

## The effect of cenosphere on thermal and rheological behavior of cenosphere loaded thermosetting polyimide

Ping Yu<sup>1</sup> (宇平), Min-zhao Xue<sup>1</sup>, Yan-gang Liu<sup>1</sup>, Xue Yang<sup>1</sup>, Lijing Pan, Yanli Zhang, Wei Wang<sup>1,2\*</sup> (王巍)

<sup>1</sup>Department of Chemical Engineering, Shanghai Jiao Tong University(上海交通大学), Shanghai 200240, P. R. China.

<sup>2</sup>Changzhou JME Advanced Materials Co. Ltd, Changzhou 213200.

**Abstract** With the goal of reducing cost of polyimide matrix and improving processability of imide oligomers, KH550-modified cenospheres were used as a lightweight filler in producing high performance thermosetting polyimides. The chemical structure, glass transition temperature, thermal curing properties, melt processability and thermal stability of the blends were prepared. The thermal curing behaviors of the blends were analyzed by using differential scanning calorimetry. The rheological properties were investigated by using a dynamic rheometry. The  $T_g$  value for the cured polyimide with 3 wt% cenospheres was 287 °C which was about 11 °C higher than that of the cured polyimide. The oligomer with addition of 3 wt% cenospheres showed a broader melt processing window and a lower minimum complex viscosity. The cured resin systems exhibited high thermal and thermal-oxidative stability.

### Keywords

thermosetting polyimide, cenosphere, thermal properties, melt processability

### 1.INTRODUCTION

Aromatic polyimide (PI) has been considered to be a particularly attractive class of high-performance materials pivotal to microelectronics packaging and advanced composites in aerospace industries [1-3]. However, PI materials exhibit poor solubility and melt processability due to the rigid backbone architecture and strong molecular interactions. Therefore, Thermosetting polyimide (TPI) terminated with reactive groups has achieved the balance between processing characteristic and thermal properties. TPI not only exhibits excellent solution and melt processability of oligomer but also keep good thermal and mechanical properties of cured resin [4-6]. Thermosetting polyimide are an important matrix resin for fiber reinforced advanced composites. However, the application of the thermosetting polyimide is limited due to its high cost. Besides lower the cost, the good processability and thermal property of composites are also required.

Cenosphere has gained much attention from researchers to produce lightweight materials in the last few decades. Cenospheres are lightweight hollow spherical particles obtained as waste residue from coal fired power plants. In 2015, more than 600 million tons of coal fly ash were produced in China [7]. Cenospheres have been incorporated in polymer matrices for producing low cost composite material. Spherical cenospheres not only reduce resin consumption but also improve the flow ability of base polymers as well. Many research have showed the improvement in thermal and mechanical properties, and also showed reduction in shrinkage by adding cenosphere as filler [8,9]. In order to improve the interaction between polyimide and cenosphere, surface treatment of cenosphere can be used as an effective method. A simple but effective surface treatment by KH550 coupling agent can optimize the adhesion between fillers-matrix. KH550 is used because it is commercially available and has special groups which provides appropriate bonds between the surface of inorganic cenospheres and organic polyimides. To the best of our knowledge, there exists no report for the use of cenosphere in blending with phenylethynyl-terminated polyimide for composites.

In fact, the composites with lightweight and high strength are playing extremely important role in some aircrafts such as helicopter. In this current study, we make an attempt to understand the thermal properties and melt processability of cenosphere filled thermosetting polyimide composites.

## 2. EXPERIMENTAL

### Materials

2,3,3',4'-Diphenyl ether tetracarboxylic acid dianhydride (a-ODPA, 99.64%), 3,4'-oxydianiline (3,4'-ODA, 99.92%) and 4-phenylethynylphthalic anhydride (PEPA, 99.94%) were obtained from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou China). Acetic anhydride (98.5%) and triethylamine (99%) were purchased from J&K Chemical Technology (Shanghai China). VS5500 cenospheres were acquired from Minnesota Mining and Manufacturing company. 3-aminopropyltriethoxysilane (KH550) was provided by J&K Chemical Technology (Shanghai China). N-Methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc) were acquired from Ling Feng Chemicals Co., Ltd. (Shanghai China) and purified by vacuum distillation over P<sub>2</sub>O<sub>5</sub> prior to use. Other solvents were all used as received from their respective vendors and without further purification.

### Synthesis of imide oligomer (TPI)

According to our previous work <sup>[10]</sup>, the synthesis of oligomer was as follows: First of all, 3,4'-ODA (10 g, 0.05 mol) and 40 mL NMP were placed into a three-necked flask equipped with magnetic stirrer and nitrogen purge. After dissolution of 3,4'-ODA, a-ODPA (12.4 g, 0.04 mol) was added into the flask and kept stirring for 6 h at room temperature. Then end-capping reagent PEPA (4.96 g, 0.02 mol) and the rest NMP were added into the flask, and the mixture was stirred for another 16 h at room temperature to obtain a amide acid solution with a solid content of 20 wt%. Then the acetic anhydride (15.3 g, 0.15 mol) and triethylamine (15.2 g, 0.15 mol) were added one by one and the mixture was stirred for 6 h at room temperature. Finally, the product (denoted as TPI) was filtered, washed with deionized water for 3 times and ethanol for 1 time. Then dried at 150 °C under vacuum until constant weight.

### Preparation of KH550-modified cenosphere (CS)

Firstly, a 500 mL solution containing deionized water (5%) and ethanol (95%) was prepared. Then, 0.2 g KH550 silane coupling agent was added into the solution. The mixture was stirred at 40 °C for 90 min. 5 g cenospheres were added into the prepared mixture with 60 °C and kept stirring for 120 min. The solid product (denoted as CS) was dried under vacuum oven at 100 °C for 24 h.

### Preparation of composites (TPI/CS)

Thermosetting polyimide containing 3 wt% KH550-modified cenosphere was prepared by melt blending. The cenosphere and phenylethynyl terminated oligomer with calculated weight fractions were mixed by the torque rheometer for 20 min at 270 °C. Then obtained TPI/CS slurry was cooled and put into a vacuum bag for test. TPI oligomer for test was also mixed by the torque rheometer for 20 min at 270 °C. Figure 1 showed the melt blending of TPI oligomer and cenosphere.

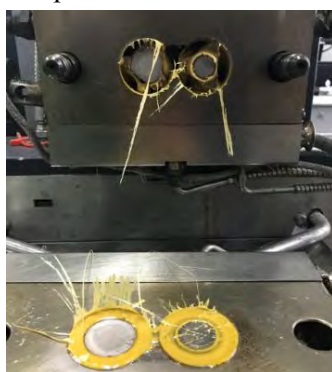


Fig. 1 the melt blending of oligomer and cenosphere.

## Characterization

Fourier transform infrared (FTIR) spectroscopy spectroscopy was recorded on Nicolet Nexus 8700 in the range of 400-4000  $\text{cm}^{-1}$ .

Differential scanning calorimetry (DSC) tests were performed on a TA DSC Q20 equipment with a nitrogen flow rate of 50 mL/min. Nearly 5 mg of the sample was heated to 500  $^{\circ}\text{C}$  at the heating rate of 20  $^{\circ}\text{C}/\text{min}$  for the first scan to observe its thermal curing behavior. After cooling to the ambient temperature, the second scan of the identical sample was measured for the  $T_g$  of the cured resin at a heating rate of 20  $^{\circ}\text{C}/\text{min}$ .

The melt rheological behavior was performed on HAAKE MARS III rheometer with a fixed strain of 5% and a fixed angular frequency of 10 rad/s. The melt viscosities of imide systems were measured from 200  $^{\circ}\text{C}$  to 380  $^{\circ}\text{C}$  at a heating rate of 4  $^{\circ}\text{C}/\text{min}$  under a continuous air flow.

The thermal stability was tested by TA Q5000 instrument, which was carried out in  $\text{N}_2$  atmosphere or air atmosphere with a heating rate of 20  $^{\circ}\text{C}/\text{min}$ .

## 3. RESULTS AND DISCUSSION

### Characterization of structures

FT-IR spectra of KH550, unmodified cenosphere and KH550-modified cenosphere were presented in Figure 2 (a) and (b). Absorption peaks observed at 1075  $\text{cm}^{-1}$  was due to the surface -OH groups of cenosphere. In the modified cenosphere spectrum, the new absorption peaks at 2979  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  are assigned to be for the  $\text{CH}_2$  stretching vibrations alkyl group of KH550.

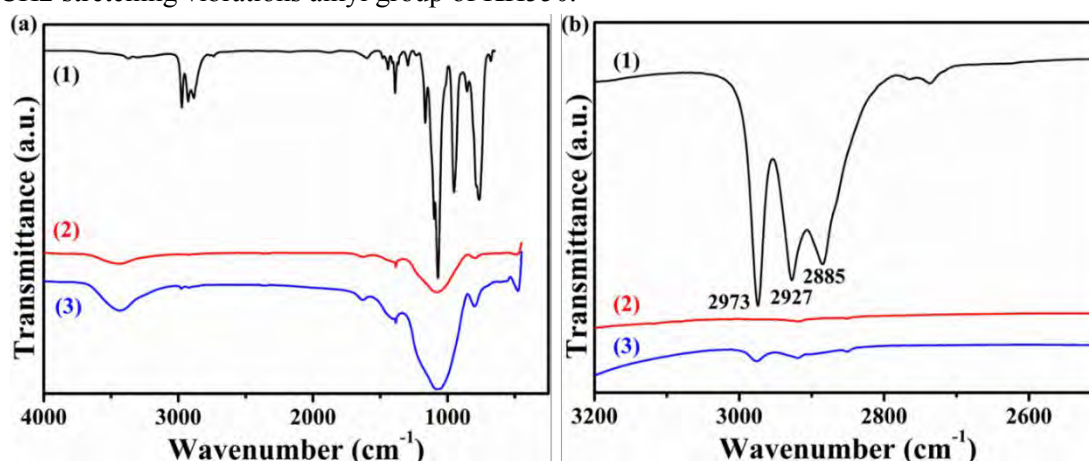


Fig. 2 (a) FT-IR spectra of (1) KH550, (2) unmodified cenosphere, (3) KH550-modified cenosphere. (b) Wavenumber between 2500 and 3200  $\text{cm}^{-1}$ .

### Thermal Properties of the blends

The typical DSC curves of TPI and TPI/CS were illustrated in Figure 3(a) and (b). It was found that TPI and TPI/CS samples exhibited similar thermal behavior. In the first scan, the two samples exhibited an endothermic shift of 183  $^{\circ}\text{C}$  and a large exothermic peak which was attributed to the thermal curing of the phenylethynyl groups. In comparison, the curing peak shifted to a higher temperature with addition of cenosphere, which was due to the reduction of crosslinking density.

In the second scan, the disappearance of the curing exothermic peaks indicated that all the phenylethynyl groups had been completely cured in the first DSC scan. Due to the high cross-linking density, the cured samples displayed a high  $T_g$  values. The  $T_g$  value for the cured TPI/CS composite was 287  $^{\circ}\text{C}$  which was about 11  $^{\circ}\text{C}$  higher than that of the cured TPI. The dispersion of the cenosphere in the cured resin may lead to less free volume around thermosetting polyimide segments and decrease the facility of the

mobility.

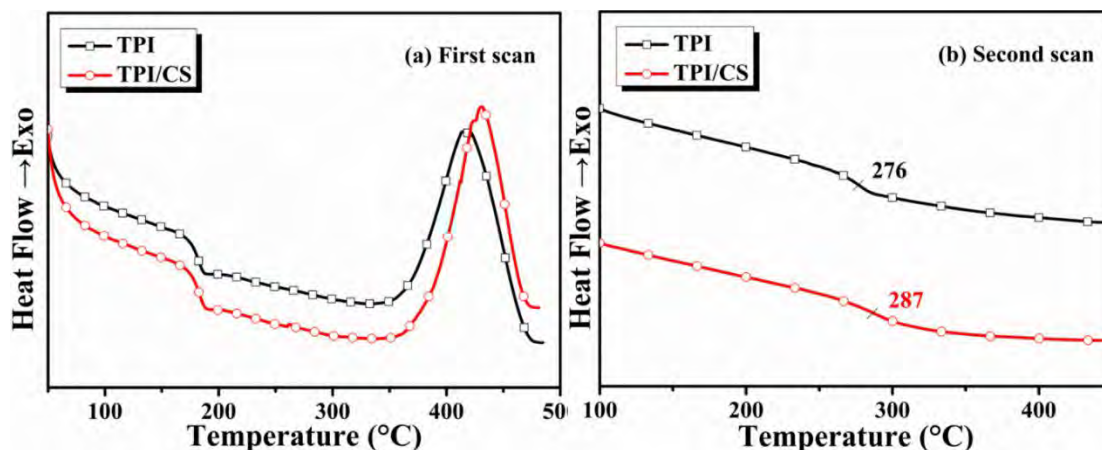


Fig. 3 DSC curves of TPI and TPI/CS (a) First scan, (b) Second scan.

### Melt processability of the blends

The melt viscosity for TPI and TPI/CS oligomers as a function of temperature was displayed in Figure 4. It was found that the melt viscosity of the two oligomers declined and finally reach the minimum value with the rise in temperature at first, and then ascended sharply due to the crosslinking of phenylethynyl groups. The minimum melt viscosities of TPI and TPI/CS oligomers were 2.0 Pa·s (315 °C) and 0.66 Pa·s (321 °C), respectively. The TPI oligomer with addition of 3 wt% cenospheres showed a broader melt processing window and a lower minimum complex viscosity. This phenomenon indicated that the processability of the oligomer was significantly improved by the addition of cenosphere. The low melt viscosity of oligomer could be adapted to a low-cost manufacturing process such as resin transfer molding (RTM). The reduction in the viscosities is the principle cause for the cenosphere with spherical structure.

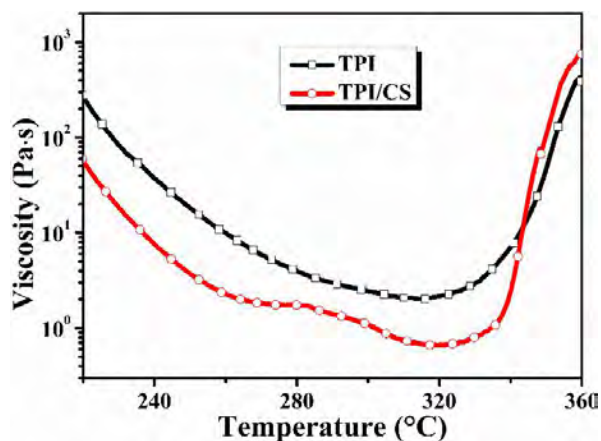


Fig. 4 Melt viscosity behaviors of TPI and TPI/CS oligomers.

### Thermal stability

Thermogravimetric analysis (TGA) was employed for determining weight changes with temperature. The TGA characterization in N<sub>2</sub> or air described in Figure 5. The thermal data for initial decomposition temperature (T<sub>d</sub>), the temperature of maximum rate of decomposition (T<sub>max</sub>), the char yield at 800°C (R<sub>w</sub>), and the onset temperature corresponding to 5% and 10% weight loss of cured polyimides are listed in Table 1.

It can be seen from the Table 1 that the cured TPI and TPI/CS samples had high thermal and thermal-oxidative stability. The T<sub>max</sub> values of the cured TPI and TPI/CS samples were 585 °C and 571 °C in N<sub>2</sub>, respectively. The T<sub>d5</sub> values of the cured TPI and TPI/CS samples were 545 °C and 518 °C in N<sub>2</sub>,

respectively. The char yield of the cured TPI and TPI/CS resins at 800 °C reached 60.4% and 60.3%, respectively. In comparison, the thermal resistance of TPI/CS resins was lower than pure TPI resin.

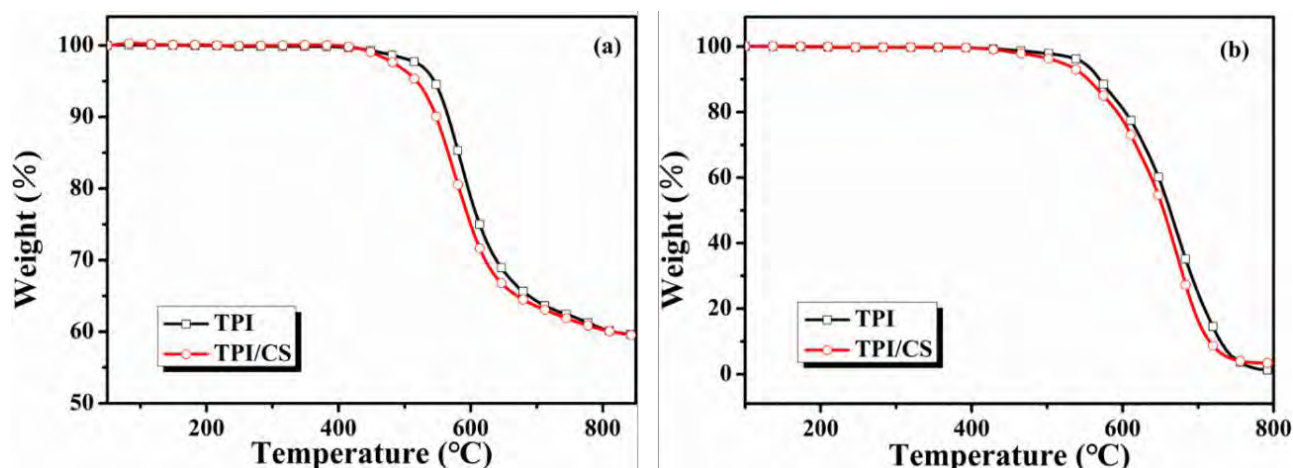


Fig. 5 TGA curves of the cured resins in (a) N<sub>2</sub> and (b) air atmosphere.

Table 1. TGA data of the cured imide compounds

Samples	TGA (N <sub>2</sub> )					TGA (air)		
	T <sub>d</sub> <sup>a</sup> (°C)	T <sub>max</sub> <sup>b</sup> (°C)	T <sub>d5</sub> <sup>c</sup> (°C)	T <sub>d10</sub> <sup>d</sup> (°C)	R <sub>w</sub> <sup>e</sup> (%)	T <sub>max</sub> (°C)	T <sub>d5</sub> (°C)	T <sub>d10</sub> (°C)
TPI	537	585	545	566	60.4	669	548	569
TPI/CS	513	571	518	548	60.3	674	519	554

<sup>a</sup> The onset decomposition temperature in N<sub>2</sub> or air atmosphere; <sup>b</sup> temperature of maximum rate of decomposition; <sup>c</sup> 5% weight loss temperature in N<sub>2</sub> or air atmosphere; <sup>d</sup> 10% weight loss temperature in N<sub>2</sub> or air atmosphere; <sup>e</sup> residual weight retention at 800 °C in N<sub>2</sub> atmosphere.

#### 4.CONCLUSION

In this research, thermal and melt viscosity properties of 3 wt% cenospheres filled thermosetting polyimide were evaluated. The T<sub>g</sub> value of cured TPI/CS resin was 287 °C, which was 11 °C higher than that of TPI. The melt processability of oligomer was improved significantly by addition of cenospheres. The cured polyimide resins had high thermal and thermal-oxidative stability. By this research work, the application potential of cenosphere as a modifier for thermosetting polyimide will be greatly broadened, especially for high-performance resin-based composite materials due to its low cost, lightweight and high thermal properties without sacrificing processability.

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