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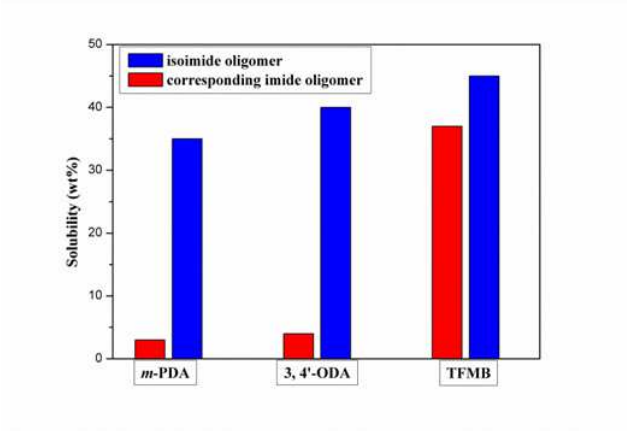
Highly soluble phenylethynyl-terminated isoimide oligomers were investigated as matrix resins which can produce high performance thermosetting polyimides and composites.



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Thermosetting polyimides and composites based on highly soluble phenylethynyl-terminated isoimide oligomers

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Highly soluble phenylethynyl-endcapped isoimide oligomers were synthesized using 2, 3, 3', 4'-biphenyltetracarboxylic dianhydride (3, 4'-BPDA) and aromatic diamines as the monomers, 4-phenylethynyl phthalic anhydride (4-PEPA) as the end-capping reagent, and trifluoroacetic anhydride as the dehydrating agent; then high performance thermosetting polyimides and composites were produced from these oligomers via the thermal crosslinking reaction of phenylethylnyl group and the material properties were fully investigated. A series of isoimide oligomers with different molecular weights and a variety of chemical architectures were prepared by polycondensation of 3, 4'-BPDA, 4-PEPA, and aromatic diamines including *m*-Phenylenediamine (*m*-PDA), 2, 2'-bis (trifluoromethyl) benzidine (TFMB), 3, 4'-oxydianiline (3, 4'-ODA), followed by cyclization with trifluoroacetic anhydride. These isoimide oligomers were characterized by means of gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), rheological measurements, intrinsic viscosity measurement, and solubility tests. Compared to their imide analogues, isoimide oligomers showed much higher solubility in low boiling point solvents, and slightly lower melt viscosity, which can be attributed to their unique asymmetric architecture. These resins were formulated into thermosetting polyimides and composites by thermal crosslinking of phenylethynyl group and conversion from isoimide to imide at elevated temperatures. The properties of the thermosets and composites were studied using mechanical property measurements, dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). The cured polyimides exhibited extremely high glass transition temperatures (T_g) up to 467 °C, and 5% weight loss temperatures ($T_{5\%}$) up to 584 °C in nitrogen atmosphere. The polyimide/quartz fiber composites possessed excellent high temperature mechanical properties due to the high glass transition temperatures of matrix resins.

1. Introduction

Aromatic polyimides are a class of polymers featured with high glass transition temperatures, high thermal stability, excellent mechanical and electrical properties, and good chemical resistance.[1-4] Therefore, polyimides have been widely utilized for a variety of applications in the electronics, automotive, and aerospace industries. In aerospace industry, thermosetting polyimides have been used as matrix resins in carbon fiber reinforced composites as replacements for metallic components in the engines and aircraft frames, due to their high strength-to-weight ratio and outstanding heat resistance. The excellent overall properties of polyimides are regarded as a consequence of their chain rigidity and strong inter- and intro-molecular interactions. However, these interactions in polyimides also give rise to high melt viscosity and limited solubility in organic solvents, which augments the difficulties in the fabrication of composites and articles.[5]

In 1970s, PMR-type (Polymerization of Monomer Reactants *in-situ*) thermosetting polyimide resins were developed to improve processability, using a methanol solution of monomers and end-capping reagent. PMR-15 (based on 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4, 4'-diaminodiphenylmethane) and PMR-Ⅱ-50 (based on 4, 4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and *p*-phenylenediamine) have been widely utilized as thermosetting resins for carbon fiber reinforced composites. These composites showed a long-term use temperature of 316 (PMR-15-based) and 371 °C (PMR-Ⅱ-50-based), respectively.[6-10] However, there are some obstacles existing in PMR-type resins and composites, including the brittleness of cured resins (low elongation at break and low impact resistance), and the release of volatiles during processing. The latter can result in voids or pin holes in the finished products.[11, 12]

Since 1985, considerable efforts had been made in the area of imide oligomers end-caped with 4-phenylethynyl anhydride (PEPA). Compared to nadic anhydride (NA) endcap, PEPA can provide a wider processing window, as well as high toughness of cured products. Among PEPA-terminated imide oligomers, PETI-5, based on 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (4, 4'-BPDA), had been extensively investigated as adhesives and composite matrix resins since it afforded polyimides with an excellent combination of thermal stability, adhesion, and toughness. However, these polyimides exhibited only a moderate glass transition temperature of 270 °C.[13] Since 2000, 3, 4'-BPDA-based, PEPA-terminated imide oligomers (TriA-PI) were developed by Yokota et al.[14] These oligomers showed improved solubility, reduced viscosity, and higher glass transition temperatures than those based on 4, 4'-BPDA, which can be attributed to the decrease of intermolecular interaction stemmed from its asymmetric and non-coplanar architecture, as well as the restricted rotation around the single bond adjacent to phthalimide. Due to their low viscosity, 3, 4'-BPDA-based resins can even be adapted to inexpensive process, such as resin transfer molding (RTM) system which is traditionally used for epoxy or bismaleimide resins.[15, 16]

Imide oligomers are usually synthesized as amide acid solution in aprotic solvents due to their limited solubility in fully imidized form.[17-19] In this route, water was released as the by-product of imidization in fabricating process. The evaporation of water and other volatiles after applying consolidation pressure can cause voids or pin holes in the finished composites. To achieve void-free laminates, many research efforts have been devoted to developing imide oligomers with high solubility in organic solvents in their fully imidized form. The synthetic strategies to improve the solubility of polyimides have been well established in the past few decades. Efficient approaches included the incorporation of flexible links (-O-, -S-, -CO-, -SO2-, -CH2-, etc.),[20-22] the attachment of bulky pendent groups,[23-26] the involvement of noncoplanar moieties, and the introduction of asymmetric monomers.[27-40] However, the thermal and mechanical properties of modified polyimides were usually compromised for better oligomer solubility in organic solvents. There is still a tradeoff between material property and oligomer solubility in organic solvents in the field of thermosetting polyimides.

Polyisoimides were considered as attractive precursors of polyimides.[41-46] Polyisoimides exhibited greater solubility, lower melt viscosity, and lower melting point than their polyimide analogues. More importantly, polyisoimides can be readily converted to the corresponding polyimides by thermal treatment, without the release of water or other volatile by-products. The combination of improved solubility and thermal convertibility to imide offered an alternative route to polyimide processing. Thus, advantages of these characteristics of isoimides have been taken in the fabrication of void-free composites. So far, most of isoimide oligomers were terminated with acetylene group to lower the melting temperature, considering that the curing temperature of acetylene group falls in the range of 180-250 °C. Thermid IP-600 and Thermid FA-700,[47] now produced by National Starch and Chemical Corp., displayed better processability compared to their imide counterparts, whereas the processability was not sufficient for big or complex articles. Recently, acetylene-terminated isoimide oligomers based on 3, 4'-BPDA, aromatic diamines, and 3-aminophenyl acetylene were developed in our group. These oligomers showed improved processability while maintaining reaseanable thermal and mechanical properties of cured resins.[48] However, to the best of our knowledge, no reports on phenylethynyl-terminated polyisoimides as matrix resins can be found in the literature.

In this study, we report the synthesis and characterization of phenylethynyl-terminated isoimide oligomers. These oligomers showed much higher solubility in low boiling point organic solvents (e.g. tetrahydrofuran and 1, 4-dioxane) than their imide counterparts, which is highly desired for the fabrication of void-free composites. The isoimide oligomers were then cured at elevated temperature, and the thermal and mechanical properties of cured polymers and composites were also investigated. The structure-property relationship for this series of thermosetting polymers was also elucidated, and some insights were provided about the design of matrix resins with a combination of high proccessability and excellent material properties.

2. Experiment

2.1 materials

m-Phenylenediamine (*m*-PDA) was purchased from Tianjin Guangfu Fine Chemical Research Institute. 3, 4'-Oxydianiline (3, 4'-ODA) and 2, 2'-Bis (trifluoromethyl) benzidine (TFMB) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. *m*-PDA and 3, 4'-ODA were purified by distillation under reduced pressure. 3, 4'-BPDA and 4-PEPA were prepared in our laboratory according to the procedures in the literatures.[49, 50] Trifluoroacetic anhydride (TFAA) was obtained from Shanghai Bangcheng Chemical Industry Co., Ltd. All other reagents were supplied by Tianjin Tiantai Fine Chemical Industry Co., Ltd. The chemicals were used as received unless specified.

2.2 Synthesis of isoimide and imide oligomers

The isoimide oligomers with a variety of molecular weights were prepared from the reaction of 3, 4'-BPDA, PEPA, and diamines (3, 4'-ODA, *m*-PDA, and TFMB) in NMP at room temperature. Three imide oligomers were also synthesized for comparison. Representative procedure for the oligomers synthesis is shown below.

2.2.1 Synthesis of isoimide oligomer (PII-PDA-2). To a flame-dried 250 ml, three-necked, round–bottomed flask equipped with nitrogen inlet/outlet and magnetic stirrer were added *m*-PDA (5.51 g, 50.98 mmol) and NMP (25 mL). The mixture was stirred at room temperature until *m*-PDA completed dissolved. Then, 3, 4'-BPDA (10.00 g, 33.99 mmol) was gradually added over 15 minutes. Another 25 mL of NMP was added to dilute the solution. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 6 hours. PEPA (8.44 g, 33.99 mmol) and NMP (50 ml) were added to the reaction mixture. The reaction mixture was then stirred at room temperature for another 12 hours. After cooled in ice-water bath, TFAA (26.82 g, 127.69 mmol), and triethylamine (10.22 g, 101.00 mmol) were added dropwise with stirring during 6 hours at 0 °C. The resulting isoimide solution was poured into a large excess amount of deionized water. The precipitate was collected by filtration, washed thoroughly with deionized water until the pH value of the filtrate reached about 7, and dried under vacuum at 60 °C for 10 hours, 110 °C for 2 hours, and 140 °C for 2 hours to yield a bright yellow powder with a yield of 95% (22.12 g). IR (KBr, cm^{-1}): 2214 (C≡C str), 1797 (C=O str), 908 (C-O-C str).

2.2.2 Synthesis of imide oligomer (PI-PDA-2). To a flame-dried 250 ml, three-necked, round–bottomed flask equipped with nitrogen inlet/outlet and magnetic stirrer were added *m*-PDA (5.51 g, 50.98 mmol), and NMP (25 mL). The mixture was stirred at room temperature until *m*-PDA completely dissolved. Then, 3, 4'-BPDA (10.00 g, 33.99 mmol) was gradually added over 15 minutes. Another 25 ml of NMP was added to dilute the solution. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 6 hours. PEPA (8.44 g, 33.99 mmol) and NMP (50 ml) were added to the mixture. The reaction mixture was then stirred at room temperature for another 12 hours. Then acetic anhydride (13.00 g, 127.38 mmol) and triethylamine (4.38 g, 43.33 mmol) were added dropwise with stirring during 6 hours at room temperature. The resulting solution was poured into a large excess amount of ethanol. The precipitate was collected by filtration, washed thoroughly with deionized water until the pH value of the filtrate was about 7, and dried under vacuum at 60 °C for 10 hours, 110 °C for 2 hours, and 140 °C for 2 hours to yield a yellow powder with a yield of 90% (20.96 g). IR (KBr, cm^{-1}): 2214 (C≡C str), 1779,1720 (C=O str), 1361 (C-N).

2.3 Processing

2.3.1 Curing of the oligomers. Isoimide oligomers in powder form were compression-molded in stainless steel mold (80 mm×100 mm) with a hot press. The isoimide oligomers (ca. 35 g) were heated to 320 °C for 40 minutes on a hot plate. Then pressure (~2 MPa) was applied and the temperature was raised to 371 °C in 20 minutes, and held at 371 °C for 2 hours. The cured resins were cooled under pressure to about 150 °C, and the pressure was subsequently released. The polyimide sheets were removed from the mold and stored under ambient condition before subjected to characterization.

2.3.2 Composite fabrication. Isoimide oligomers in tetrahydrofuran (THF) (30-35%) were filtrated to remove the insoluble impurities, and then coated onto quartz fiber cloth. The coated cloth was dried in a chamber at 60 °C for 12 hours. Laminates were fabricated in stainless steel mold (80 mm×100 mm) using a hot press process (Figure 13). A typical procedure follows: the prepregs were heated to 240 °C in 1 hour and held at 240 °C for 1 hour. The temperature was raised over 20 minutes to 310 °C, and then a pressure of about 2 MPa was applied. The temperature was ramped to 371 °C, and held at 371 °C for 2 hours under the applied pressure. After cooled to 150 °C, the pressure was subsequently released. Then the cured composite laminates were removed from the mold and stored under ambient condition before subjected to characterization.

2.4. Characterization

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 analysis system at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Thermal stability was evaluated using a Perkin-Elmer TGA 2 analysis system with a heating rate of 10 °C/min under a continuous nitrogen or air flow. Molecular weights of isoimide oligomers were measured using a PL-GPC 120 gel permeation chromatography (GPC). THF was used as the eluent, and molecular weights were determined using polystyrene standards. Fourier transform infrared spectroscopy (FTIR) was performed using a Bio-Rad Digilab Division FTS-80 spectrometer. Inherent viscosities were determined at 25 °C with an Ubbelodhe viscometer, and the concentration was 0.5 g/dL in NMP. Complex viscosity measurements were conducted on an AR2000ex rheometer (TA Instruments, USA), with a fixed strain of 5% and a fixed angular frequency of 10 rad s^{-1}. The resin disks with a diameter of 2.54 cm and a thickness of 1 mm thickness were prepared by press-molding the pretreated resin powders at room temperature. The complex viscosity (η^*) was measured from 200 to 400 °C at a heating rate of 4 °C min^{-1} under a continuous air flow. The isothermal viscosities of the resins were also measured at 280, 300, and 320 °C. Dynamic mechanical thermal analysis (DMTA) was performed on a Q800 DMTA (TA Instruments) with a frequency of 1 Hz and a heating rate of 3 °C/min from 100 to 550 °C under nitrogen atmosphere. Glass transition temperature (T_g) was determined as the peak temperature of tan δ curve. Wide angle X-ray diffraction measurements were undertaken on a D8 ADVANCE X-ray diffractometer (Germany) with a wavelength of 1.54 Å using copper radiation (40 kV, 200 mA) with a scanning rate of 3 °/min from 5 to 50°. The volume and mass fractions of the fibers in the composites were determined by loss-on-ignition test. Mechanical properties of thermosetting polyimides and composites were measured on an Instron material testing system (Model 5982, Instron, USA) under a constant displacement rate of 2.0 mm/min. Five samples were tested for each thermoset or composite, and the averages were reported. Specimens were equilibrized for 10 minutes at the targeted temperatures before the tests.

3. Results and discussion

3.1. Oligomer synthesis

It has been well documented that polyisoimides are preferred instead of polyimide when poly(amic acid)s are chemically cyclized with the use of anhydrides and acid halides derived from strong acids, and strong Lewis acids such as PCl_3.[1] As depicted in Scheme 1, three series of phenylethynyl-endcapped isoimide oligomers were prepared by a two-step procedure, using 3, 4'-BPDA and aromatic diamines (3, 4'-ODA, *m*-PDA, TFMB) as the monomers. Stoichiometric amounts of anhydride and amine groups were used in all cases. Amic acids were firstly formed by reacting anhydrides with amines in NMP, and then chemically converted into isoimide oligomers by treatment with trifluoroacetic anhydride and triethylamine. Conversely, imide oligomers were produced when amic acids were dehydrated with a combination of acetic anhydride and triethylamine. The oligomers were named by the chemical nature, diamine used, and degree of polymerization, e.g. PII-PDA-1 is the *m*-PDA-based isoimide oligomer with a degree of polymerization 1, and PI-TFMB-2 is the TFMB-based imide oligomer with a polymerization degree of 2.

FTIR spectra of PII-ODA-2, PII-PDA-2, and PII-TFMB-2 are shown in Figure 1. The bands around 1800 and 905 cm^{-1} were assigned to the characteristic absorptions of C=O asymmetric stretching and the isoimide vibration, respectively. Furthermore, no peaks can be found around 1850 cm^{-1} (for the carbonyl group of cyclic anhydride) and 1375 cm^{-1} (for the C-N bond in imide group), which demonstrated the successful synthesis of isoimide oligomers. The characteristic peaks at 2210 cm^{-1} are attributed to the stretching vibration of ethynyl C≡C group, which confirmed the existence of end group.

The intrinsic viscosities, molecular weights, and thermal properties of isoimide oligomers are summarized in Table 1. The molecular weights of the oligomers were controlled by stoichiometrically adjusting the ratios of dianhydride, diamine, and end-capping reagent. In general, the measured number average molecular weights (M_n) agreed with the calculated ones, indicating that the targeted molecular weights were achieved. The intrinsic viscosities of isoimide oligomers were in the range of 0.07-0.12 dL/g. As expected, the intrinsic viscosities increased with the increase of molecular weights. In addition, the intrinsic viscosities of isoimide oligomers were lower than those of corresponding imide oligomers due to their asymmetric architectures.

3.2. Properties of isoimide oligomers

3.2.1 Thermal properties of the isoimide oligomers. The glass transition temperatures (T_g) of isoimide oligomers were determined by DSC. The molecular weights and the structures of diamines had a great impact on the thermal properties of the oligomers. For a given diamine, the T_g values increased with the increase of molecular weights as expected. Meanwhile, the T_g values of isoimide oligomers were lower than the corresponding imide oligomers. For a given degree of polymerization, the T_g values of the isoimide oligomers followed the trend of PII-PDA-n＞PII-ODA-n＞PII-TFMB-n. This phenomenon could be attributed to the difference in the free volume of the oligomers. The flexible linkage of ether segment or the bulky pendent groups of TFMB gave rise to higher free volume, which facilitated chain mobility and led to lower T_g values. Due to their different backbone structures (imide *vs* isoimide), the T_g trend for imide oligomers was different from that for isoimide oligomers. Except for oligomers with a degree of polymerization of 1, the T_g value difference between TFMB and 3, 4'-ODA-based oligomers was minor for a given degree of polymerization.

3.2.2 Solubility of isoimide oligomers. Volatiles management is a crucial and challenging issue during the fabrication of polyimide composites. Volatiles need to be completely removed before applying pressure. Otherwise, the evaporation of volatiles will give rise to voids or pin holes and severely affect the composite properties. However, most of imide oligomers are prepared as amic acid form, which release water as the by-product of imidization at elevated temperature. Furthermore, the imidization temperature usually overlaps with crosslinking temperature of end groups, which makes the depletion of water impossible before the application of pressure. Therefore, fully imidized oligomers with good solubility are highly desired for the fabrication of void-free composites. Recently, Yokota et al reported a series of highly soluble imide oligomers (more than 30 wt.% in NMP) based on pyromellitic dianhydride (PMDA) and 2-phenyl-4, 4-diaminodiphenyl ether.[51] However, the choice of the monomers for soluble imide oligomers are usually limited, and the heat resistance of the cured articles are compromised to achieve high solubility. Furthermore, high boiling point solvents are indispensible for most of imide oligomers. From a processing point of view, low boiling point solvents are definitely preferred for high quality composites since they are much easier to remove. Isoimides can offer an efficient approach to enhancing the oligomer solubility without sacrificing chain rigidity of oligomers and consequently the thermal and mechanical properties of the cured polymers and composites. As shown in Table 2, all isoimide oligomers were soluble in DMAc, DMF, NMP, DMSO, THF and dioxane at room temperature. As illustrated in Figure 2, isoimide oligomers with a degree of polymerization of 2 showed solubility up to 35 wt.% at 30 °C and 60 wt.% at 70 °C in DMAc. In contrast, the solubility of the corresponding imide oligomers was lower than 10 wt.% at 30 °C and 20 wt.% at 70 °C in DMAc. More importantly, the solubility of three isoimide oligomers was more than 30 wt.% in the low boiling point solvents (THF and dioxane), while the solubility of PI-PDA-2 and PI-ODA-2 was lower than 5 wt.% (Figure 3). The imide oligomers based on TFMB showed much higher solubility in low boiling point solvents due to their twisted biphenyl architecture. The enhanced solubility for isoimide oligomers can be explained in terms of their asymmetric architectures, which hindered the chain packing and therefore reduced the formation of charge transfer complex. Among all the isoimide oligomers, TFMB-based ones exhibited the highest solubility due to the low polarity of fluorine and the twisted biphenyl segments. Due to their high solubility in THF and dioxane, these isoimide oligomers could be adapted to wet prepreg process to yield composites with a combination of low void contents, high glass transition temperatures, and excellent mechanical properties, while the analogous imide oligomers derived from *m*-PDA and 3, 4'-ODA are not suitable for wet prepreg process because of their limited solubility in the low boiling point solvents.

3.2.3 Rheological properties of the isoimide oligomers. The viscosity profiles of the isoimide oligomers were detailedly characterized by rheological measurements, and the results are listed in Table 3. The viscosity values of the benchmark imide oligomers, e.g. PETI-1.25K PETI-2.5K,[18] and TriA-PI (n=4.5)[14] are also included for comparison. For a given degree of polymerization, the complex viscosity of the isoimide oligomers followed the trend of PII-PDA-n＞PII-TFMB-n＞PII-ODA-n. 3, 4'-ODA-based oligomers showed much lower minimum viscosity for a given degree of polymerization, which can be contributed to their flexible ether linkage and asymmetric structure. The minimum viscosity of *m*-PDA-based oligomers was higher than that of TFMB-based ones due to the lack of flexible linkages. All isoimide oligomers displayed significantly lower viscosity compared to the benchmark imide oligomers (PETI-1.25, PETI-2.5,[18] and TriA-PI (n=4.5)[14]) with similar molecular weights. The representative rheological curves of TFMB-based isoimide oligomers are compared in Figure 4. The minimum melt viscosity of the isoimide oligomers increased as the degree of polymerization increased. Furthermore, the viscosities of the oligomers dropped as the temperature increased, down to their lowest values, and then increased sharply when the temperature reached around 340-350 °C due to the crosslinking reaction of phenylethynyl groups.

The complex viscosities for isoimide and imide oligomers as a function of temperature are compared in Figure 5. All the isoimide and imide oligomers were treated at the same temperature prior to viscosity measurements. The isoimide oligomers showed slightly lower viscosity values than the corresponding imide oligomers, which indicated their improved processability. The lower viscosity of isoimide oligomers can be explained in terms of their unique asymmetric architectures, which can reduce the chain linearity, and inter- and intro-molecular interactions.

Isoimide can be converted to imide upon heating, which can dramatically influence the viscosity of the oligomers. Therefore, the effect of pretreatment temperatures on the complex viscosity of PII-TFMB-2 was investigated. The representative complex viscosity curves for isoimide oligomers were displayed in Figure 6. For PII-TFMB-2, the minimum melt viscosity increased from 20 to 68 Pa.s when the pretreatment temperature was raised from 140 to 240 °C, due to the conversion from isoimide to imide. The conversion from isoimide to imide was also confirmed by FTIR. As illustrated in Figure 7, the absorption bands around 1806 cm^{-1}, assigned to the characteristic absorption for stretching of C=O in isoimide group, disappeared after treatment at 240 °C for 2 hours. Meanwhile, new peaks around 1780, 1720, and 1370 cm^{-1}, which represent the C=O and C-N groups in imide, appeared in FTIR spectra. FTIR results indicated that isoimide can be readily converted to imide upon heating.

The viscosity stability of oligomers has a great effect on the process window, which is very important for the composite fabrication process. Therefore, isothermal complex viscosities of representative isoimide oligomers were evaluated at 280 °C, 300 °C, and 320 °C, and the results are shown in Figure 8 and Table 4. The viscosities of the oligomers increased slowly at 280 and 300 °C, whereas increased rapidly at 320 °C due to the crosslinking reaction of phenylethylnyl groups.

3.2.4 X-ray diffraction of the isoimide oligomers. The crystallinity of isoimide oligomers was examined by wide angle X-ray diffraction. As shown in Figure 9, all of the oligomers showed amorphous patterns.

3.3. Properties of the cured resins and composites

3.3.1 Thermal and mechanical properties of the cured resins. The thermal stability of cured polyimide thermosets was characterized by thermogravimetric analysis (TGA), and the results are listed in Table 5. The $T_{5\%}$ and $T_{10\%}$ values of the thermosets in air spanned a range of 550-569 °C and 566-591 °C, respectively. As shown in Figures 10 and 11, no obvious weight loss of cured resins was detected until the temperature was ramped to 500 °C. These results demonstrate that all thermosets possessed excellent thermo-oxidative stability.

The glass transition temperatures (T_g) of cured resins were characterized via DMTA, and the results are summarized in Table 5. The T_g values of *m*-PDA and TFMB-based thermosets are much higher than those of benchmark thermosetting polyimides, such as PMR-15 (340 °C),[6-10] PETI-5 (270 °C),[13] and TriA-PI (343 °C)[14]. The incorporation of rigid diamines in isoimide oligomers accounted for the high *Tg* values of cured resins. The T_g values of most of thermosets followed the trend of PII-TFMB>PII-PDA>PII-ODA, ranging from 315 to 467 °C. The T_g values of the thermosets based on oligomers with a degree of polymerization of 1 didn't follow this trend. Thermoset based on PII-PDA-1 showed the highest T_g value. The T_g values of the thermosets are affected by two factors: crosslinking densities and chain rigidity. Thermosets based on 3, 4'-ODA showed the lowest T_g values for a given degree of polymerization, due to their flexible ether linkage. Thermosets derived from TFMB showed higher chain rigidity but lower crosslinking densities than those from *m*-PDA for a given degree of polymerization. When the crosslink densities were low, T_g values were dominated by chain rigidity since the spacers between two crosslinking sites have sufficient mobility to rotate at high temperature. Therefore, thermosets derived from TFMB with degrees of polymerization of 2, 3, and 4 exhibited higher T_g values than those from *m*-PDA. When the crosslinking density was higher, the effect of crosslinking density overrides chain rigidity due to hindered chain rotation. Therefore, T_g value of thermoset based on *m*-PDA with a degree of polymerization was higher than that based on TFMB. The temperature dependence of storage modulus and tan δ for thermosets derived from *m*-PDA-based isoimide oligomers are shown in Figure 12. The T_g values increased with the decrease of oligomer molecular weights, for a given oligomer architecture. Lower oligomer molecular weights lead to higher crosslink densities and therefore higher glass transition temperatures of cured resins.

The mechanical properties of representative cured pure resins (PII-ODA-2, PII-TFMB-2, and PII-PDA-2) are summarized in Table 6. Thermoset based on PII-TFMB-2 possessed the highest tensile strength and modulus, and flexural strength and modulus, which can be attributed to its lowest crosslinking density (highest molecular weight) and highest chain rigidity.

Thermoset based on PII-ODA-2 exhibited the highest elongation at break and lowest modulus due to its flexible ether linkage. Because of their higher crosslinking density, thermosets based on isoimide oligomers with a degree of polymerization of 2 are more brittle than those based PETI-5 and TriA-PI, which was indicated by their relatively lower tensile strength (48-90 MPa for cured resins with this work, >100 MPa for PETI-5 and TriA-PI) and elongation at break (2.6-4.1% for cured resins in this work, 32% and 14% for PETI-5 and TriA-PI, respectively).[13-14]

3.3.2 Mechanical properties of polyimide/quartz fiber composites. The isoimide/quartz fiber prepregs were prepared by coating the THF solution of isoimide oligomer onto quartz fiber cloth, followed by drying at 60 °C for 12 hours. The volatile contents of as-prepared prepregs spanned the range of 10-19%. The existence of a small fraction of volatiles can prevent the delamination between fiber and resins. Then polyimide/quartz fiber composites were fabricated from these prepregs by a high temperature compression-molding process (Figure 13). The low boiling point volatiles were readily removed by heating the prepregs at 240 °C for 1 hour under ambient pressure. The temperature was then ramped to 370 °C with a heating rate of 3 °C/minute, and held at 370 °C for 2 hours. A pressure of 2 Mpa was applied when the temperature reached 310 °C, and held until the end of this process. The cured composites were then removed from the mold, and their mechanical properties were evaluated at room temperature and 300 °C (Table 7). These composites showed similar mechanical properties at room temperature, while their mechanical properties at 300 °C followed the trend of PII-TFMB>PII-PDA>PII-ODA. This trend was identical to the trend for T_g values, which indicated that glass transition temperatures played a key role in high temperature mechanical properties. The composites maintained 75-90% of their room temperature flexural strength and 90-97% of their room temperature flexural modulus at 300 °C, which demonstrates their excellent high temperature mechanical properties.

4. Conclusion

In this work, a series of phenylethynyl-terminated isoimide oligomers were prepared using 3, 4’-BPDA and aromatic diamines (3, 4’-ODA, *m*-PDA, TFMB) as the monomers, and PEPA as the end-capping reagent. Due to their unique asymmetric architecture, these isoimide oligomers showed much higher solubility in low boiling point solvents and lower minimum viscosity, when compared to corresponding imide oligomers. High solubility in low boiling point solvents is highly desired for high quality composites fabrication. With a degree of polymerization of 2, the solubility of isoimide oligomers were up to 35 wt.% at 30 °C and 60 wt.% at 70 °C in DMAc, and more than 30 wt.% in THF and dioxane at room temperature, which makes these oligomers suitable for wet prepreg process. Furthermore, as confirmed by FTIR spectra, isoimide groups can be easily converted to the corresponding imide groups by thermal treatment. Thermosetting polyimides and polyimide/quartz fiber composites were formulated using these isoimide oligomers, and fully characterized in terms of thermal and mechanical properties. Due to the incorporation of rigid diamines, these polyimides exhibited glass transition temperatures of 315-467 °C, and 5% weight loss temperatures of 566-580 °C in nitrogen atmosphere. The flexural strength and modulus polyimide/quartz fiber composites derived from isoimide were in the range of 892-953 Mpa and 30-31 GPa, respectively. Moreover, these composites can maintain their 75-90% of their room temperature flexural strength, and 90-97% of their room temperature flexural modulus at 300 °C. Due to a combination of good processability and remarkable thermal and mechanical properties of cured resins and composites, these isoimide oligomers showed great potential in the applications of high temperature structural composites for aerospace industry. This study provided our community a new insight on how to design and prepare high performance thermosetting polyimides and composites without sacrificing processability.

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Notes and references

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Table 1. Molecular weights, inherent viscosities, and thermal properties of the oligomers

Oligomer	Mn (g/mol)		PDI (measured) [a]	η_{inh} (dL g^{-1}) [b]	T_g (°C) [c]
	Calculated	Measured [a]			
PII-PDA-1	935	1206	1.48	0.07	130
PII-PDA-2	1300	1241	1.35	0.09	157
PII-PDA-3	1668	1319	1.43	0.10	171
PII-PDA-4	2034	1424	1.48	0.12	184
PI-PDA-2	1300	- [d]	- [d]	0.11	173
PII-TFMB-1	1359	1181	1.08	0.07	119
PII-TFMB-2	1938	2237	1.92	0.09	142
PII-TFMB-3	2516	2702	1.94	0.10	155
PII-TFMB-4	3094	2886	1.96	0.11	166
PI-TFMB-2	1938	- [d]	- [d]	0.10	172
PII-ODA-1	1119	1790	2.10	0.08	128
PII-ODA-2	1578	1817	2.33	0.09	146
PII-ODA-3	2036	2028	2.10	0.12	159
PII-ODA-4	2495	1914	1.69	0.13	167
PI-ODA-2	1578	- [d]	- [d]	0.12	168

[a] Determined from GPC;

[b] Measured at a concentration of 0.5 g/dL in NMP at 25 °C;

[c] Determinded from DSC at a heating rate of 10 °C /min under a nitrogen atmosphere;

[d] Not measured due to the limited solubility in THF.

Table 2. Solubility of the oligomers

Oligomer	DMAc	DMF	NMP	DMSO	THF	dioxane	acetone	ethanol
PII-PDA-1	++	++	++	++	++	++	±	-
PII-PDA-2	++	++	++	++	++	++	±	-
PII-PDA-3	++	++	++	++	+	+	±	-
PII-PDA-4	++	++	++	++	±	±	-	-
PI-PDA-2	+	+	+	+	±	±	±	-
PII-TFMB-1	++	++	++	++	++	++	++	±
PII-TFMB-2	++	++	++	++	++	++	++	±
PII-TFMB-3	++	++	++	++	++	+	+	±
PII-TFMB-4	++	++	++	++	++	+	+	±
PI-TFMB-2	++	++	++	++	++	++	+	-
PII-ODA-1	++	++	++	++	++	++	±	±
PII-ODA-2	++	++	++	++	++	++	±	±
PII-ODA-3	++	++	++	++	+	+	±	-
PII-ODA-4	++	++	++	++	+	+	±	-
PI-ODA-2	+	+	+	+	±	±	±	-

Key: ++, soluble more than 10% at room temperature; +, soluble 5% at room temperature; ±, partially soluble on heating; -, insoluble.

Table 3. Complex viscosity data of isoimide oligomers

	Complex melt viscosity (Pa s)				Minimum melt viscosity
Oligomer	280 °C	300 °C	320 °C	350 °C	(Pa s, °C)
PII-PDA-1	2	2	2	4	2 at 295 °C
PII-PDA-2	29	17	12	18	12 at 327 °C
PII-PDA-3	186	155	128	100	99 at 347 °C
PII-PDA-4	6799	1897	1008	1396	1,000 at 322 °C
PII-TFMB-1	7	7	7	9	7 at 323 °C
PII-TFMB-2	49	23	21	70	20 at 321°C
PII-TFMB-3	88	40	25	32	24 at 329 °C
PII-TFMB-4	263	100	52	73	45 at 334 °C
PII-ODA-1	1	1	1	2	0.4 at 292 °C
PII-ODA-2	5	3	2	3	2 at 336 °C
PII-ODA-3	14	7	4	4	3 at 333 °C
PII-ODA-4	30	15	9	7	7 at 340 °C
PETI-1.25K					500 at 335 °C
PETI-2.5K					9,000 at 371 °C
TriA-PI (n=4.5)					10,000 at 320 °C

Table 4. Isothermal complex viscosity values of representative isoimide oligomers

Oligomer	Temperature (^{o}C)	Initial viscosity (Pa s)	Viscosity after 30 minutes (Pa.s)	Viscosity after 60 minutes (Pa.s)	Rate of viscosity increase (Pa s min^{-1})	
					30 min	60 min
PII-PDA-2	280	29	326	571	10	9
	300	17	241	2571	7	43
	320	12	1597	48960	53	816
PII-TFMB-2	280	47	480	1557	14	25
	300	23	1619	6735	53	112
	320	16	6152	60965	205	1016
PII-ODA-2	280	5	16	137	0.4	2
	300	3	123	1863	4	31
	320	2	1513	8210	50	137

Table 5. Thermal properties of cured polyimide thermosets

Oligomer		N$_2$			Air	
	T_g (°C)[a]	$T_{5\%}$ (°C)[b]	$T_{10\%}$ (°C)[c]	Char yield (%)[d]	$T_{5\%}$ (°C)[b]	$T_{10\%}$ (°C)[c]
PII-PDA-1	467	566	599	71	561	586
PII-PDA-2	435	584	614	72	569	591
PII-PDA-3	385	580	606	65	562	586
PII-PDA-4	374	578	605	65	564	587
PII-TFMB-1	457	560	585	62	550	566
PII-TFMB-2	440	572	591	60	552	576
PII-TFMB-3	401	580	598	60	562	583
PII-TFMB-4	390	575	593	61	558	582
PII-ODA-1	382	566	593	68	556	578
PII-ODA-2	354	567	593	66	567	586
PII-ODA-3	332	571	596	67	564	583
PII-ODA-4	315	574	599	65	568	587

[a] Obtained from DMTA at a heating rate of 3 °C/min at 1 Hz in air.

[b] Temperature of 5% weight loss determined by TGA at a heating 10 °C/min in air or nitrogen.

[c] Temperature of 10% weight loss determined by TGA at a heating 10 °C/min in air or nitrogen.

[d] Char yield resulting after a 10 °C/min scan to 800 °C in nitrogen.

Table 6. Mechanical properties of cured polyimide thermosets

Oligomers	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
PII-PDA-2	48	2.2	2.6	74	3.5
PII-TFMB-2	90	3.0	3.1	140	3.6
PII-ODA-2	52	1.7	4.3	77	3.2

Table 7. Mechanical properties of polyimide/quartz fiber composites

Property	Test temperature (^{o}C)	PII-PDA-2	PII-TFMB-2	PII-ODA-2
Volume fraction of quartz fiber		58	58	58
Mass fraction of quartz fiber		70	70	70
Flexural strength (MPa)	23	892	905	953
	300	762	810	715
Flexural modulus (GPa)	23	31	30	31
	300	30	29	28
Tensile strength (MPa)	23	543	581	564
	300	381	410	354
Tensile modulus (GPa)	23	19	22	20
	300	17	21	16
Interlaminar shear strength (MPa)	23	55	58	49
	300	44	42	31

Figure caption

Scheme 1. Synthesis of isoimide oligomers

Figure 1. FTIR spectra of isoimide oligomers

Figure 2. The solubility of oligomers in DMAc as a function of temperature

Figure 3. The solubility of oligomers in THF and dioxane at room temperature:
(a) PI-PDA-2 and PII-PDA-2, (b) PI-ODA-2 and PII-ODA-2, (c) PI-TFMB-2 and PII-TFMB-2.

Figure 4. Complex viscosity curves of PII-TFMB-n

Figure 5. Complex viscosity curves of isoimide and imide oligomers

Figure 6. Complex viscosity curves of PII-TFMB-2 with different pretreatment temperatures

Figure 7. FIIR spectra of PII-TFMB-2 with different pretreatment temperatures

Figure 8. Isothermal viscosity profiles of PII-TFMB-2

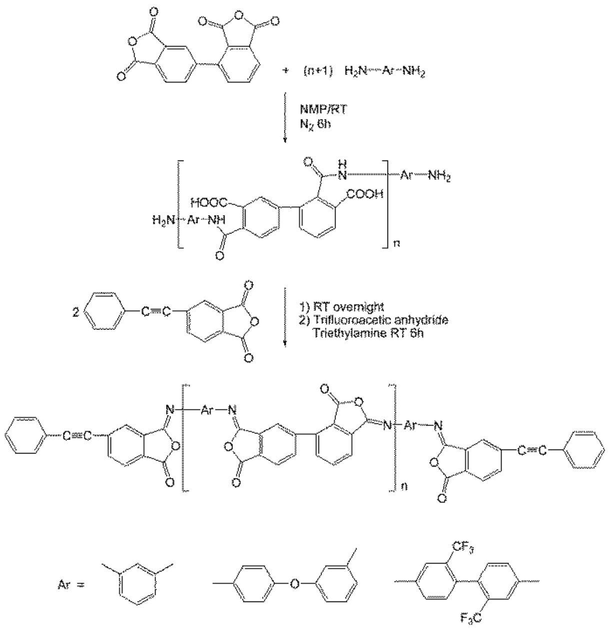
Figure 9. Wide angle X-ray diffraction diagram of isoimide oligomers

Figure 10. TGA traces of cured PII-ODA-n in air

Figure 11. TGA traces of cured PII-ODA-n in nitrogen

Figure 12. DMA curves of the cured polyimides based on *m*-PDA

Figure 13. Processing cycle for polyimide/quartz fiber composites



Scheme 1. Synthesis of isoimide oligomers

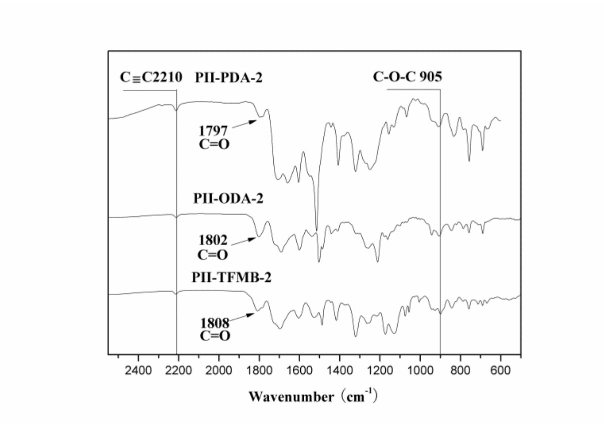


Figure 1. FTIR spectra of isoimide oligomers

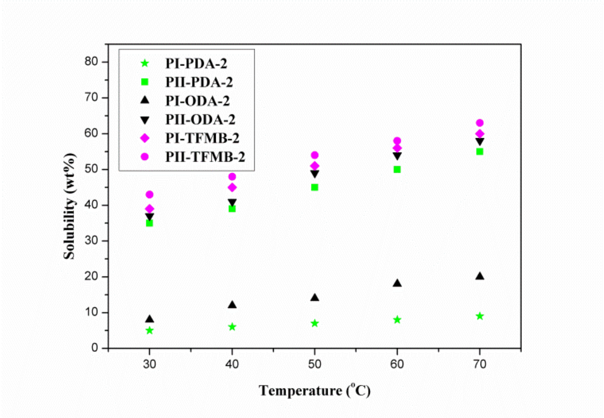


Figure 2. The solubility of oligomers in DMAc as a function of temperature

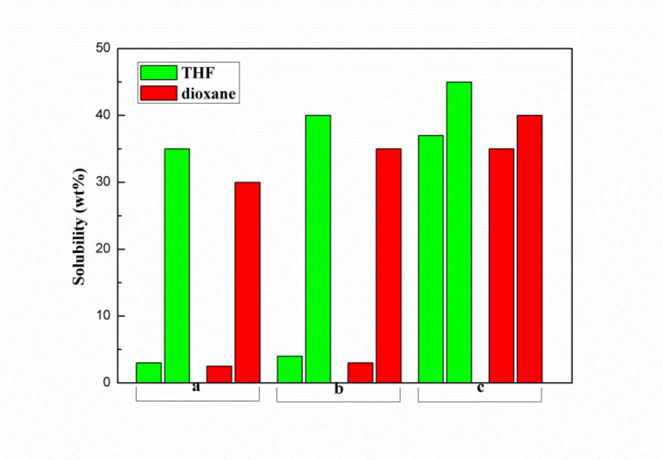


Figure 3. The solubility of oligomers in THF and dioxane at room temperature: (a) PI-PDA-2 and PII-PDA-2, (b) PI-ODA-2 and PII-ODA-2, (c) PI-TFMB-2 and PII-TFMB-2.

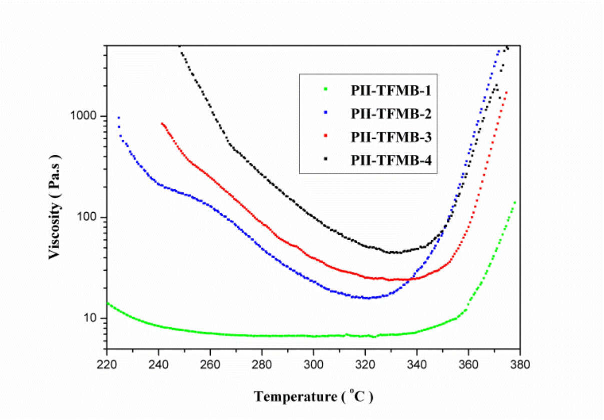


Figure 4. Complex viscosity curves of PII-TFMB-n

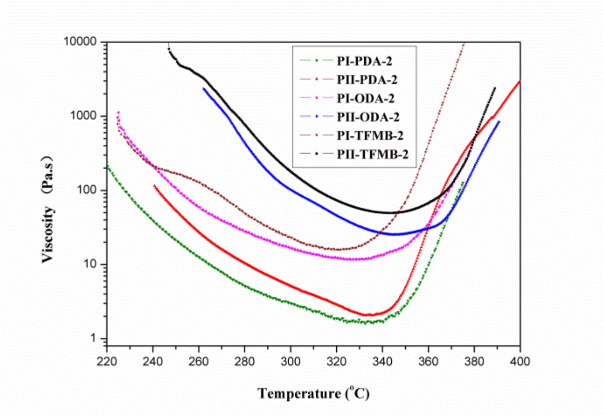


Figure 5. Complex viscosity curves of isoimide and imide oligomers

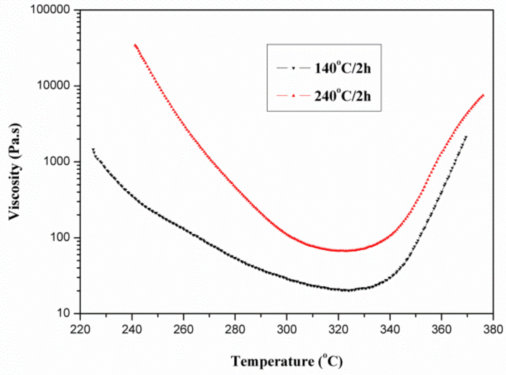


Figure 6. Complex viscosity curves of PII-TFMB-2 with different pretreatment temperatures

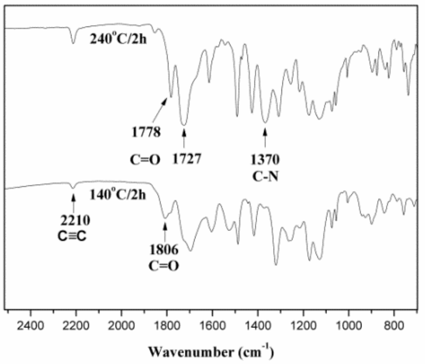


Figure 7. FTIR spectra of PII-TFMB-2 with different pretreatment temperatures

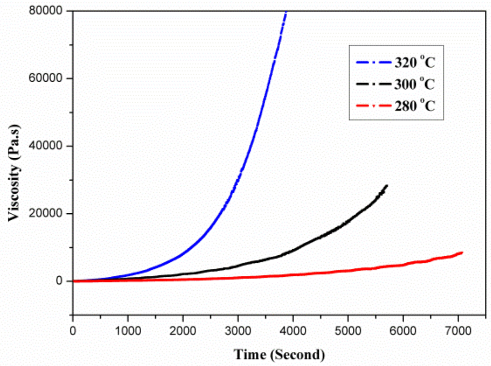


Figure 8. Isothermal viscosity profiles of PII-TFMB-2

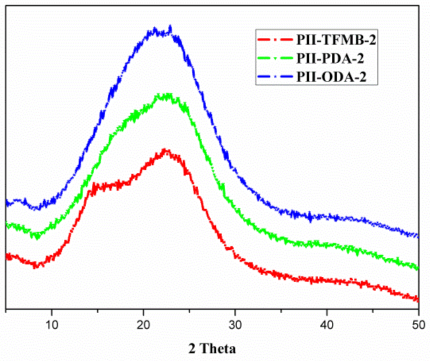


Figure 9. Wide angle X-ray diffraction diagram of isoimide oligomers

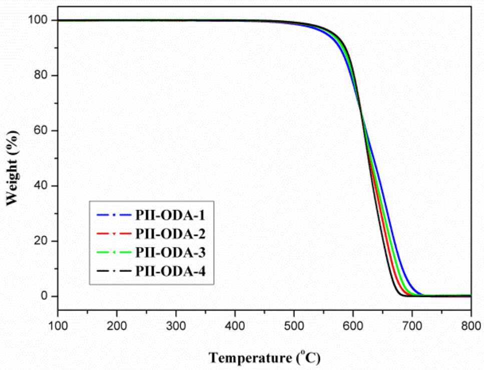


Figure 10. TGA traces of cured PII-ODA-n in air

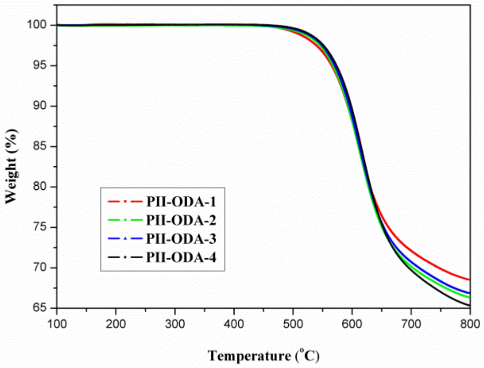


Figure 11. TGA traces of cured PII-ODA-n in nitrogen

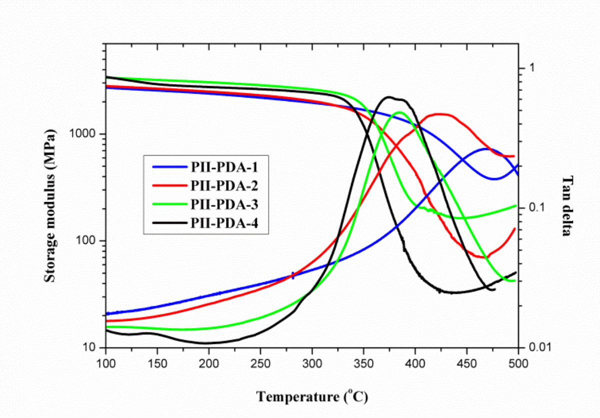


Figure 12. DMTA curves of the cured polyimdes based on *m*-PDA

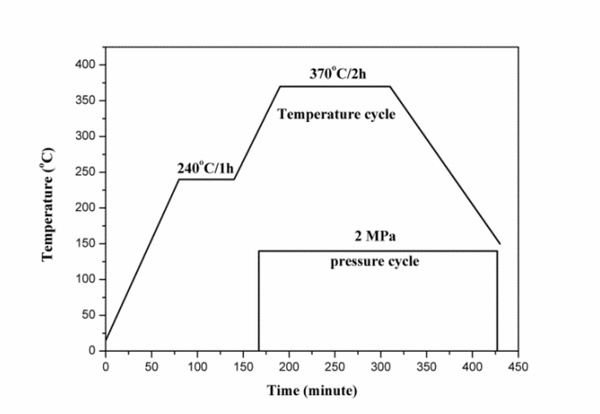


Figure 13. Processing cycle for polyimide/quartz fiber composites