times10^3$	11 ± 1	15 ± 3

Table IV. Mechanical Properties of Films Cold-Crystallized at 280°C for 1 h When Being Tested at Different Temperatures

Samples	Testing temperature (°C)	Modulus (MPa)	Max Strength (MPa)	Elongation (%)
Co-PI A	25	$(2.2 \pm 0.2)\times10^3$	90 ± 10	5 ± 2
	220	$(1 \pm 0.2)\times10^3$	18 ± 2	5 ± 1
	250	$(0.2 \pm 0.05)\times10^3$	13 ± 2	40 ± 20
	280	$(0.2 \pm 0.1)\times10^3$	10 ± 1	400 ± 100
Composite materials	25	$(2.6 \pm 0.2)\times10^3$	41 ± 10	5 ± 1
	220	$(1.6 \pm 0.2)\times10^3$	32 ± 2	10 ± 2
	250	$(0.5 \pm 0.1)\times10^3$	15 ± 2	14 ± 2
	280	$(0.2 \pm 0.05)\times10^3$	10 ± 2	10 ± 2

completely crystallized, crystal perfection cannot be improved further when being tested at 220°C and 250°C, elongations were therefore small. When the testing temperature reached 280°C, crystal structure formed previously could be perfected further as a function of tensile force, elongations therefore increased again. Like in Table III, the composite also displayed lower max strength at 25°C in comparison with the neat resin, but it displayed worse toughness at higher temperatures as evidence by lower elongation in Table IV.

Melt Viscosity Studies

Since melt processing is more desirable from both economical and environmental standpoint, the synthesis of melt processable, thermally stable resin is one of prime interest. Thermal stability of this copolyimide under harsh melting conditions had been studied by TGA. However, TGA technique by itself is inadequate for reflecting the thermal stability of polymers, because degradation reactions such as cross linking or chain extension could occur with a small accompanying weight loss. So, rheological analysis was also carried out in this article. Effect of melting temperatures on melt viscosity of co-PI A was firstly investigated. Generally, cross linking and chain extension are prone to occur with the increasing of curing temperatures, along with the increasing of molecular weight, melt viscosity increases finally. Co-PI A was melt at a certain temperature for 30 min and then was isothermally tested at 420°C for 1 h in nitrogen, because 420°C is required during injection processing of TPER PI. As is shown in Figure 8, this copolyimide displayed outstanding thermal stability. Melt viscosities increased from 12,000 Pa s to 18,000 Pa s after the samples had been melted at 410°C, 420°C, and 430°C for 30 min, respectively. After the sample was melted at 400°C for 30 min, the melt viscosity rose evidently from 6000 Pa s and reached 10,000 Pa s at last. In addition, co-PI A exhibited better thermal stability than TPER PI as evidence by lower melt viscosity after being melted at 420°C for 30 min. So co-PI A will be more suitable for melt processing.

Except for the higher T_m and higher melt viscosity, TPER PI has another shortcoming. As is shown in Figure 4(a), TPER PI displayed extremely fast crystallization rate and it started to

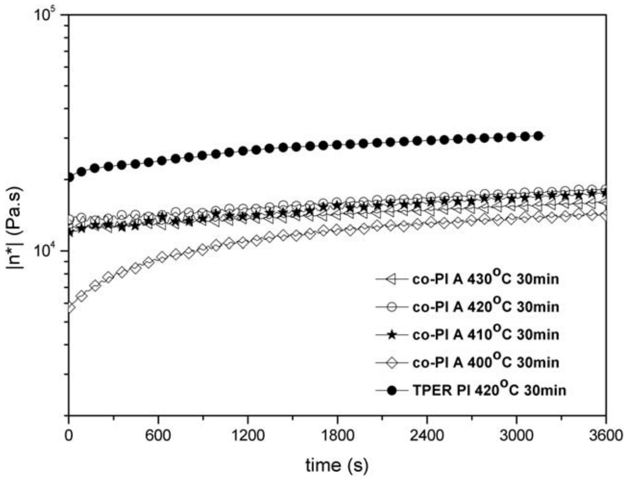

Figure 8. Effect of melting temperatures on the melt viscosities of co-PI A.

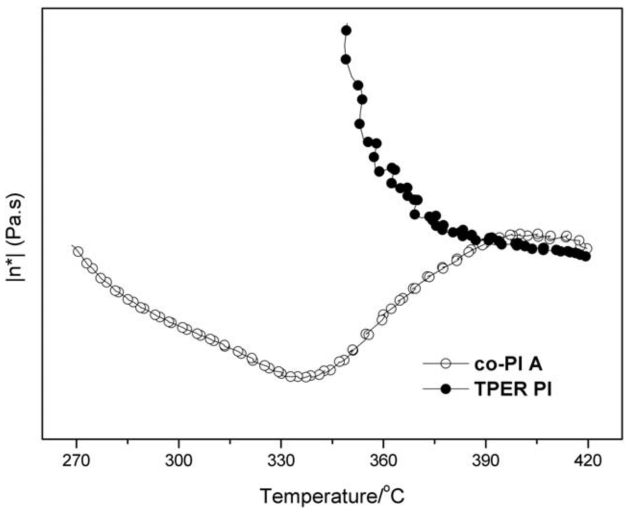

Figure 9. Melt viscosities of TPER PI and co-PI A when being cooled from 420°C at 4°C min^{-1}.

crystallize at about 360°C when being cooled from the melt. This would result in marked increase of the melt viscosity. To investigate the change of melt viscosity during cooling process, rheological analysis under nonisothermal conditions was also carried out. Samples were melted at 420°C for 30 min at first and then were cooled at 4°C/min. As is shown in Figure 9, viscosity of TPER PI increased evidently at 360°C as a result of crystallization, and this would result in a series of problems during actual processing. As soon as TPER PI was injected into a matrix, the resin started to crystallize and melt viscosity would increase remarkably, which may result in the defect of products. However, co-PI A started to crystallize at around 325°C when being cooled at 5°C min^{-1} as is shown in Figure 4(b), so the melt viscosity was expected to increase at 325°C. The resin therefore could fully fill in the matrix before the viscosity increased. Figure 9 approved this hypothesis again, and the melt viscosity of co-PI A increased remarkably around 330°C as expected. Surprisingly, the melt viscosity of co-PI A decreased remarkably at first. This should be attributed to shrinkage of the resin when temperature decreased. Since parallel plates fixture were used in this experiment, the resin disengaged the plates because of the shrinking, leading to the decrease of the melt viscosity. Anyhow, co-PI A exhibited lower melt viscosity than TPER PI during melting and after being injected into a matrix, so it should be more suitable for melt processing.

CONCLUSIONS

A semicrystalline copolyimide and glass fiber reinforced composite materials were prepared. The copolyimide exhibited lower T_m, lower melt viscosity and lower crystallization rate in comparison with TPER PI, indicating it would be more suitable for melt processing and the crystallization progress would be much easier to be controlled. The superior processability combined with great mechanical properties and excellent retention of mechanical properties at elevated temperature will make this copolyimide become a very attractive thermo-oxidative stable material in the future.

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