Preliminary exploration of processability and self-lubricating properties of polythioetherimides/PEEK blends and their composites

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Abstract. Polythioetherimides (STPI) were first synthesized from 3- and 4-chlorophthalic anhydrides, and 4,4’-oxydianiline and 1,3-bis(4-aminophenoxy) benzene by a two-step polycondensation procedure via their soluble poly (amic acid) precursors. Then a series of isomeric polythioetherimides/polyetheretherketone (STPI/PEEK) blends samples with compositions (wt%) of 30/70, 40/60 and 50/50 were prepared and characterized. The structure characterization of STPI demonstrated by FTIR, Raman and elemental analysis show that there are little S-S bonds of the copolythioetherimides chains. Thermal, rheological, ultrasonic non-destructive testing technique, mechanical measurements and dynamic thermomechanical analysis were conducted to process and assess the morphology and mechanical properties of the STPI/PEEK blends, and 30/70 weight composition of STPI/PEEK was preferred. There are few voids or air gaps in the molding samples. The samples of STPI/PEEK-30/70 show two relaxations at 164.2 °C and 243.5 °C, an average tensile modulus of 1.264 GPa, an average bending elastic modulus of 2.061 GPa and a bending strength of 78.3 MPa. Finally, the friction-wear characteristics of STPI/PEEK composites with solid lubricants such as graphite, MoS2 and PTFE were investigated, indicating a promising way to develop a STPI-based thermoplastic for tribological applications.

1. Introduction

Polymers and composites have been extensively employed in various applications as tribological components such as bearings, gears and seals, owing to their lightweight, self-lubrication, chemical stability and biocompatibility[1-3]. Thermoplastic aromatic polyimides (TPI), as a class of important high performance engineering polymers, have been extensively used as motion components under...
extreme conditions for their excellent physical and chemical properties especially their high service temperature, radiation resistance, inherent flame retardancy, and special self-lubricating properties[4-6]. Isomeric polythioetherimides (STPI), which were prepared by a two-step poly-condensation procedure via soluble poly (amic acid) precursors to give 3- or 4- nitro- (or chloro-) phthalic imide, and then reacting with sulfur or an alkali metal sulfide or hydrosulfide, such as sodium sulfide or sodium hydrosulfide as vulcanizing agents, have many different properties because of the variety of substitution positions or the difference of the arranging order[7-9]. With superior processability (low melt viscosity) and good combined properties, STPI have attracted the attention of researchers in designing lubricating materials in academic and industrial applications[10-13]. However, STPI self-lubricating composites with better wear resistance and lower friction are still a challenge. Favourable lubricating properties of the polymer may be optimized by blending STPI with other polymers[14]. Polyetheretherketone (PEEK) is an another melt-processable, semicrystalline, high performance engineering thermoplastic with a glass transition temperature (Tg) of 145°C and a melting point (Tm) of 335°C, which is known to be miscible with polyetherimide (PEI). Due to its low friction coefficient, good mechanical properties, high heat resistance, superior resistance to dynamic fatigue and good machinability, PEEK shows very attractive tribological characteristics which include superior sliding wear properties[15-16]. This well-balanced combination of mechanical and tribological properties is maintained at temperatures below the Tg. And it has become a promising material to meet the growing demand for lightweight and self-lubricating applications. Sulfur as a homologous element of oxygen, makes it reasonable to infer that STPI exhibit enough similar and unique properties compared with PEI when blending with PEEK. In fact, the thermal, dynamic mechanical relaxation and tribological behaviours of blends of PEI and PEEK has been investigated[17-22]. Although, among polyimides, PEI exhibits a relatively low coefficient of friction, the wear characteristics of the bulk polymer are not very favourable. A study conducted by Yoo and Eiss constitutes the first available report on the tribological behaviour of these blends[17]. It was found that as the content of PEI in the blends increased, wear rates also increased, and that raising the degree of crystallinity of the PEEK phase resulted in reduced wear rates. Reported dominant wear mechanisms were plowing in PEEK rich blends, and fatigue in PEI rich blends; the latter blends were found to exhibit the highest coefficient of friction.

At present, the preparation methods of polymer/inorganic composites are mainly mixing, reinforcing with fiber or fiber fabric, and filling with solid lubricants, which can improve the friction and wear properties of thermoplastics[1]. Generally, self-lubricating composites take advantage of both matrix and reinforcement. Here matrix phase is carefully combined with a lubricating phase material. As the key lubricating phase in composite materials, a large number of solid lubricants have been reported, such as soft metals, transition metal dichalcogenides, oxides, alkaline fluorides, carbon and polymers[2]. In general, graphite, Molybdenum disulfide (MoS2) and polytetrafluoroethylene (PTFE) powders are commonly used in moderate temperature[3, 23-27]. When polymer or material surfaces slide against metal counterparts under dry friction, the ability to develop a transfer film on the counter surface is determined as a crucial factor in lubricating performance, which transforms the direct contact of the friction pairs into the sliding between the soft surfaces.

In this work, a series of isomeric polythioetherimides/polyetheretherketone (STPI/PEEK) blends were prepared and investigated by thermal, rheological behaviour, ultrasonic scanning technique, mechanical measurements and dynamic thermomechanical analysis to assess processabilities, morphology and mechanical properties of the STPI/PEEK blends. Besides, the friction-wear characteristics of STPI/PEEK composites with a certain proportion of graphite, MoS2 and PTFE powders were also presented.

2. Experimental

2.1. Materials and synthesis of STPI
Polythioetherimides (STPI) phthalic anhydride capped polymers were synthesized according to literatures procedure (Scheme 1). The 3- and 4-chlorophthalic anhydrides were obtained from Shanxi Haoteng Technology Co., Ltd (China) and further purified by dehydration with xylene, giving fully anhydrides to ensure accurate reaction proportion. 4,4'-oxydianiline and 1,3-bis(4-aminophenoxy) benzene were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd (China). Anhydrous sodium sulfide was purchased from Chengdu Yuanda Chemical Co. Ltd (China). Anhydrous potassium carbonate was supplied from Chengdu Kelong Chemical Co., Ltd (China). Phthalic anhydride was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd (China). All of the other reagents were supplied from the Sinopharm Chemical Reagent Co., Ltd (China) and were of analytical grade and used as received.

PEEK (trade mark: 330PF) was supplied by Changchun Jida Engineering Research for Super Engineering Plastics Co., Ltd (China). Graphite flakes (RGB390TS) with a mean diameter of about 4 μm were purchased from Superior graphite (USA) and used as internal lubricants. Lamellar MoS₂ particles were supplied from Beijing DK Nano technology Co., Ltd (China). PTFE powders were supplied by Daikin Fluorochemicals (China) Co., Ltd.

2.2. Preparation of STPI/PEEK blend and Composites

The hot press molding technique was conventionally used to fabricate STPI/PEEK blends and composites samples. The thermal and rheological behaviours of the STPI, PEEK and their blends with different proportions were investigated to conduct processing and later analyzed in Results and discussion section. The STPI and PEEK powders were first dried respectively at 150 °C for 4 h before using and then mixed with graphite, MoS₂ and PTFE using a high-speed multifunctional pulverizer (JP-500B; Yongkang Jiupin Industry and Trade Co., Ltd, China). The mixing powders were compressed and heated to 290 °C in a mold (85 mm × 60 mm × 94 mm) and held at 20 MPa for 30 min to allow fully compressing. After cooling, specimens were cut into pre-set sizes for testing.

2.3. Characterization

FTIR, Raman, elemental analysis. FTIR spectra were carried out using PerkinElmer Frontier FTIR spectrometer (USA) by KBr pellet. Raman spectrum of STPI powders was performed at room temperature by using a laser Raman spectrometer (LabRAM HR, France) equipped with a He–Ne laser (wavelength = 632.8 nm, light power = 5 mW). Micro-Raman measurements of STPI films were carried out using a WiTec Alpha300 system (Germany) with a 532 nm wavelength incident laser light. Elemental (C, H, N, S) contents were obtained using an elemental analyzer (Vario MACRO cube, Germany). Elemental (K, Na) contents were assayed using a PerkinElmer Optima 5300 DV (USA), inductively coupled plasma optical emission spectrometer (ICP-OES). Chlorine determination of STPI resin was obtained in coal of GB/T3558-2014 method for determination of the chlorine in coal.

Thermal, Rheological, mechanical and tribological tests. The 5% weight-loss data were obtained from a TGA Q500 instrument from room temperature to 800 °C at a heating rate of 10 °C/min in nitrogen atmosphere (30 mL/min). The Tg values of the polymer blends were obtained using a DSC Q2000 instrument from room temperature to 400 °C at a heating rate of 10 °C/min in nitrogen atmosphere (50 mL/min) and cooling to 40 °C (cycle 1), and then reheated for a second DSC run (cycle 2). The inherent viscosity data were obtained with a calibrated Ubbelohde viscometer, and the measurements were carried out in N, N'-Dimethylacetamide at 30 °C. Rheological behaviors of the STPI, PEEK and their blends were studied by dynamic oscillation employing a TA instrument Discovery DHR-2 rotational rheometer in conjunction with a nitrogen or environmental temperature control. The temperature ramp was taken at 10 °C/min from room temperature to 500°C with an angular frequency of 1 Hz and an initial strain of 1.25% using 25mm-diameter parallel plates (compression mode). For the time sweep test, the test was carried out first by temperature ramp at 20 °C/min, and then holding at specified temperatures (such as 380 and 400 °C). The variation of the viscoelastic properties during test such as complex viscosity were determined as a function of time. The internal morphology of the molding samples were tested layer by layer (7 layers) using an
ultrasonic scanning technique at Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The dynamic thermomechanical performance of the samples (40 mm × 10 mm × 4 mm) were evaluated by DMA (NETZSCH DMA 242, Germany) with a mode of three-point bending mode from 30 °C to 350 °C at a heating rate of 5.0 K/min, nitrogen atmosphere with frequency of 1 Hz. The tensile and bending tests were carried out on a Shimadzu AG-X 20 KN electronic universal testing machine (40 mm × 5 mm × 2 mm for tensile test and 64 mm × 10 mm × 4 mm for bending test). Tribological tests were performed on MM-P2 screen friction and wear tester (200 N force) in air ambiance.

3. Results and discussion

3.1. Synthesis and structure characterization of STPI

As shown in Scheme 1, STPI phthalic anhydride capped polymers were accomplished in two steps through the poly-condensation reactions, giving an inherent viscosity of 0.38-0.45 dL/g. The structure characterizations of STPI demonstrated by FTIR, Raman and elemental analysis were investigated. The determinations of carbon, hydrogen, nitrogen and sulfide, and residual elements (K, Na and Cl) were summarized in Table 1, which indicated that water refluxing and washing STPI polymers as many times as possible can obviously make decrease the content of K and Na (residual carbonates). Also, there are still some sulfides residue which can be washed away, and giving an illusion that the content of Cl increased instead of decreasing. FTIR spectra and Raman spectra (Figure 1) showed that no obvious S-S bonds (around 539 cm⁻¹) of the STPI were observed, which indicated that cleavage of S-S bonds can be avoided to get STPI cross-linked during high temperature processing. In fact, comparative study on FTIR spectra of STPI before and after rheological test (temp ramp from room temperature to 500 °C in nitrogen) exhibited no distinguishing structure changes, further implying a promising application for high temperature performance.

![Scheme 1. Synthesis route of STPI resins.](image)

![Figure 1. FTIR spectra of STPI before and after rheological test (N₂), and Raman spectra of STPI.](image)
Table 1. Changes of elements content of STPI before and after refluxing and washing.

| Number of refluxing and washing times | C (68.5%) | H (3.77%) | N (5.55%) | S (6.40%) | K (0.55 mg/g) | Na (1.16 mg/g) | Cl (2.45 mg/g) |
|--------------------------------------|-----------|-----------|-----------|-----------|--------------|-------------|--------------|
| 0                                    | 68.5%     | 3.77%     | 5.55%     | 6.40%     | 0.55 mg/g    | 1.16 mg/g   | 2.45 mg/g    |
| 1                                    | 68.40%    | 3.99%     | 5.52%     | 6.26%     | 0.45 mg/g    | 1.06 mg/g   | 2.25 mg/g    |
| 20                                   | /         | /         | /         | /         | 0.17 mg/g    | 0.86 mg/g   | 8.09 mg/g    |

3.2. Thermal and rheological processing evaluation for STPI/PEEK sample preparation

Figure 2 shows the thermal properties of STPI, PEEK and their blends with weight proportions of 30%/70% for STPI/PEEK 30/70, 40%/60% for STPI/PEEK 40/60, 50%/50% for STPI/PEEK 50/50. Both of STPI and PEEK exhibit no obvious weight loss before the scanning temperature reached 450 °C, and the char yields were found to be 55.1% and 50.4%, respectively after heated to 800 °C, implying superior performance in thermal stability (Figure 2(a) and (b)).

The blends of STPI and PEEK are known to be miscible at all compositions in the amorphous state. The results of DSC heating curves vs. heating temperature from cycle 1 and cycle 2 are shown in Figure 2(c) and (d). It is suggested that the 30/70, 40/60 and 50/50 weight proportions of STPI/PEEK blends show similar behaviors with slight temperature shifts during heating and cooling. Also, it is clear that both of the temperature peaks at 179 °C and 337 °C for the STPI/PEEK 50/50 on the cycle 1.
and 2 respectively decrease in height, comparing with the other two proportions. Notably, new temperature peaks around 176 °C for all of the three proportions during cycle 1 heating (Figure 2(c)) were observed, comparing with no peaks around the temperature in Figure 2(b) and disappearance of the peak in Figure 2(d), implying there were some crystallizations by chain rearrangements for the blends of STPI/PEEK especially for PEEK. In general, the high melting temperature of STPI/PEEK blend affects processing and it is necessary to investigate the rheological behaviors of the blends to further conduct the sample preparations.

To systematically study the process characteristics and properties of the STPI/PEEK blends, temperature ramp and time sweep procedures were chosen to further investigation in air atmosphere. Viscosity measurements on 30/70, 40/60 and 50/50 weight proportions of STPI/PEEK blends were conducted at several temperatures to determine the preferred weight proportion and temperature for blend processing. The complex viscosities change as a function of temperature and time, respectively, for STPI, PEEK and their blends at specified temperatures are shown in Figure 3. It can be seen that the more the composition of PEEK, the higher the viscosity of the blends is. Further, the viscosity at 400 °C for time sweep is higher than that at 380 °C, which can be explained as some cross-linking reaction occurred in the blend system in air atmosphere, showing that there are still some improvements during the synthesis of STPI especially removal of residual sulfides. Besides, STPI/PEEK 30/70 shows a relatively lower viscosity and longer retention time with viscosity from 7120 Pa·s at 370 °C to 3600 Pa·s at 450 °C for temperature ramp. Therefore, the 30/70 weight proportion of STPI/PEEK blend was preferred to be chosen as molding thereafter.

3.3. Morphological evaluation of STPI and STPI/PEEK blends

In this section, an ultrasonic inspection method was used to evaluate the micro-voids of the samples. Actually, this is one of the ultrasonic non-destructive testing methods extensively used for polymer matrix composite parts. As shown in Figure 4, there were a few of voids or air gaps (white points) in the sample STPI and STPI/PEEK, indicating that air among the powders is not completely removed from the gap during hot press molding, and could have an impact on the properties of the composites.
3.4. Dynamic mechanical analysis

Mechanical behaviors of polymer composites have a direct influence on their friction and wear properties. As shown in Figure 5, the dynamic viscoelastic properties of STPI/PEEK blend were obtained with curves of storage modulus (E’), loss modulus (E’’) and tanδ as a function of temperature,
respectively. In the test temperature, the STPI/PEEK-30/70 blend gave two relaxations. The temperatures at 164.2 °C and 243.5 °C are for transition α and β relaxation, respectively, which is considered to be the glass transition temperatures of PEEK and STPI of the blend, respectively. Besides, the storage modulus of the sample is high, giving it good anti-wear performance. The tensile test exhibits that STPI/PEEK-30/70 sample has an average elastic modulus of 1.264 GPa, and the bending test shows that the samples give an average bending elastic modulus of 2.061 GPa and a bending strength of 78.3 MPa, which can be further improved to enhance the lubricating properties.

3.5. The Friction and Wear investigation of STPI and STPI/PEEK Composites

Figure 6 shows the variation friction coefficient of the STPI and STPI/PEEK-30/70 with graphite, MoS2 and PTFE composites as a function of sliding time under constant loading of 200 N at room temperature, of which the speed is from 6500 to 12800 r/min for STPI sample, and from zero to 6300 r/min for the other three samples, respectively. There are some fluctuations on the curves of the samples at the beginning of friction test, with the rise in the time and the speed, the friction coefficients go a stable upward. The friction coefficient of the STPI is around 0.5, which is somewhat high. After mixing with PEEK and other solid lubricants, the friction coefficients are decreased to a certain extent. In fact, the experimental system is too complicated to find out the effect of a single factor, and more friction-wear characteristics need to be further investigated.

4. Conclusion

A series of different proportions of STPI/PEEK blends and their composites filled with graphite, MoS2 and PTFE were prepared by hot press molding method and characterized. The structure characterization of STPI demonstrated by FTIR, Raman and elemental analysis show that there are little S-S bonds of the copolythioetherimides chains and some cross-linking reactions may occur in air atmosphere. There is still a long way to of some improvements during the synthesis of STPI especially removal of residue reaction reagents such as sulfides to avoid accelerating cure of STPI at high temperatures. Thermal analysis and rheological evaluations were conducted to process, and 30/70
weight composition of STPI/PEEK was preferred. Few voids or air gaps of the molding samples are detected by an ultrasonic non-destructive testing method. Dynamic thermomechanical analysis and friction characteristics show that after filling with solid lubricants such as graphite, MoS₂ and PTFE, the lubricating properties could be improved, which makes the blending of STPI and PEEK a promising way to develop a STPI-based thermoplastic for tribological applications.

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