Polym. Bull. (2012) 68:53–67
DOI 10.1007/s00289-011-0519-7

ORIGINAL PAPER

Synthesis and structural characterization of novel bionanocomposite poly(ester-imide)s containing TiO_2 nanoparticles, *S*-valine, and L-tyrosine amino acids moieties

Shadpour Mallakpour · Parvin Asadi

Received: 3 March 2011 / Revised: 19 May 2011 / Accepted: 22 May 2011 /

Abstract The incorporation of different percents of titanium dioxide (TiO_2) nanoparticles into optically active poly(ester-imide) (PEI), afforded an opportunity to prepare several novel PEI/TiO_2 bionanocomposites (BNC)s. To this point, firstly PEI was synthesized via direct polyesterification of chiral diacid monomer and an optically active phenolic diol using tosyl chloride/pyridine/*N,N*-dimethylformamide system as a condensing agent. Novel BNC polymers containing TiO_2 nanoparticles were synthesized through ultrasonic irradiation method. With the aim of γ-amido-propyl-triethoxylsilicane as a coupling agent, the surface of nanoscale TiO_2 was modified to decrease aggregation of nanoparticles in polymer matrix. The obtained PEI/TiO_2 BNCs were characterized with FT-IR, thermogravimetric analysis (TGA), scanning electron microscopy, X-ray diffraction, and transmission electron microscopy (TEM) techniques. Consequently, TEM image showed that the nanoparticles of smaller than 50 nm in diameter were uniformly dispersed in the polymer matrix. TGA data demonstrated that new synthesized PEI/TiO_2 BNCs are more thermally stable in compare to pure PEI.

Keywords TiO_2 nanoparticles · Bionanocomposite polymer · Ultrasonics irradiation · Amino acids

---

S. Mallakpour (✉) · P. Asadi
Organic Polymer Chemistry Research Laboratory, Department of Chemistry,
Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran
e-mail: mallak@cc.iut.ac.ir; mallak777@yahoo.com; mallakpour84@alumni.ufl.edu

S. Mallakpour
Nanotechnology and Advanced Materials Institute, Isfahan University of Technology,
Isfahan 84156-83111, Islamic Republic of Iran

Introduction

In new century nanotechnology as one of the key technologies is actively being sought in the quest to research on developing nanocomposites with various functions and specific properties. Relating to pure organic or inorganic material, nanocomposites have shown improved mechanical, thermal, optical, or chemical properties [1, 2]. Especially strong material, which could be synthesized by combination of polymer matrix with nanosized filler, is a highly desired object [3–5]. A major specific feature of polymer matrix nanocomposites (PMNC)s is their huge interfacial area between filler and matrix, which is considered as a key factor to intensely improve mechanical properties of a polymer matrix. Effect of fillers on the mechanical performance of nanocomposites strongly depends on their property, shape, dimension, size, aggregate degree, dispersibility, and concentration. Studies have shown that mechanical properties of PMNCs filled with smaller particle are superior to those with larger ones at micron level [6]. As one group of PMNCs, polymer-based bionanocomposites (BNC)s are among the most promising material for the production of environmentally friendly biodegradable packaging materials [7, 8]. Titanium dioxide (TiO_2) as an inert, nontoxic compound has been the focus of frequent research in recent years, particularly from the view point of its photocatalytic effect. This material is capable of decomposing organic compound and destroying bacteria, therefore, it has been applied to water and air pollutions [9–16]. For preparation of PMNCs including inorganic nanoparticles, there still remain problems related to the uniform dispersion of nanoparticles in polymer matrix [17]. The direct mixing of the nanoparticles with polymer often lead to their aggregations within polymer matrix and can reduce the expected efficiency of naocomposite by the decrease of interfacial areas between TiO_2 and polymer chains. As an approach to decrease the aggregation and also to control the size distribution of the nanosize particles, ultrasonic irradiation has been employed to synthesize the nanocomposites [18–20]. Ultrasonic has been extensively used in machining, medicine, chemistry, and preparing nanosized materials [21, 22]. Another approach to decrease the aggregation of inorganic TiO_2 is surface modification of these nanoparticles with coupling agent which usually has a long alkyl tail and shows a good compatibility with polymer matrix, therefore, allows high homogeneous dispersion of nanoparticles in organic matrix [23].

Amino acids as suitable compounds for chiral sources in organic synthesis can induce optical activity into polymers. These polymers are used in pharmaceutical industry for enantioselective separation of drugs and also are employed in dentistry, drug delivery, gene therapy, and tissue engineering as biocompatible polymers [24–27].

Polyimides with a valuable complex of toughness, insulating coatings, high thermal, and oxidative resistance have lots of applications. But alongside of these advantages, they still lack certain optimum possessions for mechanical properties [28]. One approach to rise above this drawback involves the synthesis of copolyimides such as poly(ester-imide)s (PEI)s and poly(amide-imide)s by incorporating amide or ester functionality at regular intervals in the polyimide chains. In this way the melting point of polyimides may be decreased [29, 30].

Direct polycondensation using condensing agent is a useful procedure for the synthesis of polyamides, polyesters, and other copolymers [31]. Higashi et al. reported that Vilsmeier adduct derived from arylsulfonyl chlorides and *N,N*-dimethylformamide (DMF) in pyridine (Py) was successfully used as a suitable condensing agent for the synthesis of aromatic polyesters [32]. In connection with our interest in preparing optically active polymers having amino acid in the main chain or in the side chain, herein we wish to report the synthesis and characterization of potentially biodegradable and optically active PEI which has two different types of amino acid linkages in the main chain as well as in the side chain. Subsequently, the synthesized polymer and nanosize TiO_2 were used for the preparation of novel polymer-based BNC. Silane-coupling agent was utilized to modify the surface properties of TiO_2 and also ultrasonic was taken up to simulate good dispersibility of modified TiO_2 in polymer matrix. Finally, the structure and properties of PEI/TiO_2 BNCs were characterized by different techniques such as FT-IR, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

Experimental

Materials

For synthesis of PEI, the amino acids of synthetic grade were used as purchased from Merck Chemical without further purification. *N,N*-Dimethylacetamide (DMAc), DMF, Py, *N*-methyl-2-pyrrolidone (NMP), and triethylamine (TEA) were procured from Fluka (dried over barium oxide (BaO) and then distilled under reduced pressure). Pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) and phthalic anhydride were the product of Merck Chemical Co and purified by recrystallization from a mixture of acetic anhydride and acetic acid (1:4). 5-Aminoisophthalic acid was obtained from Aldrich and recrystallized from H_2O/DMF (4/1) mixture. A commercial form of TiO_2 with average size about 35–50 nm was obtained from nanosabz Co. Coupling agent (γ-amidopropyl-triethoxylsilicane) (KH550), was purchased from Merck Chemical Co.

Techniques

Structural confirmation of PEI was done by proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra recorded in dimethyl sulfoxide (DMSO)-d_6 solution using a Bruker Avance 500 instrument (Bruker, Germany) and FT-IR spectra were also recorded on spectrophotometer (Jasco-680, Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g dL^{-1} in DMF at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Preparation of PEI/TiO_2 BNCs was carried out on a MISONIX ultrasonic XL-2000 SERIES.

Ultrasonic irradiation was performed with the probe of the ultrasonic horn immersed directly in the mixture solution system with frequency 2.25×10^4 Hz and power 100 W. Optical absorption spectra (UV–Vis) of the PEI/TiO_2 BNCs were measured at room temperature by JASCO V-750 UV–Vis/NIR spectrophotometer using solid pellets. FE-SEM measurement of PEI/TiO_2 BNC10% was carried out on a HITACHI S-4160. TEM measurements were performed on a Philips CM120 instrument, operated at an accelerating voltage of 100 kV. TGA data for polymer and PEI/TiO_2 BNCs were taken on STA503 WinTA instrument at a heating rate of 10 °C min^{-1} under argon (Ar) atmosphere. The XRD patterns were recorded by employing a Philips X'PERT MPD diffractometer (Cu K_α radiation: $\lambda = 0.154056$ nm at 40 kV and 30 mA) over the 2θ range of 10–80° at a scan rate of 0.05°/min.

Monomer synthesis

Optically active monomers based on amino acids, 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid (1) as a diacid and also *N,N'*-(pyromellitoyl)-bis-L-tyrosine dimethyl ester (2) as a phenolic diol, were prepared according to our previous works [33, 34].

Polymer synthesis

For synthesis of polymer, a Py (0.20 mL) solution of tosyl chloride (TsCl) (0.37 g; 1.94×10^{-3} mol), after 30 min stirring at room temperature, was treated with DMF (0.14 mL; 1.94×10^{-3} mol) for 30 min and the resulting solution was added dropwise to a solution of diacid (1) (0.10 g; 2.44×10^{-4} mol) in Py (0.20 mL). The mixture was maintained at room temperature for 30 min and then diol (2) (0.14 g; 2.44×10^{-4} mol) was added to this mixture and the whole solution was stirred at room temperature for 30 min and then at 120 °C for 4 h. As the reaction proceeded, the solution became viscous and then the viscous liquid was precipitated in 30 mL of methanol to give 0.20 g of PEI (86% yield) [35].

PEI: FT-IR Peaks (KBr): 3419 (m, br), 2954 (m), 1778 (m), 1724 (s), 1678 (m), 1548 (w), 1505 (m), 1452 (m), 1382 (m), 1364 (s), 1215 (m), 1184 (w), 1167 (m), 1112 (m), 1018 (m), 917 (w, br), 887 (w), 833 (w), 712 (w), 633 (w), (cm^{-1}). ^{1}H-NMR (500 MHz, DMSO-d_6): δ 0.81 (CH_3), 0.98 (CH_3), 2.70 (CH), 3.32 (CH_2), 3.67 (OCH_3), 4.54 (CH, chiral center), 5.32 (CH, chiral center), 6.90 (4H aromatic), 7.24 (4H aromatic), 7.87 (4H aromatic), 8.48 (3H aromatic), 8.58 (2H aromatic), 10.35 (NH), (ppm).

Surface modification of TiO_2

The experiment procedure of modified TiO_2 nanoparticle refers [36]. Before reaction, TiO_2 nanoparticles were dried at 500 °C for about 7 h, then 0.30 g of the dried TiO_2 was dispersed in 10 mL of acetone for 3 min. 0.30 mL of KH550 (10% wt of TiO_2 nanoparticles) was dissolved in 10 mL of distilled water and was added to the mixture under ultrasonic irradiation. The whole blend was mixed for 30 min and then centrifuged and the precipitate was washed twice with ethanol and distilled water, respectively to completely remove the residual KH550 and then dried in vacuum at 60 °C for 4 h.

Preparation of PEI/TiO_2 BNCs

0.10 g dried polymer and different amount of modified TiO_2 (5, 10, 15, 20, and 25 wt%) were mixed and were added into 10 mL of absolute ethanol. The reactions occurred by ultrasonic irradiation with the probe of the ultrasonic horn immersed directly in the mixture solution systems for 4 h at 30 °C. Then, the mixtures were centrifuged for 10 min and washed with ethanol and distilled water, respectively. Finally, the obtained products as PEI/TiO_2 BNCs were dried in vacuum at 80 °C for 6 h and kept for further characterizations.

Result and discussion

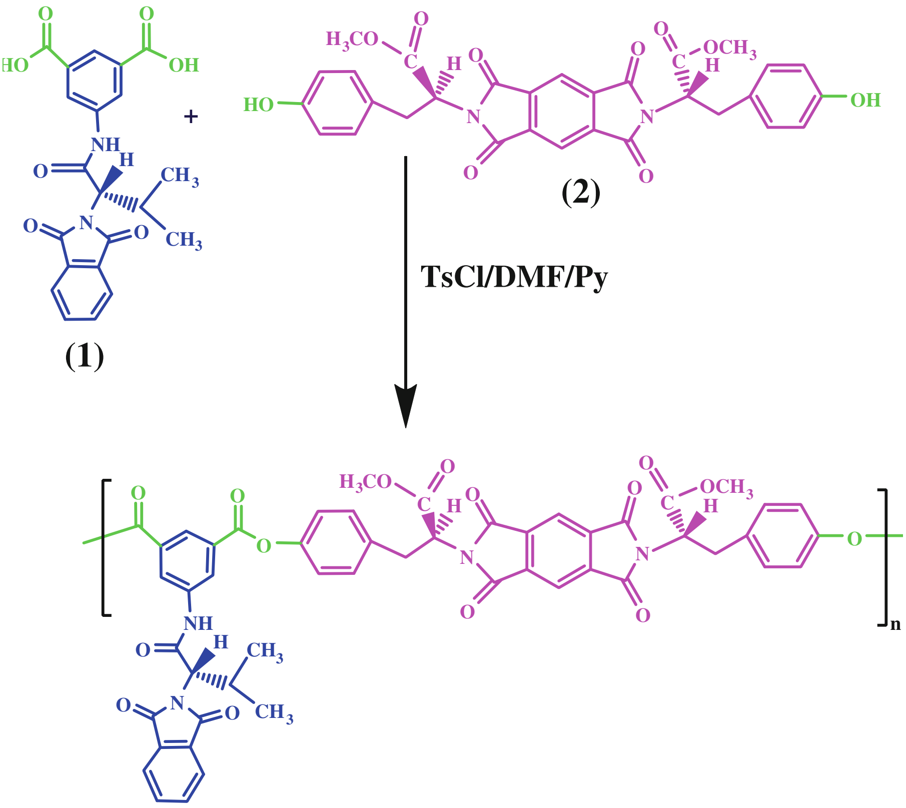
Synthesis of monomers

By the condensation reaction of an equimolar amount of phthalic anhydride and *S*-valine, in reflux acetic acid, corresponding imide acid was synthesized and then was reacted with thionyl chloride in dichloromethane. The obtained diacid chloride was converted to diacid (1) thought reaction with 5-amino isophthalic acid in dry DMAc in the presence of TEA. For the preparation of *N,N*'-(pyromelliticdiimido)-bis-L-tyrosine dimethyl ester (2) as a diol, L-tyrosine was added to a methanol solution containing thionyl chloride and stirred at room temperature to obtain white, powdery, L-tyrosine methyl ester hydrochloride which was deprotoned with TEA in CH_2Cl_2 to obtain L-tyrosine methyl ester. The obtained compound was reacted with pyromellitic dianhydride in reflux DMF so that yellow precipitate was collected in a mixture of cold water/concentrated HCl as a diol (2).

Polymer synthesis

Polycondensation of aromatic diacid 1 with diol 2, using Vilsmeier adduct as a condensing agent was performed in the following way: (Scheme 1), TsCl was dissolved in Py to yield sulfonium salt and after a certain period of time (aging time) the solution was treated with DMF for 30 min to form Vilsmeier adduct. The reaction mixture was added to a solution of diacid in Py to form activated acid. After 30 min powder of diol was added and the whole solution was maintained at room temperature and elevated temperature for a period of time.

The optically active synthesized PEI with 86% yield had a moderate inherent viscosity of 0.33 dL/g (at concentration of 0.5 g dL^{-1} in DMF at 25 °C). Incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotation of polymer. This polymer showed a relatively high optical rotation ($[\alpha]_D^{25} = -19.2$ measured at a concentration of 0.5 g/dL in DMF at 25 °C) and is, therefore, optically active.



Scheme 1 Synthesis of amino acid containing PEI

Characterization of polymer

The structure of synthesized polymer was confirmed as PEI by means of FT-IR. The FT-IR spectrum of PEI showed absorption of amide N–H bond appeared around 3419 cm^{-1} (hydrogen band) and the peaks at 1778 (C=O imide group), 1721 cm^{-1} (C=O ester group) and 1605 cm^{-1} (C=O amide group) confirm the presence of different carbonyl groups in the polymer chains. The absorption bands appeared around 3013–3100 and 2850–2930 cm^{-1} are related to the corresponding aromatic and aliphatic C–H stretching vibration, respectively. This PEI exhibited absorptions at 1382 and 725 cm^{-1} which showed the presence of the imide heterocycle in this polymer.

The ^{1}H-NMR (500 MHz) spectrum of PEI is shown in Fig. 1. The appearance of the N–H proton of amide group around the 10.30 ppm indicates the amide group in the polymer's chain. The absorption of aromatic protons was appeared in the range of 6.90–8.58 ppm. The protons of the chiral centers for *S*-valine and L-tyrosine appeared at 4.54 and 5.32 ppm, respectively. Appearances of the methoxy (O-CH_3) protons at 3.68 ppm as a single peak indicate the presence of ester group in the

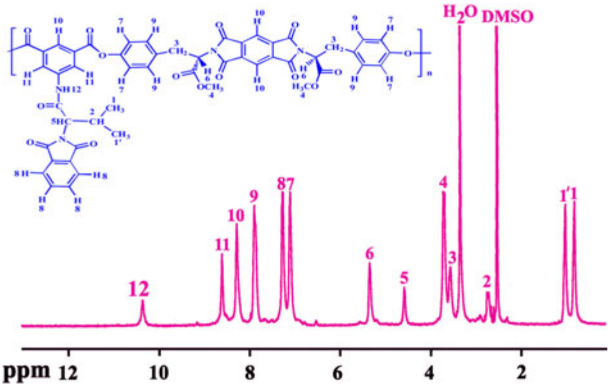


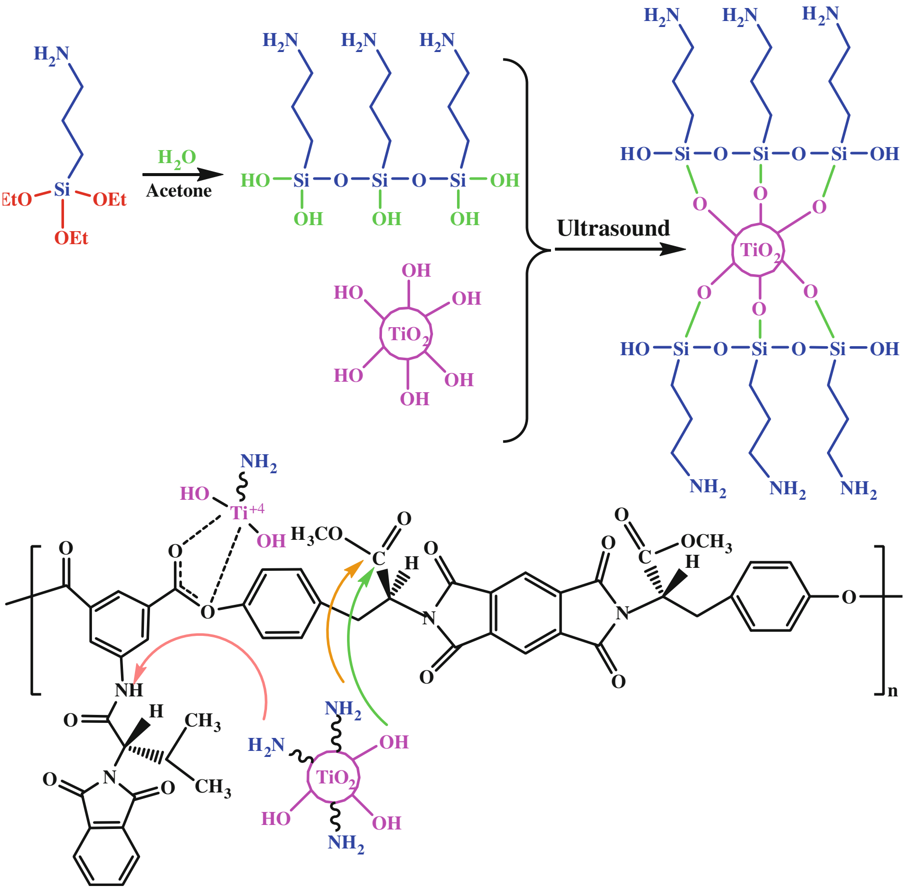
Fig. 1 ^{1}H-NMR (500 MHz) spectrum of PEI in DMSO-d_6 at R.T

polymer's side chain. The absorption of CH_2 of diol appeared at 3.35 ppm. In spectrum of PEI, the peak of the C–H isopropyl group of *S*-valine appeared at 2.70 ppm and the absorptions of the diastereotopic CH_3 proton groups of *S*-valine appeared at 0.81 and 0.98 ppm. The elemental analyses result for PEI is also in agreement with calculated values of carbon, hydrogen, and nitrogen in the polymer.

Quantitative solubility of PEI was determined using 0.05 g of the polymer in 1 mL of solvent. Synthesized polymer is soluble in organic polar solvents such as DMAc, DMF, NMP, and in sulfuric acid at room temperature and is insoluble in solvents such as chloroform, methylene chloride, acetone, cyclohexane, tetrahydrofuran, and water. The good solubility of this PEI is due to the presence of bulky group in side chain, which prevents the packing of the macromolecules and facilitates the diffusion of solvent molecules among the polymer chains.

Surface modification of TiO_2 and preparation of PEI/TiO_2 BNCs

For the synthesis of PEI/TiO_2 BNCs, nanoscale TiO_2 was dispersed in polymer matrix through ultrasonic irradiation technique. The dispersity of nanoparticles in organic polymer is one of the hot stop puzzles of researches and applications, because TiO_2 nanoparticles will aggregate badly in polymer matrix and cause size to be extended up to few micrometers. In this work, silane-coupling agent was used to modify the surface properties of TiO_2. When γ-amidopropyl-triethoxylsilicane (with a trade name KH550) transferred in the water, ethoxy groups were hydrolyzed and sol–gel took place to form Si–O–Si bonds. Then, by reaction with hydroxyl groups of TiO_2, the alkyl groups of coupling agent were placed on the surface of nanoparticles. The alkyl chain of coupling agent has a good compatibility with polymer matrix and allows a highly dispersion of TiO_2 in organic matrix. There are some suggestions for interaction of modified nanoparticles with PEI (Scheme 2). One offer is that TiO_2 was bonded with two oxygen atoms of a carboxylate group via a bidentate coordination to Ti^{4+} cation. The other suggestion is the formation of H-bond between a carboxylate group and the amine group or the surface hydroxyl



Scheme 2 Modifying TiO_2 nanoparticles with KH550 and their interactions with PEI

group of TiO_2. And also interaction of amine group with amide group in the side chain can be supposed.

Characterization of PEI/TiO_2 BNCs

The FT-IR spectra of the TiO_2, modified TiO_2, pure PEI and PEI/TiO_2 BNCs are shown in Figs. 2 and 3. The characteristic peak (in Fig. 2a) showed the existence of hydroxyl group (–OH, 3423 cm^{-1}) and Ti–O–Ti bonds (540–643 cm^{-1}). It can be clearly seen (in Fig. 2b) that the FT-IR spectrum of modified TiO_2 reveals new bands compared to the unmodified TiO_2, with maxima at the wavenumbers of 2870–2928, 1605, 1050, and 910–950 cm^{-1}, respectively. The bands at 2870–2928 cm^{-1} can be, respectively, ascribed to C–H symmetrical and asymmetrical stretching absorptions of the CH_2 group of the coupling agent. The newly formed band at 1050 and 910–960 cm^{-1} can be assigned to the stretch vibration of Si–O–Si and Ti–O–Si bonds, respectively. The peak at 1605 cm^{-1} indicates the

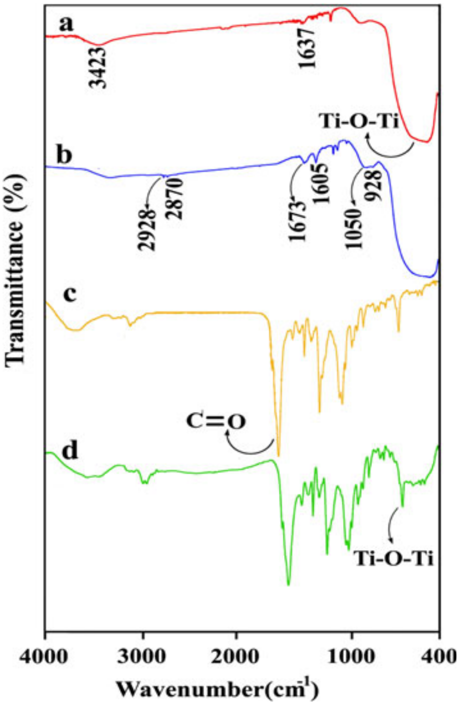


Fig. 2 FT-IR (KBr) spectra of **a** TiO_2, **b** modified TiO_2, **c** pure PEI, and **d** PEI/TiO_2 BNC 10%

presence of the bending vibration of N–H bond. These results showed that the coupling agent was grafted onto surface of TiO_2 by chemical bond.

The FT-IR spectra of PEI/TiO_2 BNCs are shown in Fig. 3. It is noticed that the PEI/TiO_2 BNCs maintain the features of the pure PEI and modified TiO_2.

The XRD patterns of PEI and PEI/TiO_2 BNCs were recorded for characterization of morphology. For PEI (Fig. 4), it could be observed that except one crystalline peak, there is a lack of any diffraction peak in the range of 2θ angle, and this observation suggested the presence of a little proportion of crystalline phase compared to an amorphous one. This may be due to the presence of the aromatic structures in the main chain, which limit the molecular mobility of the polymer. The XRD pattern of modified TiO_2 is in a good agreement with that of standard TiO_2 crystallites. It means the presence of KH550, did not have any great influence on the morphology of nanoparticles. As it is clear, modified TiO_2 nanoparticles are in two different crystal forms (anatase and rutile), which is in agreement with the used commercial TiO_2 nanoparticles.

XRD patterns of PEI/TiO_2 BNCs are suggesting that the samples prepared under the present experimental conditions have crystalline peaks according to pure TiO_2 nanoparticles and average crystallite size was calculated as 35–50 nm using Sherrer's equation. This is in agreement with the used TiO_2 nanoparticles. Sherrer's equation is as follows:

$$D = 0.9\lambda/\beta\cos\theta$$

Fig. 3 FT-IR (KBr) spectra of **a** PEI/TiO_2 BNC 5%, **b** PEI/TiO_2 BNC 10%, **c** PEI/TiO_2 BNC 15%, **d** PEI/TiO_2 BNC 20%, and **e** PEI/TiO_2 BNC 25%

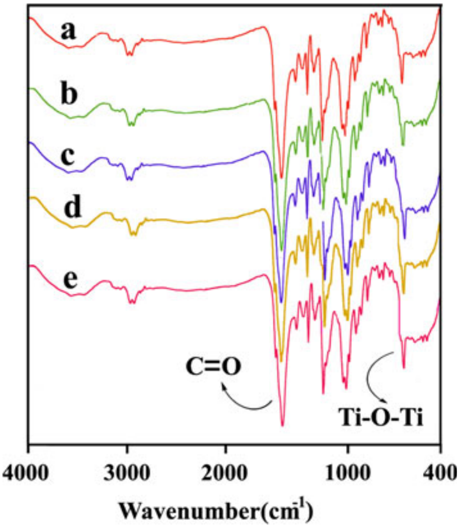
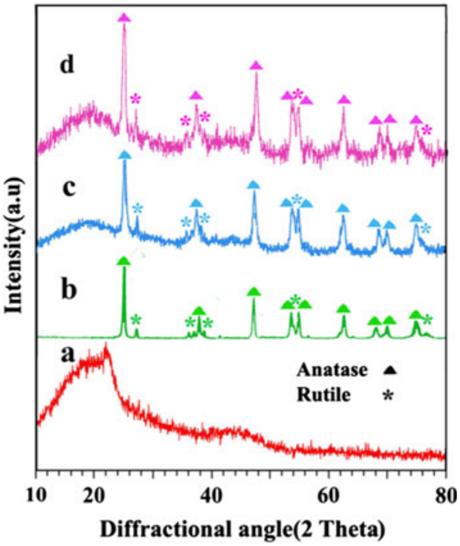


Fig. 4 XRD pattern of **a** pure PEI, **b** TiO_2, **c** PEI/TiO_2 BNC 5%, and **d** PEI/TiO_2 BNC 10%



where D is the crystallite size, λ is a wavelength of the radiation, θ is Bragg's angle and β is the full width at half maximum.

For promoted study, FE-SEM of PEI/TiO_2 BNC10% was carried out (Fig. 5). FE-SEM is widely used to elucidate the phase morphology of polymers. From FE-SEM images, any aggregation or phase separation has not been observed. This shows the method for the preparation of PEI/TiO_2 BNCs used in this study could make the inorganic part well dispersed into polymer matrix and gave uniform and homogeneous distribution of TiO_2 nanoparticles in these BNCs.

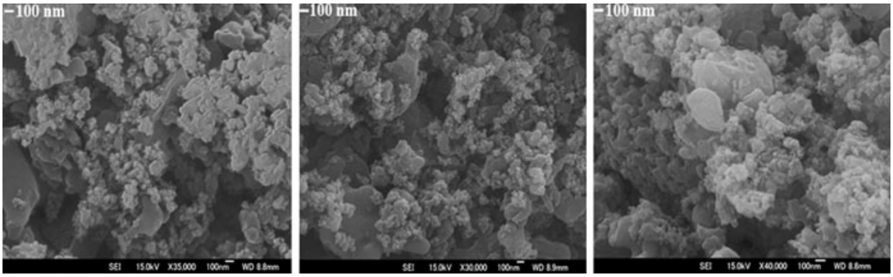


Fig. 5 FE-SEM micrograph of the PEI/TiO_2 BNC 10%

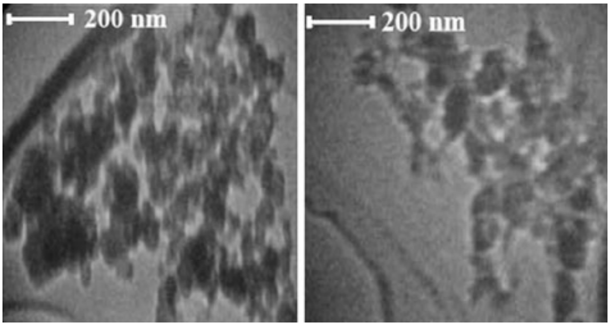


Fig. 6 TEM micrograph of the PEI/TiO_2 BNC 5%

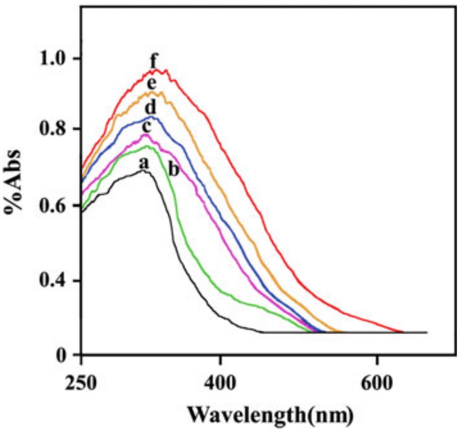
Figure 6 shows the TEM micrographs of PEI/TiO_2 BNC 5 wt%. It is natural to believe that a homogenous dispersion of nanoparticles in material will bring best result. In these images, no aggregation is visible between the modified TiO_2 nanoparticles and relatively satisfactory dispersion of nanoparticles can be observed. This indicates that modification cause easier dispersion during composite processing. From FE-SEM and TEM images, it was estimated that the particle size of the resulting PAIs are around 30–60 nm.

Figure 7 shows the UV spectra of different PEI/TiO_2 BNCs. It can be seen that all of the samples have absorption below the region of 400 nm and the percentage of absorption increase in proportion to the amount of TiO_2 nanoparticles. Therefore, the resulting PEI/TiO_2 BNCs can block out the UV rays, but are transparent to visible light.

Thermal properties

The thermal properties of the PEI and PEI/TiO_2 BNCs were evaluated by TGA technique at a heating rate of 10 °C/min under Ar atmosphere (Fig. 8). Thermal stability of these compounds were studied based on 5 and 10% weight loss (T_5, T_{10}) and residue at 800 °C (char yield). As observed from the Fig. 8, with increasing amount of TiO_2 in polymer matrix, thermal stability was increased. This can be due

Fig. 7 UV–visible absorption spectra of **a** PEI/TiO_2 BNC 5%, **b** PEI/TiO_2 BNC 10%, **c** PEI/TiO_2 BNC 15%, **d** PEI/TiO_2 BNC 20%, **e** PEI/TiO_2 BNC 25%, and **f** pure TiO_2



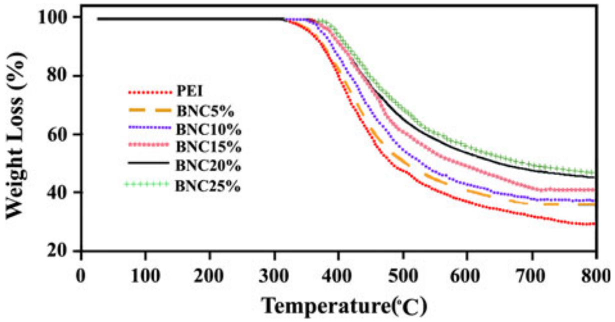


Fig. 8 TGA thermograms of PEI and PEI/TiO_2 BNCs under Ar atmosphere and a heating rate of 10 °C/min

to thermally stable TiO_2 lattice and presence of physical crosslink which restrict the movement of chains. In fact TiO_2 as an inorganic compound is thermally stable and prevent from thermal degradation. The thermo analyses data are summarized in Table 1.

Char yield can be applied as decisive factor for estimated limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation [37].

$$\mathrm{LOI} = 17.5 + 0.4\ \mathrm{CR},$$

where CR = char yield.

The PEI/TiO_2 BNCs have good LOI values above 30 which were calculated from their char yield at 800 °C. On the basis of LOI values, the more amounts of TiO_2, the more LOI values and, therefore, these PEI/TiO_2 BNCs can be classified as self-extinguishing BNCs.

Table 1 Thermal properties of the PEI and PEI/TiO_2 BNCs

Polymer	Decomposition Temperature (°C)		Char yield (%)[b]	LOI[c]
	T_5^a	T_{10}^a		
PEI	350	367	27	28.3
PEI/TiO_2 BNC (5 wt%)	350	370	35	31.3
PEI/TiO_2 BNC (10 wt%)	370	400	40	33.5
PEI/TiO_2 BNC (15 wt%)	375	380	40	33.5
PEI/TiO_2 BNC (20 wt%)	390	400	55	39.5
PEI/TiO_2 BNC (25 wt%)	390	400	58	40.7

[a] Temperature at which 5 and 10% weight loss were recorded by TGA at heating rate of 10 °C min^{-1} in a Ar atmosphere

[b] Weight percent of the material left undecomposed after TGA at maximum temperature 800 °C in a Ar atmosphere

[c] Limiting oxygen index (LOI) evaluating at char yield at 800 °C

Conclusions

To briefly conclude, we have described the preparation of new biodegradable and optically active PEI. The polymerization was carried out by the reaction of chiral synthesized dicarboxylic acid and phenolic diol based on amino acids using Vilsmeier adduct as a condensing agent. This polymer with good yield and moderate inherent viscosity was thermally stable and soluble in common organic solvents. Novel PEI/TiO_2 BNCs were synthesized via an approach allowing the incorporation of nanoscale TiO_2 within polymer matrix by ulterasonication. Although dispersion of nanoparticles is a key property to obtain organo–inorgano hybrid composite, so by effective surface modification of TiO_2 nanoparticles using KH550, they were uniformly dispersed into PEI matrix without aggregation. Morphology study of resulting PEI/TiO_2 BNCs showed well-dispersed TiO_2 nanoparticles in the polymer matrix by FE-SEM and TEM analyses. TGA data indicated that thermal stability of the PEI/TiO_2 BNCs have enhanced with increasing TiO_2 nanoparticles content. Due to presence of amino acid group on the PEI backbone, it could be classified under environmentally benign polymers. Combining nano-sized bioactive materials with biopolymer could produce materials with greater bioactivity and better thermal properties. Therefore, because of the existence of both natural amino acid and TiO_2 nanoparticles in these novel nanocomposites, it would be appropriate to name them as bionanocomposites polymers which may be expected to have biodegradability as well as biocompatibility properties.

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 like to thank Dr. Ashrafi for helpful discussions.

References

1. Doyle ME (2006) Nanotechnology: a brief literature review. Food Research Institute, University of Wisconsin-Madison, Madison
2. Owpradit W, Mekasuwandumrong O, Panpranot J, Shotipruk A, Jongsomjit B (2011) Synthesis of LLDPE/TiO_2 nanocomposites by in situ polymerization with zirconocene/dMMAO catalyst: effect of [Al]/[Zr] ratios and TiO_2 phases. Polym Bull 66:479–490
3. Caseri W (2000) Nanocomposites of polymers and metals or semiconductors: historical background and optical properties. Macromol Rapid Commun 21:705–722
4. Lachman N, Wagner HD (2010) Correlation between interfacial molecular structure and mechanics in CNT/epoxy nano-composites. Compos Part A 41:1093–1098
5. Wang YW, Chen WC (2010) Synthesis, properties, and anti-reflective applications of new colorless polyimide-inorganic hybrid optical materials. Compos Sci Technol 70:769–775
6. Goren K, Chen L, Schadler LS, Ozisik R (2010) Influence of nanoparticle surface chemistry and size on supercritical carbon dioxide processed nanocomposite foam morphology. J Supercrit Fluids 51:420–427
7. Almasia H, Ghanbarzadeha B, Entezami A (2010) Physicochemical properties of starch–CMC–nanoclay biodegradable films. Int J Biol Macromol 46:1–5
8. Mallakpour S, Soltanian S (2010) Studies on syntheses and morphology characteristic of chiral novel poly(ester-imide)/TiO_2 bionanocomposites derived from L-phenylalanine based diacid. Polymer 51:5369–5376
9. Wan T, Feng F, Wang YC (2006) Structure and thermal properties of titanium dioxidepolyacrylate nanocomposites. Polym Bull 56:413–426
10. Yang JL, Zhang Z, Zhang H (2005) The essential work of fracture of polyamide 66 filled with TiO_2 nanoparticles. Compos Sci Technol 65:2374–2379
11. Marques PAAP, Trindade T, Neto CP (2006) Titanium dioxide/cellulose nanocomposites prepared by a controlled hydrolysis method. Compos Sci Technol 66:1038–1044
12. Linsebigler AL, Lu G, Yates JT (1995) Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chem Rev 95:735–758
13. Sunada K, Watanabe T, Hashimoto K (2003) Studies on photokilling of bacteria on TiO_2 thin film. J Photochem Photobiol A 156:227–233
14. Tong Y, Li Y, Xie F, Ding M (2000) Short communication preparation and characteristics of polyimide—TiO_2 nanocomposite film. Polym Int 49:1543–1547
15. Yu JC, Ho W, Lin J, Yip H, Wong P (2003) Photocatalytic activity, antibacterial effect, and photoinduced hydrophilicity of TiO_2 films coated on a stainless steel substrate. Environ Sci Technol 37:2296–2301
16. Hoffmann MR, Martin ST, Choi W, Bahneman DW (1995) Environmental applications of semiconductor photocatalysis. Chem Rev 95:69–96
17. Hamming LM, Qiao R, Messersmith PB, Brinson C (2009) Effects of dispersion and interfacial modification on the macroscale properties of TiO_2 polymer–matrix nanocomposites. Compos Sci Technol 69:1880–1886
18. Mohan YM, Murthy PSK, Sreedhar B, Raju KM (2006) Swelling and thermal characteristics of ph sensitive crosslinked poly(acrylamide-*co*-calcium methacrylate) superabsorbent copolymers. J Appl Polym Sci 102:1–12
19. Chen J, Zhou YM, Nan QL, Ye XY, Sun YQ, Wanga ZQ, Zhang SM (2008) Synthesis and characterization of polyurethane/CdS–SiO_2 nanocomposites via ultrasonic process. Appl Surf Sci 255:2244–2250
20. Feng W, Zhang TR, Liu Y, Lu R, Zhao YY, Li TJ, Yao JN (2002) Sonochemical preparation of photochromic nanocomposite thin film based on polyoxometalates well dispersed in polyacrylamide. J Solid State Chem 169:1–5
21. Mason TJ (1997) Ultrasound in synthetic organic chemistry. Chem Soc Rev 26:443–451
22. Erikson KR, Fry FJ, Jones JP (1974) Ultrasound in medicine—A review. IEEE Trans Sonics Ultrasonics 21:144–170
23. Joni IM, Purwanto A, Iskandar F, Okuyama K (2009) Dispersion stability enhancement of titania nanoparticles in organic solvent using a bead mill process. Ind Eng Chem Res 48:6916–6922
24. Itsuno S (2005) Chiral polymer synthesis by means of repeated asymmetric reaction. Prog Polym Sci 30:540–558

25. Cornelissen JJLM, Rowan AE, Nolte RJM, Sommerdijk NAJM (2001) Chiral architectures from macromolecular building blocks. Chem Rev 101:4039–4070
26. Zhang Y, Lu Z, Deng X, Liu Y, Tan C, Zhao Y, Kong X (2003) Photochromism and holographic recording in polymer film containing chiral azo molecules derived from amino acid. Opt Mater 22:187–192
27. Mallakpour S, Dinari M (2009) Preparation of thermally stable and optically active organosoluble aromatic polyamides containing L-leucine amino acid under green conditions. Polym Bull 63:623–635
28. Ghaemy M, Alizadeh R (2009) Synthesis of soluble and thermally stable polyimides from unsymmetrical diamine containing 2,4,5-triaryl imidazole pendent group. Eur Polym J 45:1681–1688
29. Mallakpour S, Khani M (2007) Novel optically active poly(amide-imide)s derived from *N*-trimellitylimidolsoleucine and different diisocyanates. Polym Bull 59:587–596
30. Mallakpour S, Kowsari E (2005) Synthesis of organosoluble and optically active poly(ester-imide)s by direct polycondensation with tosyl chloride in pyridine and dimethylformamide. Polym Bull 55:51–59
31. Higashi F, Mashimo T (1986) Direct polycondensation of hydroxybenzoic acids with thionyl chloride in pyridine. J Polym Sci Part A 24:1697–1701
32. Higashi F, Ong CH, Okada Y (1999) High-molecular-weight copolyesters of dihydroxybenzophenones by “induced” copolyesterification using TsCl/DMF/Py as a condensing agent. J Polym Sci Part A 37:3625–3631
33. Mallakpour S, Kolahdoozan M (2007) Synthesis and properties of thermally stable and optically active novel wholly aromatic polyesters containing a chiral pendent group. Eur Polym J 43:3344–3354
34. Mallakpour S, Tirgir F, Sabzalian MR (2011) Synthesis and structural characterization of novel biologically active and thermally stable poly(ester-imide)s containing different natural amino acids linkages. J Polym Res 18:373–384
35. Mallakpour S, Asadi P (2010) Novel chiral poly(ester-imide)s with different natural amino acids in the main chain as well as in the side chain: synthesis and characterization. Colloid Polym Sci 288:1341–1349
36. Chen J, Zhou Y, Nan Q, Ye X, Sun Y, Zhang F, Wang Z (2007) Preparation and properties of optically active polyurethane/TiO2 nanocomposites derived from optically pure 1,10-binaphthyl. Eur Polym J 43:4151–4159
37. Van Krevelen DW, Hoftyzer PJ (1976) Properties of polymers, 3rd edn. Elsevier Scientific Publishing, New York