

Preparation and Characterization of Poly(amide-imide)/ZnO Nanocomposites Containing Pendent Benzoxazole and Benzimidazole Segments^{*}

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Abstract In the present investigation, novel poly(amid-imide)/zinc oxide nanocomposites (PAI/ZnO NCs) containing benzoxazole and benzimidazole pendent groups with different amounts of modified zinc oxide nanoparticles (ZnO NPs) were successfully prepared *via* the *ex situ* method. Poly(amid-imide) (PAI) was prepared by direct polycondensation of 2-[3,5-bis(*N*-trimellitimidoyl)phenyl]benzoxazole (DCA) with 5-(2-benzimidazole)-1,3-phenylenediamine (DAMI) and provided the polymeric matrix with well-designed groups. The surface of ZnO NPs was functionalized with 3-aminopropyltriethoxysilane (APS) coupling agent to have a better dispersion and enhancing possible interactions of NPs with functional groups of polymer matrix. The amount of APS bonded to the ZnO surface was determined by thermogravimetric analysis. PAI/ZnO nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). SEM analysis showed that the modified ZnO nanoparticles were homogeneously dispersed in polymer matrix. In addition, TGA data indicated an enhancement of thermal stability of the nanocomposite compared with the neat polymer.

Keywords: Poly(amide-imide); ZnO nanoparticles; Nanocomposites; Surface modification; Pendent group.

INTRODUCTION

Recently, polymer/inorganic nanocomposites as a new generation of high-level materials have attracted the attention of researchers because they are able to produce superior properties over the parent polymer or inorganic hybrid materials. Properties of polymer-inorganic nanocomposites are not only the sum of the individual contributions of both phases but are usually combined and improved. Indeed, the hybrid materials retain the advantageous features of both polymeric materials (such as light weight, versatility in tailoring chemical, physical and mechanical properties, low manufacturing cost, easy shaping and processability, *etc.*) and inorganic filler (such as high strength, heat stability, and chemical resistance). Moreover, the presence of inorganic filler is able to change deeply the thermo-mechanical, optical, electrical, and magnetic properties of a polymeric matrix. Obviously, these properties are strongly dependent on the nature of the constituents as well as the shape, size distribution and crystallinity of the incorporated particles^[1–3].

Among all the potential nanofillers for fabrication of nanocomposites, zinc oxide nanoparticle (ZnO NP) is of significant scientific and industrial interest with very large surface area, easy availability, biocompatibility, outstanding mechanical properties, intensive ultraviolet absorption, as well as high thermal and chemical stability, making it one of the most employed materials to be used as reinforcing fillers in composites. Therefore,

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it has been widely used for applications ranging from solar cells^[4], UV absorbers^[5], biosensors^[6], piezoelectric devices^[7] and optoelectronics^[8]. However, the homogeneous dispersion of nanoparticles in polymers is difficult due to the incompatibility at the interphase between the hydrophobic matrix and the hydrophilic oxide surface. In addition, nanoparticles tend to strongly aggregate, hence degrading the properties of the resultant nanocomposite materials. A combination of suitable surface treatments of the NPs and appropriate dispersion techniques is required to circumvent this problem, as the NPs are added to a polymer matrix. Producing excellent integration and an improved interface between inorganic filler and the polymer matrix, surface modification of inorganic particles is a popular technique^[9]. Two approaches are generally proposed for surface modification of inorganic NPs^[10, 11]: 1) chemical treatment (surface pretreatment of NPs by coupling agent or grafting polymerization) and 2) physical treatment (through covering the NPs with surfactant treatment or polymer encapsulation). By applying the two mentioned strategies, nanoparticle agglomeration will be alleviated considering their large surface area and high surface energy and the dispersion stability of nanoparticles in polymer matrices will be improved. In physical treatment, the reaction between organic surfactant or polymer and particles results in weak secondary forces such as van der Waals, hydrogen and electrostatic forces while in the chemical treatment there is a strong covalent attachment^[10]. Among the possible techniques for chemical modification of inorganic particles, coupling agent treatment is the most popular and the easiest technique to be applied^[11]. Silane coupling agents can effectively reduce the hydrophilic nature and surface energy of the particles consequently reducing agglomerations and increasing matrix interactions^[9]. Silanization treatment by 3-aminopropyltriethoxysilane (APS) was targeted in this study for chemical modification of ZnO particles.

Aromatic polyimides (PIs) are well recognized as a class of high performance polymers due to their resistance to high temperatures, mechanical stress, and variety of chemicals^[12, 13]. One of the problems with high-performance PIs is their poor solubility or processability, and they do not react below their decomposition temperature that causes their application as engineering materials to be restricted. Therefore, the incorporation of new functionalities to make polyimides more tractable without deteriorating their own excellent properties has become an important target of polyimide chemistry. To overcome these limitations, synthetic efforts have been centered on increasing their solubility in organic solvents without sacrificing the above mentioned outstanding properties. New synthetic methods have been focused on improving solubility and processability through the synthesis of new diamine or dianhydride monomers. Attempts in this field include the incorporation of bulky substituents as pendent groups^[14], flexible bridging linkages^[15], and structurally unsymmetrical segments^[16] into the polymer backbone. However, copolymerization is another popular synthetic approach for obtaining processable and soluble polyimides^[17–19]. The replacement of polyimides by copolyimides such as poly(amide-imide)s (PAIs) may be useful in the modification of the intractable nature of polyimides. PAIs are a class of high performance polymeric materials while having the property advantages of both polyamides and polyimides that means they possess thermal stability balanced with processability^[20, 21].

In the present study, we have tried to fabricate and characterize novel poly(amid-imide)/zinc oxide nanocomposites (PAI/ZnO NCs) having benzoxazole and benzimidazole pendent groups through the ultrasonic method. First, to prevent the agglomeration of ZnO NPs in the PAI matrix and to improve their interactions with the polymer, the surface of them was treated by APS as a silane coupling agents. The PAI was prepared during polycondensation reaction of 2-[3,5-bis(*N*-trimellitimidoyl)phenyl]benzoxazole (DCA) with 5-(2-benzimidazole)-1,3-phenylenediamine (DAMI) in the presence of triphenyl phosphite (TPP) as an activating agent. Subsequently, PAI/ZnO NCs were fabricated by adding different amounts of modified ZnO NPs (5 wt%, 10 wt%, and 15 wt%) into the PAI matrix under the ultrasonic irradiation. The obtained NCs were characterized by the Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA).

EXPERIMENTAL

Materials

All chemicals were purchased from Merck and Aldrich Chemical Co. Trimellitic anhydride, ethanol (anhydrous), glacial acetic acid (purity > 99%), triphenyl phosphite (TPP) and polyphosphoric acid (PPA) were purchased from Merck and were used without further purification. *N*-Methyl-2-pyrrolidone (NMP) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. 2-Aminophenol (Merck) was recrystallized from distilled water. Aromatic diamines, including 1,2-phenylenediamine and 1,3-diaminobenzoic acid were recrystallized from ethanol. Nanosized ZnO powder was purchased from Neutrino Co. (Tehran, Iran) with average particle size of about 25–30 nm and dried in a vacuum oven at 150 °C for 3 h before surface modification. 3-Aminopropyltriethoxysilane (APS) (99% purity, 0.946 g/mL, Aldrich) was used as received.

Synthesis of Monomers

2-[3,5-Bis(*N*-trimellitimidoyl)phenyl]benzoxazole (DCA)

The dicarboxylic acid monomer (DCA) was synthesized by using a two-step procedure as described previously^[22].

FTIR (KBr, cm⁻¹): 3400–2500, 1780, 1730, 1603, 1557, 1452, 1360, 1238, 1085, 926, 870, 722; ¹H-NMR (DMSO-d₆, δ): 13.77 (broad, carboxylic acid, 2H), 8.44 (m, 4H), 8.34 (d, 2H), 8.11 (d, 2H), 7.94 (d, 1H), 7.83 (m, 2H), 7.46 (m, 2H); ¹³C-NMR (DMSO-d₆, δ): 165.9, 165.7, 162.2, 160.8, 150.3, 141.3, 136.7, 135.5, 134.8, 133.2, 132.0, 128.4, 127.5, 126.0, 125.1, 123.9, 123.5, 123.0, 120.1, 111.0; Elemental analysis. Calculated for C₃₁H₁₅N₃O₉: C, 64.93; H, 2.64; N, 7.33; Found: C, 64.56; H, 2.73; N, 7.51.

Diamines

Aromatic diamines, including 5-(2-benzoxazole)-1,3-phenylenediamine (DAMO, mp = 226–230 °C)^[22] and 5-(2-benzimidazole)-1,3-phenylenediamine (DAMI, mp = 246–247 °C)^[23] were synthesized according to our previous works.

Polymer Synthesis (PAI)

The PAI was prepared *via* a direct condensation reaction, according to the previously reported procedure^[22]. Briefly, a mixture of 0.372 g (0.65 mmol) DCA and 2.5 mL NMP was stirred under nitrogen atmosphere and heated to 70 °C to dissolve DCA. Pyridine (0.6 mL), 0.7 mL TPP, and 0.25 g calcium chloride were added to the reaction mixture. The mixture was stirred and heated to 110 °C. An equal molar amount of diamine DAMI (0.146 g, 0.65 mmol) was then added to this mixture. The resulting mixture reacted at 110 °C for 5 h. After the completion of polymerization, the viscous mixture was poured into methanol. The precipitated polymer was filtered and washed thoroughly with methanol and hot water and then dried under a vacuum to give 0.430 g (87%) of PAI. The inherent viscosity of polymer was 0.43 dl g⁻¹ measured at a concentration of 0.5 g/dl in *N,N*-dimethylacetamide (DMAc) at 30 °C.

IR (KBr): 3400–3200, 1778, 1724, 1667, 1611, 1585, 1361, 1276, 1101, 870, 770, 725 cm⁻¹; ¹H-NMR (DMSO-d₆, δ): 12.74 (s, imidazole proton, 1H), 10.82 (s, amide protons, 2H), 6.76–8.35 (m, aromatic protons, 20H); Elemental analysis: Calcd. for (C₄₄H₂₃N₇O₇)_n: C, 69.38%; H, 3.04%; N, 12.87%. Found: C, 69.54%; H, 3.11%; N, 12.66%.

Surface Functionalization of ZnO NPs with APS (APS-ZnO NPs)

Silane grafting reaction onto the surface of oxide nanoparticles was carried out in ethanol. The dried ZnO NPs (3.0 g, 36.8 mmol) was added into absolute ethanol (60 mL) and was ultrasonicated for 45 min. Then, 0.60 g (2.7 mmol) APS (20 wt%) based on the content of ZnO) was added to the dispersed solution. The resulting colloidal suspension was ultrasonically stirred for one hour and precipitated by centrifugation. The precipitated nanoparticles were rinsed with absolute ethanol to remove the excessive APS. The redispersion and centrifugation were repeated with fresh ethanol until no APS could be detected by FTIR in the ethanol solution after centrifugation. The white APS-ZnO NPs were dried under vacuum at 50 °C for 24 h.

Fabrication of PAI/ZnO Nanocomposites

The fabrication of PAI/ZnO nanocomposites was carried out by the following procedure. Different amounts of APS-ZnO NPs (5 wt%, 10 wt% and 15 wt%) were mixed with PAI (0.1 g) and the mixture was dispersed in 20 mL of absolute ethanol, then it was irradiated under ultrasound waves for 4 h. After irradiation, the solvent was removed and the obtained solid was dried in vacuum at 80 °C for 4 h.

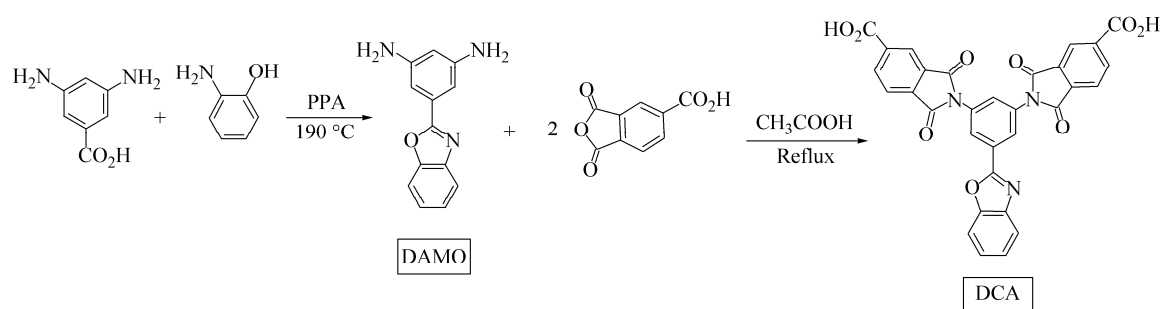
Techniques

^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker AV-500 FT-NMR spectrometer in DMSO- d_6 , at 25 °C with frequencies of 500.13 and 125.77 MHz for the ^1H and ^{13}C spectra, respectively. Multiplicities of proton resonance are assigned as singlet (s), doublet (d), triplet (t) and multiplet (m). FTIR spectra were recorded on a Bruker Tensor-27 spectrometer for the measurement of infrared absorption spectra for monomer, polymer and nanocomposites in the spectral range between 4000 and 400 cm^{-1} with KBr pellet. Inherent viscosity (η_{inh}) of polymer was determined for solution of 0.5 g/dl in DMAc at 30 °C using a Canon-Fenske viscometer. Elemental analyses were carried out with a Perkin-Elmer model 2400 C, H, N analyzer. The morphologies of the samples were determined with a Hitachi S-4160 scanning electron microscope (SEM) at an acceleration voltage of 15 kV. Wide-angle X-ray diffraction (XRD) patterns for each polymeric film were performed with an X'Pert PRO MPD diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) at a scanning rate of 0.02 (°)/min over a range of $2\theta = 10^\circ$ – 80° . Thermo-gravimetric analyses (TGA) were conducted with a Perkin Elmer instrument in nitrogen atmosphere (20 cm^3/min) at a heating rate of 10 K/min, from 25 °C to 800 °C and equilibrate at 30 °C for 5 min.

RESULTS AND DISCUSSION

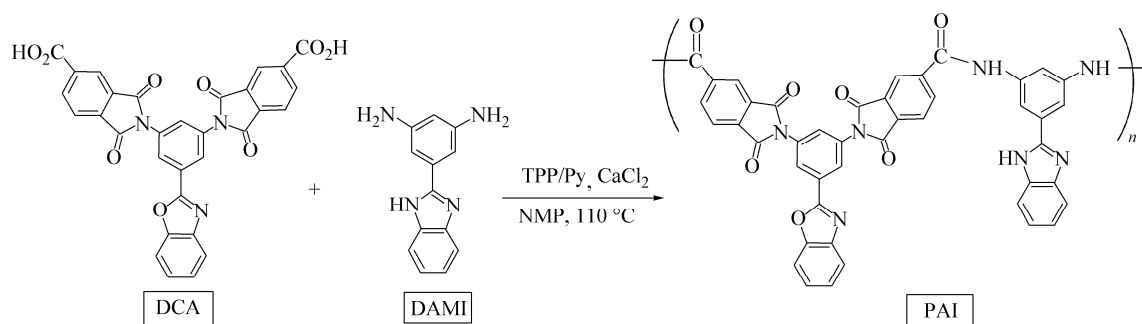
Monomer and Polymer Synthesis

Compound 2-[3,5-bis(*N*-trimellitimidoyl)phenyl]benzoxazole (DCA) containing pendent benzoxazole group has been previously synthesized through a two-step synthetic procedure starting from 3,5-diaminobenzoic acid and 2-aminophenol outlined in Scheme 1^[22]. First, the 5-(2-benzoxazole)-1,3-phenylenediamine (DAMO) was prepared *via* a cyclodehydration reaction of 3,5-diaminobenzoic acid with an equivalent amount of 2-aminophenol in the presence of polyphosphoric acid (PPA) as the condensation agent and solvent at 190 °C. In the second step, dicarboxylic acid monomer (DCA) was prepared by the condensation of the diamine (DAMO) with two mole equivalents of trimellitic anhydride in refluxing glacial acetic acid. The condensation reaction between the amines and anhydride groups as well as the subsequent cyclodehydration reaction was carried out in the heterogeneous solution.



Scheme 1 Synthesis route of dicarboxylic acid monomer (DCA)

As shown in Scheme 2, the PAI was prepared from compound DCA with 5-(2-benzimidazole)-1,3-phenylenediamine (DAMI) by a direct condensation reaction using TPP/pyridine system as a condensing agent (Yamazaki process).

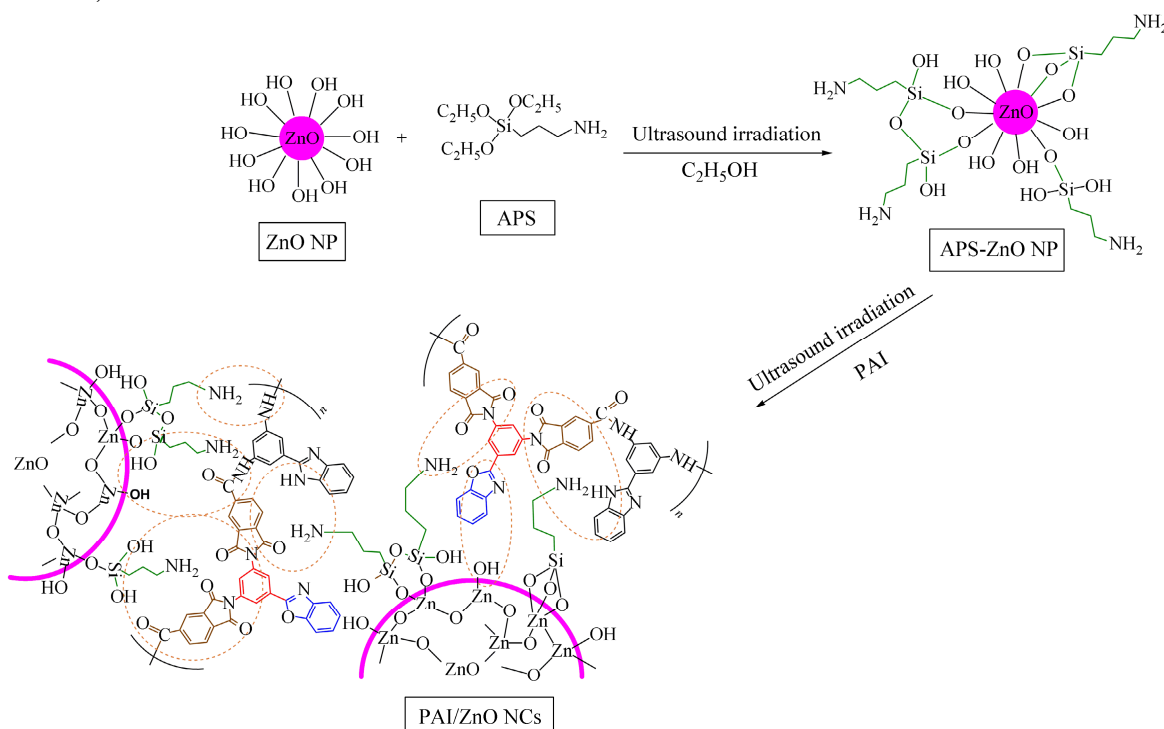


Scheme 2 Synthesis of poly(amid-imide) (PAI)

Surface Treatment of ZnO NPs and Fabrication of the PAI/ZnO NCs

The major aim for surface modification of ZnO NPs is to prevent the agglomeration of NPs in polymer matrix and to improve the compatibility of ZnO filler with polymer matrix. In this study, the surface of ZnO nanoparticles was treated using APS. A substitution reaction can take place between the hydroxyl surface groups of the ZnO nanoparticles and the ethoxyl groups from the coupling agent, thereby changing the ZnO surface to be more hydrophobic with better affinity to organic matrix^[24, 25]. Silanol groups of APS generated by hydrolysis can interact with hydroxyl groups on the ZnO NPs surface and form the modification layer with NH₂ groups. The surface modification process is illustrated in Scheme 3.

PAI/ZnO NCs were prepared *via* a solution blending method. Different amounts of APS-ZnO NPs (5 wt%, 10 wt% and 15 wt%) were loaded into neat PAI and the mixture was dispersed in absolute ethanol, under ultrasonic irradiation. Due to the high local pressure and temperature produced during sonication, the APS-ZnO NPs could be completely dispersed in PAI. When functionalized NPs are embedded into PAI matrix, weak interactions such as electrostatic and hydrogen bonding between the N—H and C=O groups of PAI with the NH₂ groups of coupling agent could generate a relatively suitable stabilization of the NPs in the polymer matrix (Scheme 3).



Scheme 3 The proposed interaction of APS with ZnO NPs and schematic representation for the fabrication of PAI/ZnO NCs

FTIR Study

The FTIR spectra of raw and modified ZnO, PAI, and the corresponding nanocomposites were recorded to corroborate the success of the surface modification treatment and to obtain information about the nanoparticle-polymer interactions (see Fig. 1). In the spectrum of raw ZnO (Fig. 1a), a broad peak between 3350 cm^{-1} and 3450 cm^{-1} is due to the stretching vibrations of the OH group on the nanoparticle surface. The appearance of peaks at 1582 cm^{-1} and 1425 cm^{-1} is attributed to the vibration of Zn–O bonds. Further, a broad and intense peak appears at 450 cm^{-1} that corresponds to the stretching of Zn–O bonds^[24]. The spectrum of APS-ZnO (Fig. 1b) reveals some new peaks compared to those of pristine nanoparticles. The bands at 2970 cm^{-1} and 2820 cm^{-1} are assigned to symmetrical and asymmetrical stretching vibrations of C–H in CH_3 and CH_2 groups, respectively. The N–H bending vibration of primary amine appeared at 1578 and 1509 cm^{-1} . Furthermore, the peak at 1018 cm^{-1} can be attributed to the Si–O–Si asymmetric stretching, and that at 878 cm^{-1} is assigned to Zn–O–Si symmetrical stretching vibrations^[25]. The appearance of these bands proves that the functional groups of APS were successfully attached onto the ZnO surface.

The spectra of PAI and PAI/ZnO NCs are also shown in Fig. 1. Neat PAI (Fig. 1c) shows characteristic absorption bands for the imide ring at around 1781 and 1725 cm^{-1} (imide-I), which is indicative of the asymmetrical and symmetrical C=O stretching vibration. The other absorption peaks at 1355 (imide-II), 1080 (imide-III), and 724 cm^{-1} (imide-IV) were assigned to axial, transverse, and out-of-plane vibrations of the cyclic imide structure, respectively^[19]. The N–H stretching bands of the amide and imidazole could be observed at 3350 cm^{-1} , and the C=O stretching band of amide group at 1670 cm^{-1} , the C=N stretching band oxazole and imidazole segments at 1611 cm^{-1} and the N–H bending and C–N stretching bands at 1550 cm^{-1} could also be observed^[22]. The FTIR spectra of nanocomposites (Figs. 1d–f) are almost similar to that of pure PAI spectrum (Fig. 1c). Due to the hydrogen interaction between NH_2 or free OH groups of modified ZnO NPs and different functional groups of PAI, the characteristic functional group peaks of these NCs shift to lower frequencies along

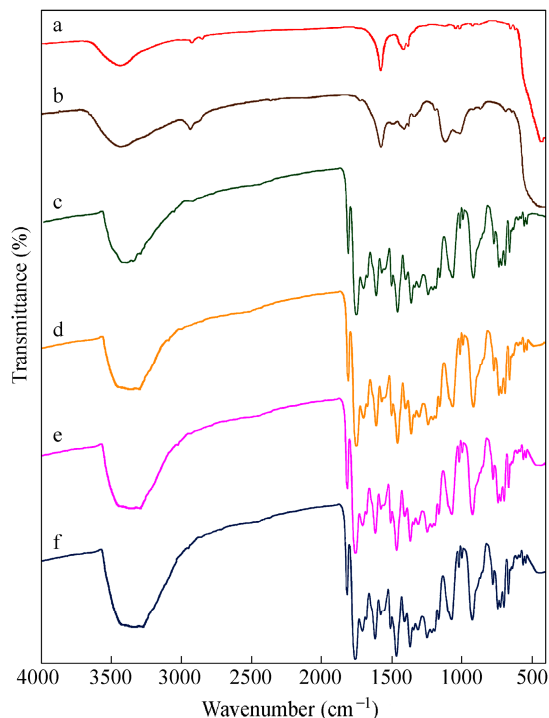


Fig. 1 FTIR spectra of (a) pristine ZnO NPs, (b) APS-ZnO NPs, (c) neat PAI and PAI/ZnO NCs with different APS-ZnO NPs contents: (d) 5 wt%, (e) 10 wt% and (f) 15 wt%

with the broadening and diminution in the intensity in comparison to those of the neat PAI. Moreover, a new broad absorption band in the range of 400–550 cm^{-1} could be attributed to the Zn–O stretching bonds. This confirmed the existence of ZnO NPs in the polymer matrix. While the loading of the ZnO NPs was increased, the intensities of Zn–O bands became more obvious. Since the characteristic peaks of PAI and ZnO both present on NCs spectra, it is clear that PAI/ZnO nanocomposites were successfully synthesized.

X-ray Diffraction

The crystallinity of the APS-ZnO NPs, neat PAI, and PAI/ZnO nanocomposite with 10 wt% loading was examined by XRD in the region of $2\theta = 10^\circ$ – 80° , as shown in Fig. 2.

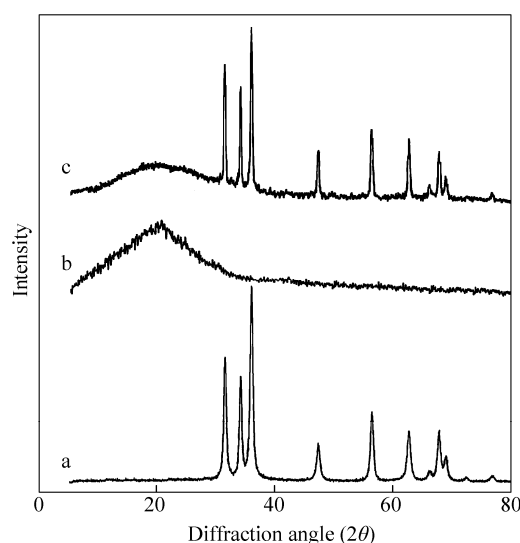


Fig. 2 XRD patterns of APS-ZnO NPs (a), pure PAI (b) and PAI/ZnO NC (10 wt%) (c)

The bare nanoparticles show characteristic peaks at 2θ value of 31.8° , 34.4° , 36.3° , 47.6° , 56.6° , 62.9° , 66.4° , 67.9° , 69.1° , 72.6° and 77.0° can be assigned to (100), (002), (101), (102), (110), (103), (112), (200), (201), (004) and (202) crystal planes of pure ZnO with hexagonal wurtzite structure and the lines match well with the normal values reported by JCPDS (No. 36-1451). The modified nanoparticles (APS-ZnO NPs) display an almost identical pattern to that of the unmodified counterparts. This corroborates the fact that the coupling agent does not influence the crystalline structure. As the figure indicates, it can be observed that the PAI is an amorphous polymer (the broad hump centered at $2\theta = 20^\circ$) and exhibits no anisotropic behaviors, which can be attributed to the presence of bulky benzoxazole and benzimidazole pendent groups which increased the disorder in the chains and hindered dense chain packing, thus, reducing the interchain interactions of the polymer. The XRD pattern of PAI/ZnO (10 wt%) nanocomposite shows characteristic peaks of PAI and ZnO indicating that the morphology of ZnO NPs has not been changed during the process. Further, the average crystallite size of ZnO obtained from the plane of PAI is about 28 nm, as estimated from the full-width at half maximum (FWHM) of 101 diffraction peak using the Scherrer formula^[26]. This is in agreement with the size of used ZnO nanoparticles.

Morphological Analysis

The surface morphology of neat PAI and the corresponding nanocomposites was investigated by SEM, and typical images are shown in Fig. 3. As can be observed (Fig. 3a), the surface of neat PAI is smooth and uniform. However, some transparent spots could be readily observed in the micrographs of the nanocomposites, (Fig. 3b). Comparing the smooth surface of neat PAI and the spongy surface of PAI/ZnO nanocomposite (15 wt%) it could be determined that these protuberant dots should be ZnO NPs, indicating that ZnO NPs have influence on the

surface morphology of polymer. Hence, the incorporation of APS-ZnO nanoparticles into PAI matrix could successfully result in a nanocomposite with a high degree of homogeneity.

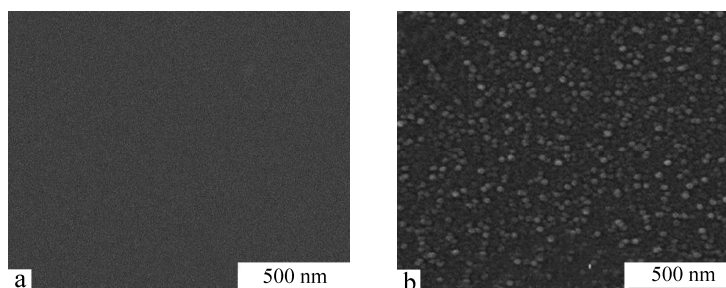


Fig. 3 Typical SEM micrographs of pure PAI (a) and PAI/ZnO nanocomposite (15 wt%) (b)

Thermal Stability

Figure 4 shows representative TGA thermograms obtained under a nitrogen atmosphere of raw and functionalized ZnO, neat PAI and its nanocomposites with 5 wt%, 10 wt% and 15 wt% loadings. To estimate the amount of silane coupling agents on the ZnO nanoparticle surface, TGA technique was performed on both the unmodified and surface modified ZnO nanoparticles. As can be seen from the curves, the bare nanoparticles had a very small weight loss (~ 1.7 wt%) below 300 °C, probably due to the removal of physically and chemically adsorbed water on their surface. Two weight losses are detected regarding the APS-ZnO nanoparticles, the one around 300 °C related to the decomposition of physically adsorbed APS and the other centered at about 450 °C arising from the degradation of the coupling agent covalently bonded to the nanoparticles^[27]. The weight loss (at 750 °C) of the unmodified ZnO nanoparticles and the APS-modified ZnO were 2.1% and 5.2% respectively, after achieving the thermogram plateaus during heating. Comparing the TGA curves of raw and modified ZnO, it is deduced that about 3.1 wt% of the total weight loss of the APS-ZnO is due to the detachment of the coupling agent. Therefore, the percentage of modification (M) of ZnO nanoparticles by APS and the grafting efficiency (E_g) were calculated from TGA at 750 °C as shown in the following Eqs. (1) and (2)^[28].

$$M (\%) = (\text{Weight loss of APS-ZnO}) - (\text{Weight loss of ZnO}) \quad (1)$$

$$E_g (\%) = (m_{\text{APS grafted}} / m_{\text{APS introduced}}) \times 100 \quad (2)$$

where, $m_{\text{APS grafted}} = M \times [m_{\text{ZnO}} / (100 - M)]$.

Values of the percentage of modification (M) and the grafting efficiency of APS onto the surface of ZnO nanoparticles are 3.1 and 15.9, respectively.

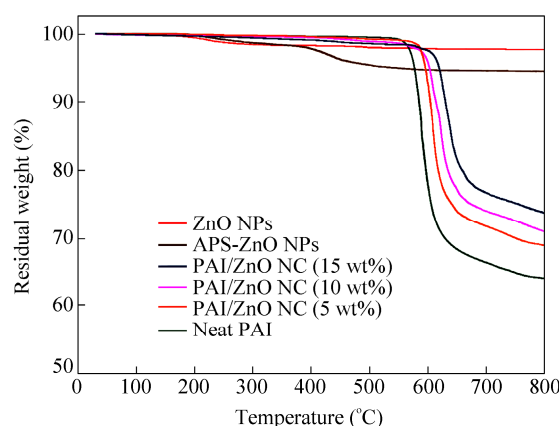


Fig. 4 TGA curves obtained for ZnO, APS-ZnO, PAI and the corresponding nanocomposites with 5 wt%, 10 wt%, and 15 wt% loading

TGA technique was also applied to determine the effect of the modified ZnO NPs on the thermal stability of the NCs. The TGA curves of neat PAI and its nanocomposite with different contents of APS-ZnO under nitrogen flows are shown in Fig. 4. In TGA, three parameters were measured: the temperature of thermal degradation at 5% (T_5) weight loss, the temperature at 10% (T_{10}) weight loss, and the yield of charred residue under nitrogen flow at 800 °C. The summary of TGA results is listed in Table 1. As shown in Fig. 4, neat PAI shows good thermal stability due to the existence of various linkages such as imide and amide groups in polymer backbones. The onset of decomposition temperature of the NCs was higher than that of neat PAI, shifting toward higher temperatures as the amount of modified-ZnO was increased. The improvement of thermal property of PAI/ZnO NCs can be attributed to the homogeneous dispersion of modified-ZnO NPs in polymer matrix and the hydrogen bonding between OH and NH₂ groups on the surface of APS-ZnO NPs and nitrogen atoms or carbonyl group of PAI matrix. Moreover, the high thermal conductivity of ZnO should facilitate heat dissipation within the composite, resulting in enhanced thermal stability^[29]. The char yield of the pure PI is 64%, while that of the PAI/ZnO NCs with 5 wt%, 10 wt% and 15 wt% of ZnO nanoparticles were 69%, 71% and 74%, respectively (Table 1).

Table 1. Thermal parameters obtained from TGA analysis of PAI and the nanocomposites reinforced with different loadings of APS-ZnO NPs

Sample	Decomposition temperature (°C)		Char yield ^b (%)	OI ^c (%)
	T_5^a	T_{10}^a		
Neat PAI	574	587	64	43.1
PAI/ZnO (5 wt%)	593	601	69	45.1
PAI/ZnO (10 wt%)	602	613	71	45.9
PAI/ZnO (15 wt%)	618	629	74	47.1

^a Temperature obtained at 5% (T_5) and 10% (T_{10}) weight loss;

^b Percentage weight of material left undecomposed at 800 °C;

^c Oxygen index (OI) parameter evaluated at char yield at 800 °C

The nanoparticles not only enhance the thermal stability of the matrix, but also promote stable char formation; hence they have an important effect on the flame retardant ability of the nanocomposites. The char residues under inert atmosphere can be correlated with the Oxygen Index (OI) through the equation developed by van Krevelen: $OI \times 100 = 17.5 + 0.4CR$, where CR is the char residue in wt% at 800 °C^[30]. The limiting OI (LOI) is defined as the minimum amount of oxygen in a nitrogen-oxygen mixture that is just sufficient to maintain combustion after ignition. Since air comprises approximately 21% oxygen by volume, any material with a LOI less than this will burn easily in air. Conversely, the burning behavior and tendency to propagate flame for a polymer with a LOI greater than 21 will be reduced or even zero after removal of the igniting source^[31]. The better flame retardancy of PAI/ZnO NCs than the neat PAI can be attributed to the presence of ZnO NPs acting as an insulator and mass transport barrier that hinders the escape of volatile products generated during the decomposition process and also prevents oxygen from reaching the matrix^[27].

CONCLUSIONS

In the present investigation, a series of new PAI/ZnO nanocomposites containing bulky benzimidazole and benzoxazole pendent groups in the structure of polymer matrix have been successfully synthesized *via* embedding ZnO nanoparticles into PAI matrix through the ultrasonic irradiation technique. In order to improve compatibility of ZnO NPs and reduce the agglomeration of them in the organic matrix, the ZnO surface was grafted with 20 wt% of APS as a coupling agent to form APS-ZnO. The presence of the coupling molecule on the surface of NPs was confirmed by FTIR spectroscopy and TGA analysis. The chemical structure and morphology of different nanocomposites were characterized by different techniques. FTIR and XRD data confirmed the presence of ZnO nanoparticles in the PAI matrix. SEM images showed that the ZnO nanoparticles were homogeneously dispersed in the polymer matrix. The results obtained from the thermal analysis of the PAI/ZnO NCs prove an improvement in the thermal properties in comparison with the neat PAI and this increase goes to be higher when the NP content increases.

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