

A facile route for the preparation of novel optically active poly(amide–imide)/functionalized zinc oxide nanocomposites containing pyromellitoyl-bis-L-phenylalanine moieties

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Received: 13 June 2011 / Revised: 5 August 2011 / Accepted: 8 August 2011 /
Published online: 18 August 2011
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Abstract In the present investigation, at first, the surface of zinc oxide (ZnO) nanoparticles was treated with a silane coupling agent of γ -methacryloxypropyl-trimethoxy silane (KH570), which introduces organic functional groups on the surface of ZnO nanoparticles. Secondly, optically active poly(amide–imide) (PAI) was synthesized via solution polycondensation of *N,N'*-(pyromellitoyl)-bis-phenylalanine diacid chloride **1** (**M-1**) with 4,4'-diaminodiphenylsulfone **2** (**M-2**). The polycondensation of diacid chloride with aromatic diamine was carried out with *N,N*-dimethylacetamide/triethylamine systems. Finally PAI/ZnO nanocomposites (NCs) containing 4, 8, and 12% of nanoparticles were successfully fabricated through ultrasonic irradiation technique. The obtained NCs were characterized by Fourier transform-infrared (FT-IR) spectroscopy, thermogravimetry analysis, X-ray powder diffraction, UV–Vis spectroscopy, scanning electron microscopy (SEM), field emission-scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The FT-IR spectroscopy indicated that the silane coupling agent was anchored on the surface of ZnO nanoparticles. SEM, FE-SEM, and TEM images were showed ZnO nanoparticles were dispersed homogeneously in PAI matrix.

Keywords Polymers · Nanostructures · Ultrasonic techniques · Surface properties

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Introduction

Semiconductor nanoparticles are receiving much attention owing to their novel physical and chemical properties, in comparison with the bulk semiconductor. Recently, zinc oxide (ZnO) has been found highly attractive because of its remarkable application potential in photo-catalysts [1], solar cells [2], chemical sensors [3, 4], piezoelectric transducers [5], UV shielding, and bio-imaging [6–8]. ZnO is an n-type semiconductor as well as TiO₂. Only these two metal oxides, among the 3d transition metal oxide semiconductor series, have sufficient stability on photo-excitation state. The band gap energy of ZnO is 3.37 eV. Their stability can be justified with decreasing the possibility of electron–hole recombination. This phenomenon is related to dissimilar parity of produced photo-excited electron–hole pair under UV irradiation [9, 10]. Compared to the corresponding inorganic or polymeric components, polymer-inorganic hybrid materials usually allow one to couple advantages associated with the inorganic phase to polymers. Accordingly, the integration of inorganic nanoparticles into polymeric materials leads to a new class of functional materials [11–13]. Therefore, the introduction of ZnO filler into polymeric matrix can modify the optical (e.g., shielding from UV and NIR radiation), electrical, and mechanical properties [14–20]. Consequently, these nanocomposites could be widely applied in coatings, rubbers, plastics, sealant, fibers, and other applications.

The interfacial interactions between the nanoparticles and polymer matrix play a crucial role in determining the quality and properties of the nanocomposite [21]. However, ZnO nanoparticle possesses large specific surface area and high surface energy, which may cause agglomeration of particles in polymer matrix and decline in performance of the nanocomposites. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles. Various processing methods, e.g., sol–gel and molecular capping, have been employed to form finely dispersed ZnO nanoparticles in either organic or inorganic matrix [22–26].

Poly(amide–imide) (PAI) contains both amide and heterocycle imide structures along the main chain of the polymer backbone and possesses high thermal stability, good chemical resistance, excellent mechanical properties, and hydrogen bonding interaction, being a promising matrix candidate for hybrid materials [27].

In the present investigation, we wish to report the synthesis and characterization of optically active PAI which was prepared by polycondensation reaction of *N,N'*-(pyromellitoyl)-bis-phenylalanine diacid chloride **1** (**M-1**) with 4,4'-diaminodiphenylsulfone **2** (**M-2**). Also, the ZnO nanoparticles were treated with coupling agent of γ -methacryloxypropyltrimethoxy silane (KH570) to introduce organic functional groups on the surface of ZnO. Then optically active PAI/zinc oxide nanocomposites (PAI/ZnO NCs) were synthesized under ultrasonic irradiation conditions. The resulting novel NCs are characterized by several techniques.

Experimental

Materials

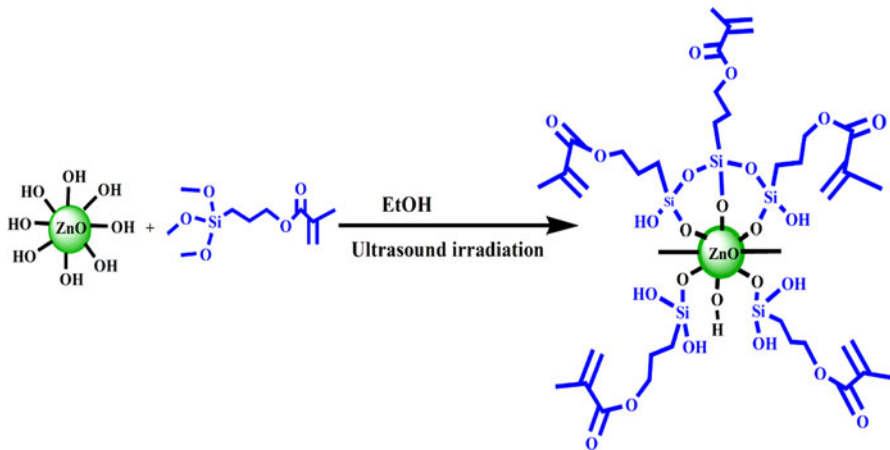
All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel–deHaen AG (Seelze, Germany), and Merck Chemical Co. 4,4'-Diaminodiphenylsulfone **2** (**M-2**) was used as obtained without further purification. *N,N*-dimethylacetamide (DMAc) was dried over BaO, then distilled in vacuum. L-Phenylalanine was used as obtained without further purification. The silane coupling agent KH570 obtained from Merck Chemical Co. Nanosized ZnO powder was purchased from Neutrino Co. with an average particle size of 25–30 nm.

Equipments

A Jasco-680 Fourier transform-infrared (FT-IR) spectroscopy (Japan) was employed to examine the chemical bonds on the polymer and NCs. Spectra of solids were obtained with KBr pellets. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon–Fenske routine viscometer (Germany) at the concentration of 0.5 g/dL at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermogravimetric analysis (TGA) is performed with a STA503 win TA at a heating rate of 10 °C/min from 25 to 800 °C under nitrogen. The XRD pattern was acquired by using a Philips Xpert MPD X-ray diffractometer. The analysis was measured on sample powders. The diffractograms were measured for 2θ , in the range of 10°–100°, using Cu K α incident beam ($\lambda = 1.5418 \text{ \AA}$). The dispersion morphology of the nanoparticles on PAI matrix was observed using scanning electron microscope (SEM, XL30, Philips) and field emission-scanning electron microscopy [FE-SEM, HITACHI (S-4160)]. Transmission electron microscopy (TEM) images were obtained using a Philips CM 120 microscope with an accelerating voltage of 100 kV. Images of SEM, FE-SEM, and TEM were collected from powder samples. UV–Vis absorption of PAI/ZnO NCs was measured in solid state on a UV–Vis spectrometer JASCO V-750 in the spectral range between 200 and 800 nm. The reaction was performed by a MISONIX ultrasonic liquid processor, XL-2000 SERIES. Ultrasound was a wave of frequency 2.25×10^4 Hz and power 100 W.

Surface functionalization of ZnO nanoparticles

KH570 was used to modify ZnO nanoparticle. Typical steps were given as follows: nano ZnO was dried at 110 °C in an oven for 24 h to remove the adsorbed water. 0.20 g of dried nano ZnO with absolute ethanol was sonicated (through an ultrasonic instrument MISONIX, 100 W) in an ice bath for 15 min, then 0.09 g of KH570 (molar ratio of KH570 to ZnO was 1:15) was added to this mixture and sonicated for 20 min. The mixture was filtered and dried at 60 °C for more than 24 h (Scheme 1).



Scheme 1 Reaction of ZnO nanoparticles with KH570

Monomer synthesis

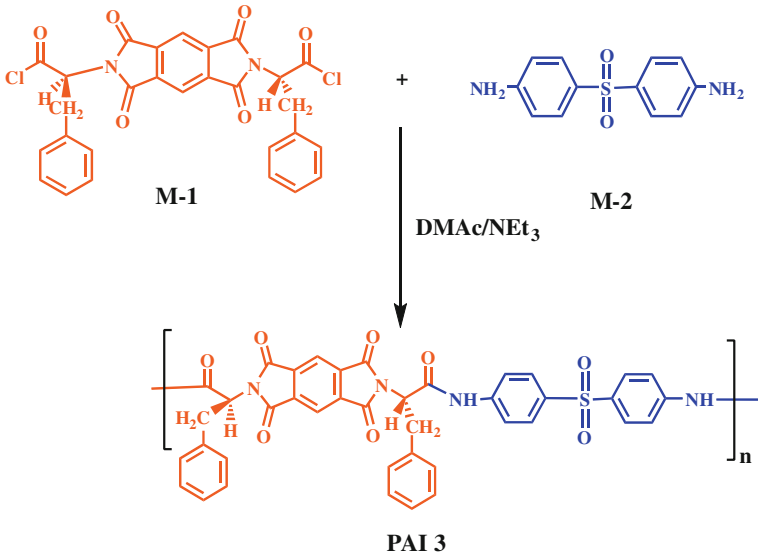
N,N'-(Pyromellitoyl)-bis-*L*-phenylalanine diacid chloride **1** (**M-1**) was prepared by procedure reported elsewhere [28].

Polymer synthesis

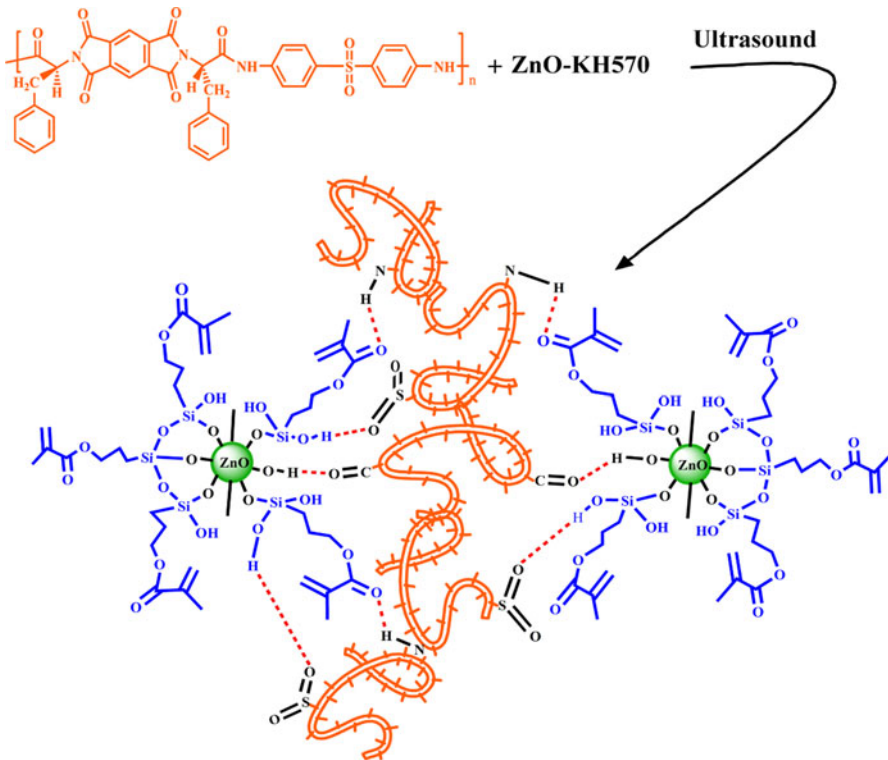
The PAI was synthesized by a typical procedure shown in Scheme 2 [29]. The general procedure consisted of adding of **M-1** to a cooled stirred solution of **M-2** in DMAc as a solvent. After the reagents dissolved completely, trimethylamine (NEt_3) was added and reaction was allowed to proceed for 2 h. The reaction mixture was stirred for 5 h. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80 °C for 10 h under vacuum to yield the solid polymer **3**, and the specific rotation was measured ($[\alpha]_D^{25} = -134$, at a concentration of 0.5 g/dL in DMF at 25 °C).

Preparation of the PAI/ZnO NCs

The procedure for the preparation of PAI/ZnO NCs is shown in Scheme 3; 0.10 g of PAI was dispersed in 20 mL of absolute ethanol. A uniform colloidal dispersion was obtained after sonication for 15 min at room temperature. The suspension was mixed with different amounts of surface modified ZnO nanoparticles (4, 8, and 12 wt% of PAI). The resulting mixture was sonicated for 4 h. After irradiation, the solvent was removed and the obtained solid was dried in vacuum at 80 °C for 2 h.



Scheme 2 Polycondensation reactions of **M-1** with aromatic **M-2**



Scheme 3 Preparation of PAI/ZnO nanocomposites

Results and discussion

Surface modification of ZnO nanoparticles

The surface of ZnO nanoparticles was treated by KH570 silane coupling agent. The reaction mechanism is illustrated in Scheme 1. In water or alcohol, KH570 hydrolyzes to trihydroxyl compounds with one unsaturated bond. The hydroxyl group on the surface of ZnO will replace with OCH₃ of the KH570 to bond to it [30–33].

FT-IR spectra of the ZnO nanoparticles, pure KH570, and ZnO–KH570 nanoparticles are shown in Fig. 1. The FT-IR spectrum of ZnO (Fig. 1a) show main absorption bands at 3434, 1577, and 1384 cm⁻¹, which correspond to the O–H mode, asymmetric, and symmetric C=O stretching modes of zinc acetate, respectively. The peak at 424 cm⁻¹ is the characteristic absorption of Zn–O bond. In the KH570 spectrum (Fig. 1b), the bands at 1720, 1637, and 1165 cm⁻¹ belong to C=O, C=C, and C–O vibrations, respectively. The peak at 900 cm⁻¹ originates from the Si–O stretching of SiOH groups due to the hydrolysis of KH570. It is also found that the infrared spectrum of the coupling agent (KH570) treated ZnO nanoparticles exhibits absorptions at 3428 cm⁻¹ (–OH), 2929 cm⁻¹ (–CH₂ stretching), 1718 cm⁻¹ (C=O of the KH570), 1636 cm⁻¹ (C=C), 1170 cm⁻¹ (SiOH), 939 cm⁻¹ (Zn–O–Si), and 817 cm⁻¹ (Si–O–Si). Such results indicate that the silane molecules have been successfully grafted onto the surface of ZnO nanoparticles.

Synthesis and characterization of polymer

The monomer **1** was synthesized according to the reported procedure [28]. PAI **3** was synthesized by the polycondensation reactions of an equimolar mixture of **M-1**

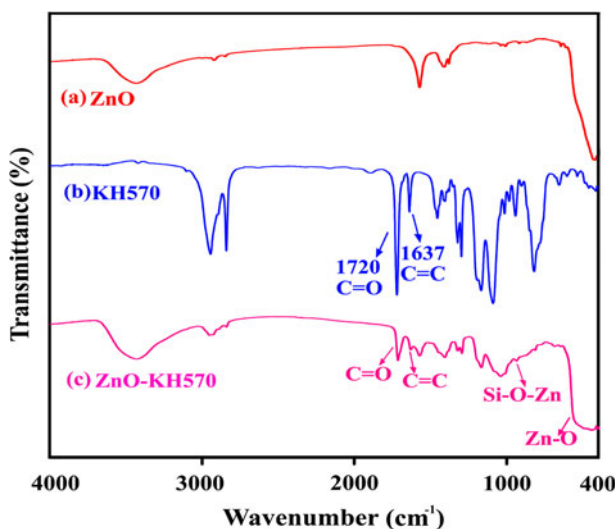


Fig. 1 FT-IR spectra of ZnO nanoparticle and modified ZnO nanoparticle

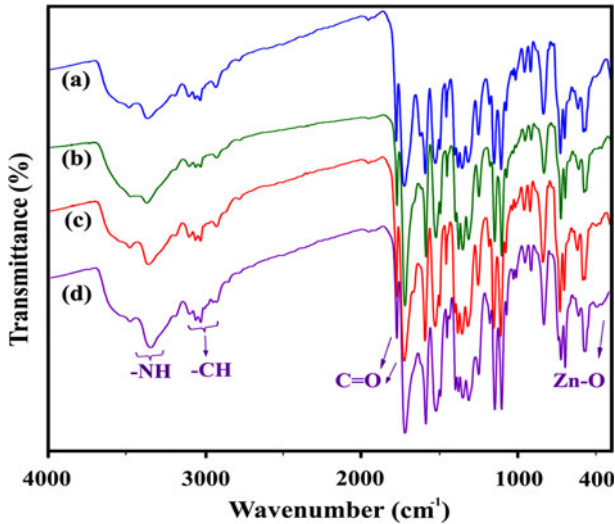


Fig. 2 FT-IR spectrum of the PAI/ZnO–KH570 NCs: (a) PAI3, (b) PAI/ZnO (4%), (c) PAI/ZnO (8%), (d) PAI/ZnO (12%)

with aromatic diamines **M-2** in DMAc/ NEt_3 systems (Scheme 3) [29]. The inherent viscosity of the resulting polymer was 0.17 dL/g and the yield was 85%. The resulting polymer showed optical rotation, which indicated that, the polymer is optically active and chirality was introduced into the backbone of the polymer. The structure of this polymer was confirmed as PAI by means of FT-IR, ^1H NMR spectroscopy, and elemental analysis [29]. The FT-IR spectrum of polymer (Fig. 2a) showed absorptions around 3360 cm^{-1} (N–H), and two overlapped carbonyl (amide and imide's C=O) absorptions at 1776 , 1725 , and 1663 cm^{-1} , respectively. Absorption at 1380 and 727 cm^{-1} indicate the presence of the imide heterocycle in this polymer structure. Absorptions at 1251 and 1150 cm^{-1} are due to the sulfone moiety (SO_2 stretching).

Characterization of PAI/ZnO nanocomposites

FT-IR spectra

Figure 2b–d shows the FT-IR spectra of the PAI/ZnO–KH570 nanoparticles (4, 8, and 12%, respectively). The spectra of the novel NCs clearly exhibit the characteristic absorption peaks corresponding to polymeric groups. The absorptions at 1776 , 1663 , 1590 , and 1150 cm^{-1} manifest the existence of PAI. The incorporation nano ZnO in PAI caused the slight changes in the intensities of absorption bands at 1725 and 1663 cm^{-1} as well as the formation of new absorption bands in the range of $600\text{--}400\text{ cm}^{-1}$. Peak around $600\text{--}400\text{ cm}^{-1}$ is attributed to the zinc–oxygen stretching of ZnO. This confirmed the presence of ZnO nanoparticles present in the PAI matrix. This indicates that there is no chemical linkage between

PAI and ZnO nanoparticles. Therefore, the comparatively weak interaction is thought to be a hydrogen bond, and also short-ranged steric and electrical interaction among active sites of ZnO and different functional groups of PAI. The modified nanoparticles were deposited on the surface of PAI matrix, which can be observed from the XRD data and photographs of FE-SEM as well as TEM.

X-ray diffraction patterns

The XRD patterns of ZnO–KH570 (a), PAI/ZnO (12%) (b), PAI/ZnO (8%) (c), PAI/ZnO (4%) (d), and PAI (e) are shown in Fig. 3. In Fig. 3a, a series of characteristic peaks at 2θ values: 31.8 (100), 34.4 (002), 36.2 (101), 47.6 (102), 56.6 (110), 62.9 (103), 66.4 (200), 67.9 (112), and 69.1(201) are noticed, which are in accordance with the zincite phase of ZnO (International Center for diffraction data, JCPDS 5-0664). No peaks due to impurity were observed, which suggests that high purity ZnO was obtained after modification. In addition, the peak was widened implying that the particle size is rather small. The average crystallite size D was calculated by the Debye–Scherrer formula ($D = K\lambda/\beta\cos\theta$), where K is the Scherrer constant, λ the X-ray wavelength, β the peak width at half-maximum, and θ is the Bragg diffraction angle. From the Debye–Scherrer formula, we obtained the crystallite diameter as 22–30 nm. Figure 3b–d shows the XRD pattern of NCs with 12, 8, and 4% of ZnO nanoparticles, respectively, indicating that the morphology of ZnO nanoparticles has not been changed during the process and the intensity of diffraction peaks increases with increasing ZnO content. Pure PAI was totally amorphous in nature, which did not show any sharp diffraction peaks.

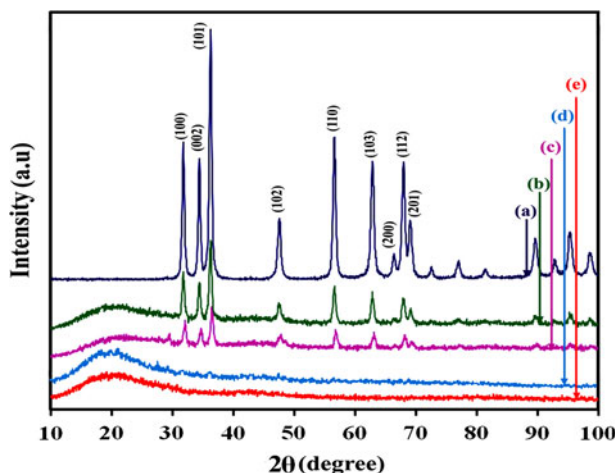


Fig. 3 XRD patterns of (a) ZnO–KH570, (b) PAI/ZnO (12%), (c) PAI/ZnO (8%), (d) PAI/ZnO (4%), and (e) pure PAI3

Distribution of ZnO nanoparticles in PAI matrix

The morphology before and after ZnO deposition on the surface of PAI polymer were confirmed by the SEM and FE-SEM. Figures 4 and 5 show the SEM and FE-SEM of PAI and PAI/ZnO (12%), respectively. The morphology of pure PAI seems to be smooth and consisting of spherical-shaped spheres, as depicted in Figs. 4a and 5a–d. The average mean diameter of pure PAI polymer is between 500 and 700 nm. PAI/ZnO NC with 12% ZnO content is shown in Figs. 4b and 5e, f. The white spots are ZnO nanoparticles. The results showed that ZnO nanoparticles were homogeneously dispersed in PAI matrix and their average particle size was below 100 nm.

TEM image of PAI NC with 12% ZnO is shown in Fig. 6a and b. The central black spot and translucent parts show ZnO nanoparticles and PAI polymer, respectively. TEM indicated that the ZnO particles were well dispersed in the polymer matrix and remain a diameter size from 30 to 50 nm, representing that the KH570 coupling agent play an important role in dispersing the nanoparticles. From FT-IR, XRD, FE-SEM, and TEM results it is clear that the modified ZnO nanoparticles were successfully dispersed in polymer matrix. In modified ZnO, the organic chains of KH570 can fulfill steric hindrance between inorganic nanoparticles and prevent their aggregation. The modified nanoparticles might be dispersed absolutely and will combine with PAI via the H-bonding of C=O coupling agent with -NH, C=O, and SO₂ groups in PAI.

The unmodified -OH groups on the surface of ZnO nanoparticle can bond to the amide group (C=O) of PAI through interchain hydrogen bonding. The details for fabrication mechanism of PAI NCs are displayed in Scheme 3.

Thermal analysis of PAI NCs

The TGA curves of PAI and PAI/ZnO NCs are shown in Fig. 7 and resulting TGA data are summarized in Table 1 that including temperatures at which 5% (T_5), 10%

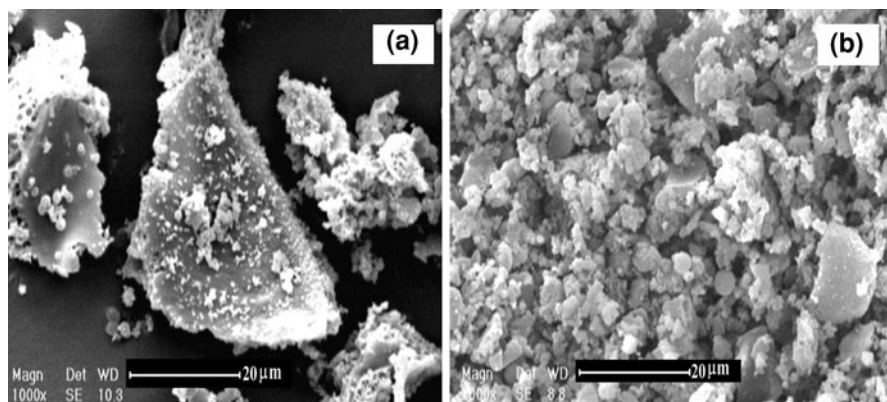


Fig. 4 SEM micrographs of **a** pure PAI3 and **b** PAI/ZnO (12%)

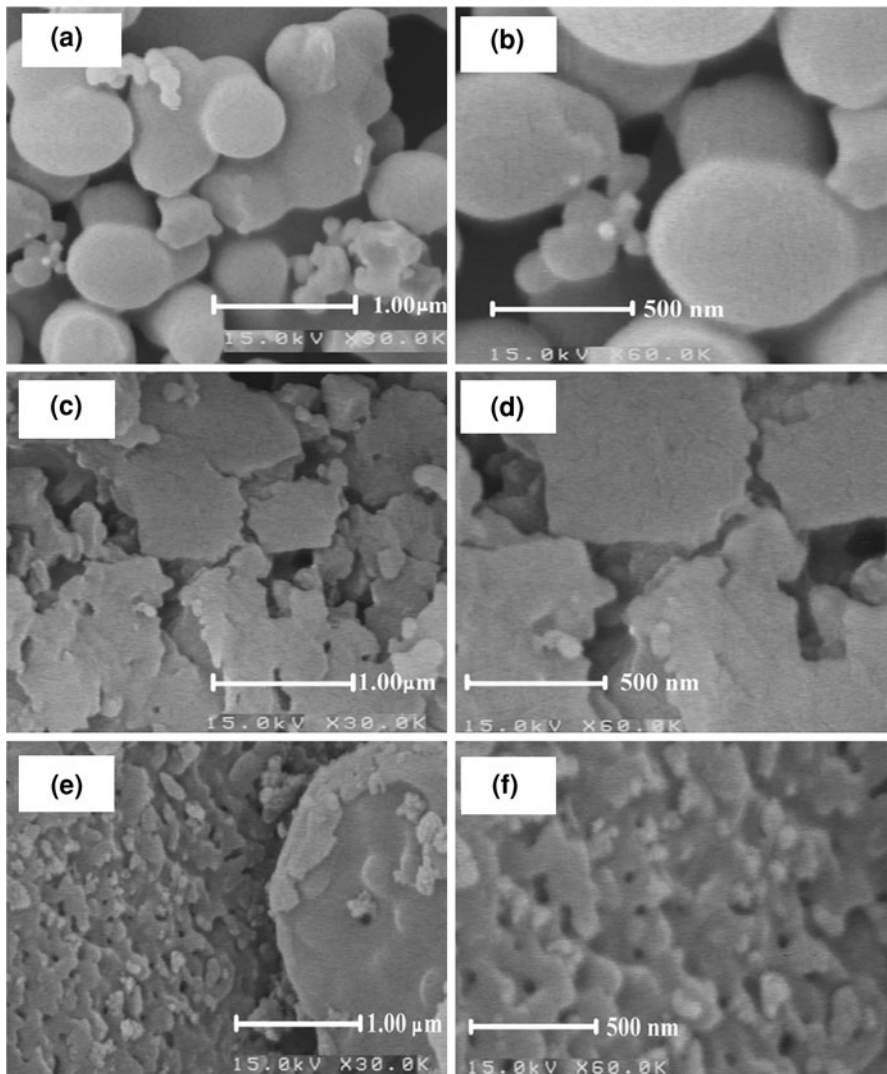


Fig. 5 FE-SEM images of **a–d** PAI3, and **e, f** PAI/ZnO (12%)

(T_{10}) degradation occur and char yield at 800 °C. The initial decomposition temperatures of the nanocomposites with different ZnO contents (4, 8, and 12%) are about 370 °C. These values are related to the decomposition of pristine polymer matrix. The char yields at 800 °C of the nanocomposites with different ZnO content are higher than that of pure PAI. This enhancement in the char formation is ascribed to the high heat resistance exerted by the ZnO, because the ZnO nanoparticles have high thermal stability, so the incorporation of ZnO nanoparticles can improve the thermal stability of the nanocomposites.

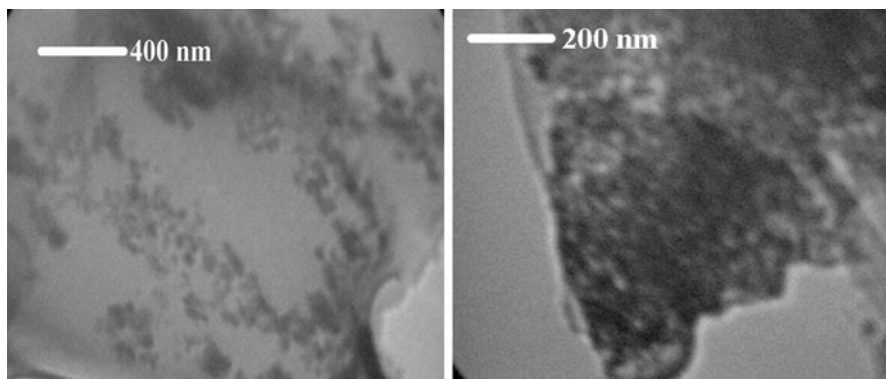


Fig. 6 TEM micrograph of PAI/ZnO (12%)

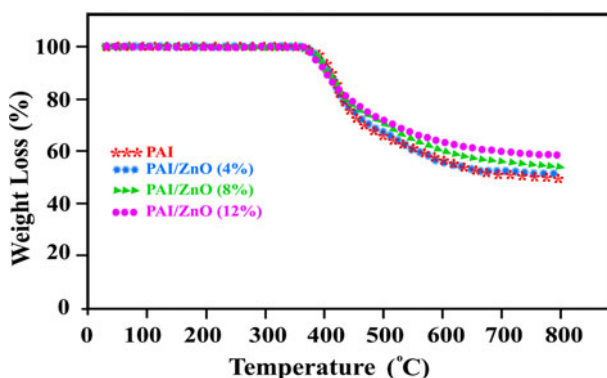


Fig. 7 TGA thermograms of PAI3 and PAI/ZnO NCs with different ZnO content

UV/vis absorption

Figure 8 shows the UV/vis absorption spectra of pure PAI, ZnO–KH570 and PAI/ZnO NCs containing different amount of ZnO nanoparticles in solid state, respectively. The maximum absorption peak of pure PAI and ZnO are shown at near 338 nm, however, the maximum of PAI/ZnO NCs red shifted to some extent up to 360 nm, as well as spectrum became slightly broad between 350 and 500 nm with increase in the ZnO content, because of a wide band gap with a large refractive index and exciton binding energy of ZnO. The observed absorption is around the UV region indicating that, this type of nanocomposite could be used as a paint-on or spray-on coating to shield against UV light.

Conclusions

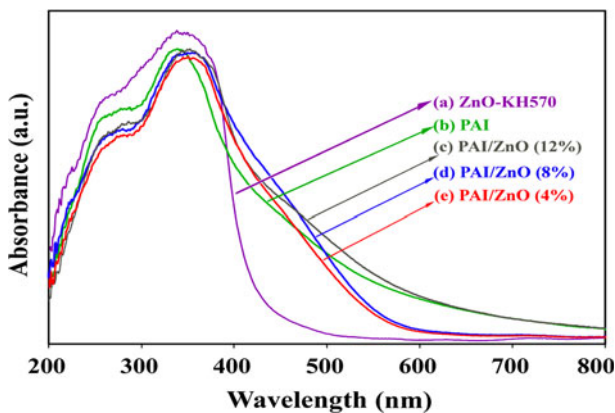
Polycondensation reaction of chiral **M-1** with **M-2** furnished an optically active PAI containing L-phenylalanine amino acid moiety using DMAC/NET₃ systems. This

Table 1 Thermal properties of the PAI and PAI/ZnO nanocomposites

Polymer	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield (%) ^b
PAI	383	410	50.0
PAI/ZnO (4%)	383	410	51.7
PAI/ZnO (8%)	391	409	53.1
PAI/ZnO (12%)	391	409	58.3

^a Temperature at which 5 and 10% weight loss was recorded by TGA at heating rate of 10 °C/min under a nitrogen atmosphere

^b Weight percentage of material left undecomposed after TGA analysis at a temperature of 800 °C under a nitrogen atmosphere

**Fig. 8** UV–visible absorption spectra of ZnO–KH570, PAI3, and PAI/ZnO NCs

synthetic polymer is expected to be biodegradable due to presence of amino acids in the polymer structure. ZnO nanoparticles functionalized with KH570 as a bifunctional coupling agent was used to fabricate a PAI polymeric NCs. KH570 modified to introduce organic functional groups on the surface of ZnO, which improved their compatibility and led to better dispersion of ZnO nanoparticles in polymer matrix. PAI/ZnO NCs are successfully synthesized by ultrasonic irradiation process. The data obtained from FT-IR spectroscopy, XRD and TGA analysis infer that the morphology of PAI/ZnO NCs arises from interchain hydrogen bonding between the ZnO nanoparticles and the PAI matrix. From SEM, FE-SEM, and TEM images, the ZnO particles show a uniform dispersion in the PAI matrix.

Acknowledgments We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from National Elite Foundation (NEF), Iran Nanotechnology Initiative Council (INIC) and Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged. We also thank to Mr. M. Dinari for helpful discussions.

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