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Polyimide–silver nanocomposite containing phosphine oxide moieties in the main chain: Synthesis and properties

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Abstract

New flame-retardant polyimide–silver nanocomposite containing phosphine oxide moiety in the main chain was synthesized by a convenient ultraviolet irradiation technique. A precursor such as $AgNO_3$ was used as the source of the silver particles. Polyimide **6** as a source of polymer was synthesized by polycondensation reaction of bis (3-aminophenyl) phenyl phosphine oxide **4** with pyromellitic anhydride **5** in the presence of *iso*-quinoline as base and in *m*-Cresol solution. The resulting composite film was characterized by FTIR spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetry (TGA) and differential scanning calorimetry (DSC). The average size of the nanometer Ag particles is about 10 nm. The temperature of 5 and 10% weight loss and also the char yield at 600 °C of polyimide–silver nanocomposite **6a** were higher than the pure PI **6**.

Keywords: Flame-retardant; Polyimide–silver nanocomposite; Phosphine oxide moiety

Polyimides (PIs), especially aromatic polyimides, are the most famous high-performance synthetic polymers with versatile properties, such as high transition temperatures, good chemical resistance, excellent mechanical properties, and outstanding thermal and thermo-oxidative stability. These properties have made polyimides widely used in many fields including aerospace, electronics, and other modern industries [1]. With the development of nanotechnology, the investigation on polyimide-based nanocomposites or hybrids with inorganic particles such as metals, metal oxides, zeolites, organoclay and carbon nanotubes have been explored to further enhance the properties of PI materials [2–6]. Also incorporating a chemically reactive phosphorus-containing monomer into the polymer backbone is one of the most efficient methods of improving the flame retardancy of polymers [7,8]. In this article a new polyimide (PI)–silver nanocomposite containing phosphine oxide moiety in the main chain was prepared by using ultraviolet irradiation technique at room temperature.

1. Experimental

Fourier transform infrared (FTIR) spectra were recorded on Galaxy Series FTIR 5000 spectrophotometer (England). Thermal Gravimetric Analysis (TGA and DTG) data were taken on a Mettler TA4000 System under N_2

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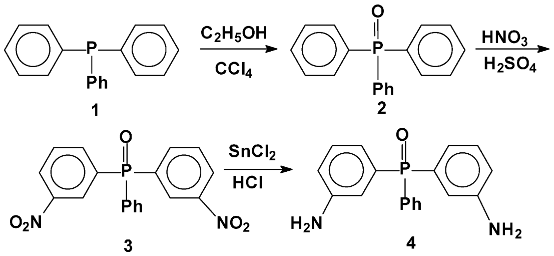


Scheme 1. Synthetic route of diamine **4**.

atmosphere at a rate of 10 °C/min. The morphology of nanocomposite film was investigated on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV. Differential scanning calorimetric analysis were performed on differential scanning calorimeter (Du Pont 910) at a heating rate of 10 °C/min. Limited oxygen indexes (LOI) were measured on a Stanton Redcraft flame meter. X-ray diffraction (XRD) were performed on Philips X-Pert (Cu-Ka radiation, λ = 0.15405 nm).

Bis (3-aminophenyl) phenyl phosphine oxide **4** was prepared in a three-step reaction by using simple organic compounds such as triphenyl phosphine according to a typical procedure that was shown in Scheme 1 [9].

A quantity of 5 mmol bis (3-aminophenyl) phenyl phosphine oxide **4**, 5 mmol pyromellitic anhydride **5** and two drops of *iso*-quinoline were dissolved in 25 mL *m*-cresol, consecutively. The mixture was stirred at room temperature for 2 h and then at 180 °C for 3 h. The obtained PI solution was precipitated in 100 mL ethanol. The precipitate was immersed in distilled water and ethanol for 2 h, and then washed with distilled water and ethanol several times to remove the residual *m*-cresol. The inherent viscosity of this soluble PI is 0.65 dL/g.

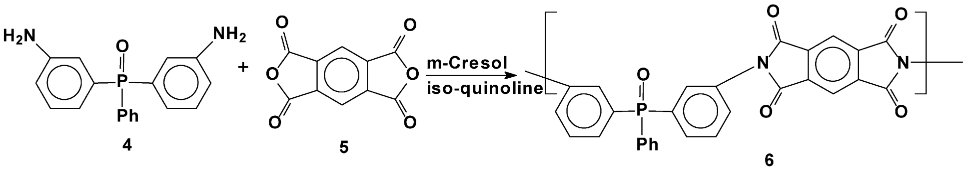
A 250 W high-pressure mercury lamp was used as the ultraviolet irradiation source. The $AgNO_3$ was introduced as the source of Ag nanoparticles. First a solution such as 1.0 g soluble PI in 7.0 mL of 1-methyl-2-pyrrolidone (NMP) and also a solution of 1.0 mmol $AgNO_3$ and 1.2 mmol trifluoroacetic acid (TFA) in 5.0 mL NMP were prepared. Then the two solutions were mixed and irradiated for 12 h to ensure the complete reduction of $AgNO_3$ under ultraviolet irradiation at room temperature. The product was precipitated quickly to distilled water and washed with distilled water for several times. Then the sample was dried in vacuum, redissolved in chloroform by sonication and was cast on a glass substrate and dried at 50 °C in vacuum for two days.

2. Results and discussion

Bis (3-aminophenyl) phenyl phosphine oxide **4** was prepared by using a three-step reaction from the simple organic compounds such as triphenyl phosphine **1**, as shown in Scheme 1. At first triphenyl phosphine **1** was oxidized to triphenyl phosphine oxide **2**, then compound **2** was converted to bis (3-nitrophenyl) phenyl phosphine oxide **3** by using concentrated nitric acid in the presence of sulfuric acid. Bis (3-nitrophenyl) phenyl phosphine oxide **3** was reduced to bis (3-aminophenyl) phenyl phosphine oxide **4** with $SnCl_2{\cdot}2H_2O$ (Scheme 1).

Polyimide **6** was synthesized by reaction of an equimolar mixture of diamine **4** with pyromellitic anhydride **5** in *m*-cresol solution and in the presence of *iso*-quinoline as a base (Scheme 2).

The FTIR spectrum of PI **6** exhibits characteristic absorption peaks for C=O unsymmetrical stretching of imide groups (at 1780 cm^{-1}), C=O symmetrical stretching of imide groups (at 1720 cm^{-1}) and C–N stretching of imide groups (at 1380 cm^{-1}). These bands show PI **6** has been successfully synthesized. In addition, no obvious difference between the infrared spectra of the pure PI **6** and the PI-silver nanocomposite **6a** was observed.



Scheme 2. Synthetic route of PI **6**.

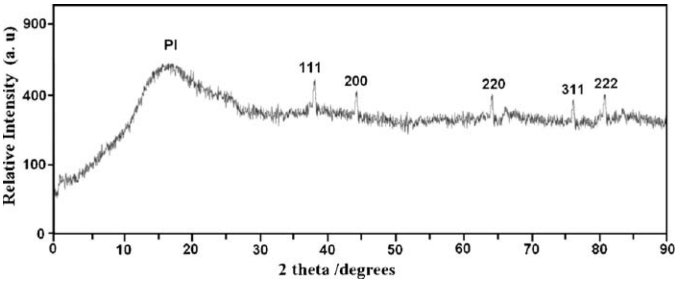


Fig. 1. XRD of polyimide–silver nanocomposite **6a**.

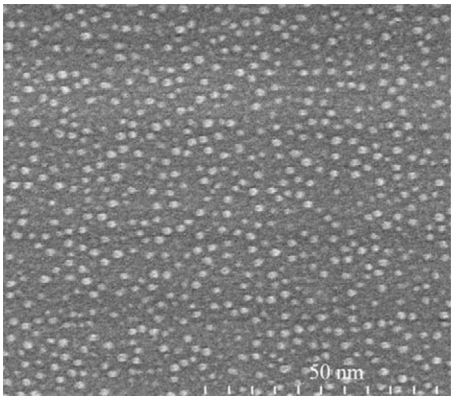


Fig. 2. TEM of polyimide–silver nanocomposite film **6a**.

The XRD patterns of polyimide–Ag nanocomposite **6a** further confirmed the incorporation of silver nanoparticles in the composites as shown in Fig. 1. The weak reflection centered at a 2θ value around 20° was characteristic of the amorphous polyimide [10]. Another five sharp diffraction peaks at 2θ values of 38.2°, 44.4°, 64.5°, 77.3° and 81.5° corresponded to Bragg's reflections from the (1 1 1), (2 0 0) (2 2 0), (3 1 1) and (2 2 2) planes of Ag and were in good agreement with the reported data [11]. These data which are close to the reported data in the JCPDS file No. 4-783.

The TEM micrograph of the PI-silver nanocomposite **6a** in Fig. 2 shows that the silver nanoparticles were homogeneously dispersed in polyimide matrix. The average size of the nanometer Ag particles is about 10 nm calculated from the half-peak width using the Scherrer formula. Also the content of Ag nanoparticles is around 10% of polyimide matrix of nanocomposite film **6a**.

The thermal properties of pure polyimide **6** and polyimide–silver nanocomposite **6a** were investigated by TGA (in a nitrogen atmosphere at a heating rate of 10 °C/min) and DSC experiments and the results are summarized in Table 1. The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600 °C for these samples are summarized in Table 1. The temperature of 5 and 10% weight loss and also the char yield at 600 °C of polyimide–silver nanocomposite **6a** were higher than the pure PI **6**. The content of Ag nanoparticles the char yield at

Table 1
Thermal and flame-retardant behaviors of polyimide **6** and polyimide–silver nanocomposite **6a**.

Polyimide	T_g [a]	T_5 (°C) [b]	T_{10} (°C) [c]	Char yield (%) [d]	LOI [e]
6	153	325	375	53	30
6a	160	375	400	62	32

[a] The glass-transition temperatures (T_g) were measured by DSC.

[b] Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 °C/min in N_2.

[c] Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N_2.

[d] Percentage weight of material left undecomposed after TGA analysis 600 °C.

[e] Limited oxygen index (LOI).

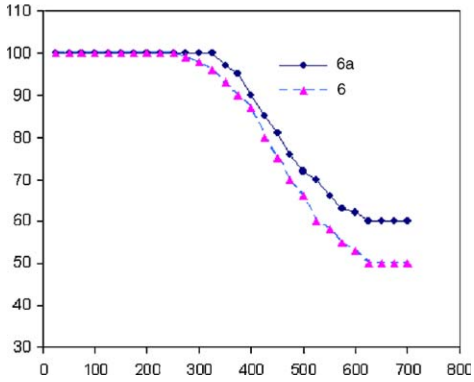


Fig. 3. TGA thermograms of PI **6** and polyimide–silver nanocomposite film **6a**.

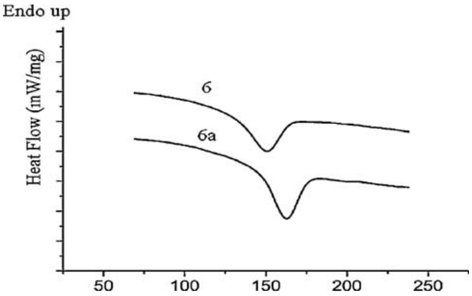


Fig. 4. DSC thermograms of PI 6 and polyimide-silver nanocomposite film **6a**.

600 °C of polyimide–silver nanocomposite **6a** is around 20%. The higher thermal stability of nanocomposite **6a** can be attributed to the presence of inorganic silver nanoparticles into the polyimide matrix (Fig. 3).

Also the T_g of nanocomposite **6a** was higher than pure polyimide **6** (Fig. 4). The increase in the T_g can be attributed to the strong interaction between the silver nanoparticles and polar imide chain.

The flame-retardant behavior of these samples was examined by measuring the limiting oxygen index (LOI). As can be seen from Table 1, the pure PI **6** had LOI value of about 30, the LOI value of the PI-silver nanocomposite **6a** was higher than that of pure PI **6**, and an increase in LOI value can be attributed to the presence of inorganic silver nanoparticles in polyimide matrix (Table 1).

3. Conclusion

In this work, a polyimide–silver nanocomposite film was successfully prepared by a convenient reduction of silver by ultraviolet irradiation technique. The high char yield and good LOI data of this nanocomposite film can be related to the presence of inorganic silver nanoparticles in the polyimide matrix. These properties can make this nanocomposite attractive for practical applications such as processable high-performance engineering plastics.

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