ORIGINAL ARTICLE

Chiral bio-nanocomposites based on thermally stable poly (amide-imide) having phenylalanine linkages and reactive organoclay containing tyrosine amino acid

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Abstract Montmorillonite clay modified with the bioactive trifunctional L-tyrosine amino acid salt was used as a reactive organoclay (OC) for the preparation of poly(amide-imide) (PAI)/OC hybrid films. One of the functional groups of the L-tyrosine as the swelling agent formed an ionic bond with the negatively charged silicates, whereas the remaining functional groups were available for further reaction with polymer matrix. The soluble PAI with amine end groups including phenylalanine amino acid was synthesised under green condition using molten tetra-butylammonium bromide by direct polymerization reaction of chiral diacid and 2-(3,5-diaminophenyl)benzimidazole. PAI/OC bio-nanocomposites films containing different contents of OC were prepared via solution intercalation method through blending of OC with the PAI solution. X-ray diffraction and transmission electron microscopy revealed that the dispersion of silicate layers in the PAI created an exfoliated structure as a result of using the trifunctional groups of the swelling agent. The structure and thermal behavior of the synthesised materials were characterized by a range of methods, including X-ray diffraction, Fourier transform infrared spectroscopy, ¹H-NMR, electron microscopy, elemental and thermogravimetric analysis techniques.

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Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, 84156, 83111 Isfahan, Islamic Republic of Iran Thermogravimetric analysis results indicated that the addition of OC into the PAI matrix was increased in the thermal decomposition temperatures of the resulted bio-nanocomposites.

Keywords Bio-nanocomposites $\cdot \alpha$ -Amino acids \cdot Layered silicate \cdot Poly(amide-imide) \cdot L-Tyrosine \cdot Green chemistry

Introduction

In synthetic polymer chemistry, it seems that one of the most challenging tasks is constructing functional polymeric systems that could be as effective as those in living systems. In this respect, today, the optically active synthetic macromolecules have received considerable attention. Due to their specific chiral structure, optically active polymers have significant applications such as catalysts for asymmetric synthesis and chiral stationary phases for the direct optical resolution of enantiomers (Chen et al. 2007; Koyam et al. 1997; Mallakpour and Dinari 2011a; Samui et al. 2002). A large number of studies on chiral materials are devoted to amino acids and carbohydrates. Amino acids as constitutional components of proteins with a high degree of functionality and chirality play an important role in the synthesis of bio-compatible and degradable polymers. Of these, macromolecules that contain amino acid units are potentially useful in many different medical applications such as bio-erodible sutures, tissue engineering scaffolds and drug delivery matrices (Wang et al. 2009; Mallakpour et al. 2011). L-Tyrosine is the only major natural nutrient amino acid containing an aromatic hydroxyl group. This kind of the amino acid can be used to improve memory and mental

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alertness, act as an appetite suppressant, control depression and anxiety and enhance physical performance (Eversloh et al. 2007; Garlick 2005).

Montmorillonite (MMT), as one of the most commonly used clays, is a type of layered silicate that has gained considerable interest in recent years for the preparation of nanocomposites. Anionically charged layers of magnesium/aluminum silicates and small cations such as sodium or potassium those are located in silicate interlayer galleries present chemical structures of MMT. The presence of ion and ionic bonds makes MMT a hydrophilic subject and prevents it from being compatible with organic polymer matrix. Modification through replacing the small cation existing in the interlayer regions with organic cations, that are usually named cation exchange, is a way to render the hydrophilic layer silicate organophilic and also make long-drawn-out interlayer space which makes it easy to come into polymers chain and therefore, leads to the striking development of polymer-clay nanocomposite (Chao et al. 2008; Delozier et al. 2003; Yin et al. 2009; Wang et al. 2004). These excellent property improvements result from the combination of organic polymers and only a 2-5 % addition of the dispersed nanophase (Liang et al. 2003).

Among the heat-resistant and high-performance polymers, polyimides (PIs) have received considerable scientific and technological attention due to their outstanding performance, dielectrical and mechanical properties and thermal and chemical stability. During the past decade, interest in aromatic PIs has been increased in response to increasing technological applications in a variety of fields such as aerospace, automobile and microelectronics (Ishii et al. 2010; Li et al. 2008; Nguyen and Wang 2010; Zhai et al. 2007). At the same time, aromatic PIs, like other aromatic and heterocyclic polymers, are quite intractable to process because they are usually infusible and insoluble in organic solvents. The highly regular and rigid polymer backbones are generally responsible for the difficulty of processing. Recently, many efforts have been centered on promoting the processability and solubility of aromatic PIs through the change in monomer construction. These structural modifications such as flexible bridging linkages into the polymer backbone, incorporation of bulky substituents along the polymer or the synthesis of co-polyimides such as poly(ester-imide)s and poly(amide-imide)s (PAIs) by incorporating amide or ester functionality at regular intervals in the PI chain could provide better solubility and processability (Karatas et al. 2007; Li and Li 2003; Li et al. 2005; Lina et al. 2004; Liang et al. 2003; Xu et al. 2006; Mallakpour and Dinari 2011b; Mallakpour and Khani 2010). Benzimidazole (BI) as one bulky group has a wide variety of reported activities, especially antimicrobial, antitumor, antiviral, antifungal,

antioxidant, antiulcer, antiamoebic, antihistaminic, anthelmintic and antihypertensive ones (Koprowska-Ratajska et al. 2009). The use of BI in PI structure combines the characteristics and properties of six membered imides and BIs and makes the polymer a good candidate for high-performance thermoplastics. Consequently, polymers modified with BI groups have shown high glass transition temperatures, excellent thermal stability and good solubility in common organic solvents (Abdalla et al. 2002; Chung et al. 2001; Huang et al. 2009; Ivarez-Gallego et al. 2007).

Lately, a research subject that is related to well-dispersed clay platelets in various polymer matrices to prepare polymer-clay nanocomposite (PCNs) materials has attracted increasing attention because PCNs exhibit great potential for a wide range of commercial applications. There are considerable publications associated with the preparation and properties of PI-clay nanocomposite. PIsilica hybrid materials show outstanding thermal stability, mechanical strength and physical properties when applied in various applications, including patterned electronic devices, optical waveguide materials, high-refractive index materials, high transparency materials, non-linear optical materials, photovoltaic devices, and fuel cells (Ma et al. 2010; Yeh et al. 2005; Yu et al. 2004, 2010). In a proper clay-polymer hybrid composite, engineering polymers are encapsulated between smectite clay particles approximately 1 nm in thickness (Lan et al. 1994).

The need to develop new cleaner chemical processes makes ionic liquids (ILs) optional solvents for chemical reaction. Non-volatility of ILs is an important property but an interest in ILs also arises from other properties such as non-flammability, high chemical/thermal stability, low toxicity and favorable conductivity. It has been shown that IL can also be advantageously used for polymer synthesis (Absalan et al. 2010; Mallakpour and Dinari 2012a; Palacio and Bhushan 2010; Zhao et al. 2008).

Generating optically active polymers based on amino acids in our previous work was a guide to consider amino acid for modification of MMT. Our interest in applying amino acid as a swelling agent stems from the fact that amine group of amino acid can provide cation (-⁺NH₃) which can form an ionic bond with the negatively charged silicate layers of MMT and acid functional groups can react with polymers chains. In this work, at first, diamine monomer containing BI pendant group was synthesised and then reacted with diacid containing natural amino acids in IL environment to make PAI in which pendant BI groups can improve solubility of polymer in organic solvent while maintaining thermal stability. Then the synthesised PAI was employed to prepare PAI/MMT bio-nanocomposite (BNC) films in which MMT was modified with tyrosine amino acid. This amino acid with three functional groups interacted with silicate layer and improved the compatibility of MMT with polymer matrix.

Experimental

Characterization

Preparation of the modified clay

The modification of the clay was carried out as follows: according to our previous work (Mallakpour and Dinari 2012b), 2 g of Cloisite Na⁺ was dispersed separately in 150 mL of hot deionized water for 6 h at 80 °C. The required amount of L-tyrosine was protonated with stoichiometric amount of concentrated HCl in 50 mL of deionized water and heated at 80 °C for 3 h. These two solutions were mixed and the contents were vigorously stirred for 6 h at 60 °C. The mixture was filtered through a Whatman[®] filter paper and then washed about five times with deionized water to remove superficially protonatedtyrosine sorbed on the surface.

Synthesis of 2-(3,5-diaminophenyl)-benzimidazole

For the preparation of 2-(3,5-diaminophenyl)-benzimidazole (1), at first, the corresponding dinito was synthesised from the reaction of 1,2-phenylenediamine and 3,5-dinitrobenzoyl chloride using methanesulfonic acid and P_2O_5 as condensation media. Then, diamine 1 was fabricated by the reduction of the dinitro precursor using palladium on activated carbon (Pd/C) and hydrazine monohydrate in refluxed ethanol (yield: 77 %) (Ayala et al. 2005; Ivarez-Gallego et al. 2007; Mallakpour and Dinari 2012c). Melting point: 242–243 °C, FT-IR (KBr, cm⁻¹): 3,409 (s, br), 3,063 (w), 1,607 (s), 1,577 (s), 1,484 (w), 1,446 (m), 1,274 (w), 841 (m) and 743 (s).

Synthesis of PAI

For the synthesis of the PAI, at first, chiral *N*,*N*'-(pyromellitoyl)-bis-L-phenylalanine diacid was prepared according to our previous works (Mallakpour and Dinari 2011a). Then, an optically active PAI was prepared by the following procedure: a mixture of 0.10 g (2.36×10^{-4} mol) of diacid 2 and 0.30 g (9.42×10^{-4} mol) of TBAB was ground until a powder was formed and then transferred into a 25 mL round-bottom flask and 0.06 g (2.36×10^{-4} mol) of diamine 1 was added to the mixture. It was heated until homogeneous solution was formed and then triphenyl phosphite (TPP) (0.49 mL, 3.70×10^{-3} mol) was added. After that, the solution was stirred for 12 h at 120 °C. The viscous solution was precipitated in 30 mL of methanol. The white solid was filtered off and dried to give 0.14 g (91 %) of white PAI. The specific rotation was $[\alpha]_D^{25} = -78.27$ (measured at a concentration of 0.5 g/dL in DMF at 25 °C) (Mallakpour and Dinari 2012c).

FT-IR peaks (KBr, cm⁻¹): 3,479 (br), 3,165 (w), 3,038 (w), 2,937 (m), 1,771 (s), 1,720 (s), 1,634 (m), 1,602 (w), 1,498 (m), 1,456 (m), 1,385 (s), 1,366 (s), 1,258 (w), 1,226 (m), 1,170 (m), 1,079 (m), 1,045 (w), 941 (s), 918 (m), 881 (m), 828 (m), 733 (s), 700 (s), 631 (m), 568 (s) and 492 (w).

An amine end-capped PAI chain was produced by adding the excess amount (1 %) of diamine 1 near the end of the polymerization reaction.

Preparation of the PAI/OC BNC films

The novel BNCs were prepared by mixing the appropriate amounts of the PAI and OC in DMAc as a solvent in a flask for a particular concentration. The solution was agitated to high speed stirring at 80 °C for 2 h and then at 40 °C for 20 h for uniform dispersion of OC platelets in the polymer matrix. Various compositions of OC (2, 5, 10 and 15 wt %) were prepared by mixing various amounts of OC to the PAI solution. Thin BNC films of uniform thickness were obtained by pouring the hybrid solutions into Petri dishes, followed by solvent evaporation at high temperature. These films were further dried at 80 °C to a constant weight.

FT-IR peaks (KBr, cm⁻¹) for BNC 2 %: 3,400 (br), 3,102 (w), 2,970 (w), 2,928 (m), 2,890 (w), 1,800 (w), 1,778 (m), 1,730 (s), 1,622 (m), 1,580 (m), 1,460 (w) 1,383 (s), 1,345 (m), 1,226 (m), 1,148 (m), 1,065 (m), 910 (m), 750 (s), 654 (m), 610 (m), 563 (w), 520 (m) and 465 (m).

FT-IR peaks (KBr, cm^{-1}) for BNC 5 %: 3,415 (br), 3,102 (w), 29,73 (m), 1,800 (w), 1,776 (m), 1,722 (s), 1,616 (m), 1,575 (w), 1,484 (m), 1,383 (s), 1,342 (m), 1,238 (m), 1,156 (w), 1,082 (m), 910 (m), 751 (m), 657 (m), 560 (w), 523 (w) and 464 (m).

FT-IR peaks (KBr, cm⁻¹) for BNC 10 %: 3,420 (br), 3,108 (w), 2,971 (m), 2,931 (w), 2,876 (w), 1,805 (w), 1,777 (m), 1,722 (s), 1,618 (m), 1,565 (w), 1,488 (m), 1,462 (m) 1,383 (s), 1,345 (m), 1,217 (m), 1,154 (w), 1,082 (m), 910 (w), 750 (m), 650 (m), 619 (w), 523 (m) and 465 (s).

FT-IR peaks (KBr, cm⁻¹) for BNC 15 %: 3419 (br), 3,103 (w), 2,960 (m), 2,937 (w), 1,775 (m), 1,720 (s), 1,620 (m), 1,580 (w), 1,488 (m), 1,463 (m) 1,380 (s), 1,342 (w), 1,223 (m), 1,154 (m), 1,080 (w), 1,050 (m), 917 (w), 754 (w), 654 (m), 578 (m), 525 (m) and 456 (s).



L-Tyrosine Modified Organoclay

Scheme 1 Preparation of organosoluble and thermally stable chiral PAI/OC BNCs

Results and discussion

Preparation of monomers and neat PAI

Diamine 1 was prepared via the reduction of dinitro precursors by using hydrazine hydrate as the reducing agent and Pd/C as the catalyst. By this procedure, pure diamine 1 was attained after recrystallization (Scheme 1).

Chiral diacid 2 was prepared by the condensation reaction of one equimolar of PMDA and two equimolars of L-phenylalanine amino acid in the refluxing acetic acid, as shown in Scheme 1.

Because of the rapid emergence of ILs as green solvents and replacement of a volatile and toxic organic solvent in the polymerization with a nonvolatile solvent, in this study, novel PAI was synthesised in green route by using molten TBAB as an IL media. Phosphorylation polymerization technique has been successfully applied to synthesize new organosoluble PAI by the direct polycondensation of imidecontaining dicarboxylic acid 2 with aromatic diamine 1 (Scheme 1). The inherent viscosity of the PAI under optimized condensations was 0.58 dL/g and the yield was 91 %. The specific rotation of this polymer is $[\alpha]_D^{25} = -78.27$, confirming the optical activity of this polymer.

Preparation of OC

The OC chosen for dispersion in high-performance polymers needed enough thermal stability to withstand the high temperature used to cure these polymers. This condition led to the selection of thermally stable molecules for surface modification of the MMT. In this study, positively charged L-tyrosine amino acid swelling agent was chosen to replace the chemically synthesised surfactant for the modification of clay. This molecule has three functional groups of amine, hydroxy and acid in which the amine is protonated and is attached to the surface of the Cloisite Na^+ while the other group is free to participate in the polymerization reaction (Mallakpour and Dinari 2011c, 2012b).

Preparation of the PAI/OC BNC films

Novel optically active PAI/OC BNC films containing 2, 5, 10 and 15 % of OC were successfully fabricated using functionalized OC and amine end-capped PAI chains in dry DMAc through solution intercalation technique (Scheme 1). These new families of homogeneous transparent materials are the combinations of organic polymers and layered silicates blended with each other at ultrafine phase dimensions. The uniform distribution of organically modified nanoclay in polymer matrices can lead to enhancements of physical, morphological, and mechanical properties in the resulting BNCs. The transparency of BNC films was decreased gradually by the addition of clay, and the films became semitransparent and brittle at high loading of OC.

Characterization

¹H-NMR and FT-IR spectra

The structures of new synthesised compounds were confirmed by FT-IR and ¹H-NMR spectroscopy techniques. In the ¹H-NMR spectrum of PAI, the emergence of the N–H



Fig. 1 1 H-NMR (500 MHz) spectrum of 1 H-NMR spectrum of chiral PAI

protons of BI and amide group at 12.60–12.80 and 10.35–10.51 ppm indicates the presence of these groups in the polymer chain (Fig. 1). The resonance of aromatic protons appeared in the range of 6.85–8.25 ppm. The proton of the chiral center appeared as multiplets in the range of 5.23–5.37 ppm. The absorption of the diastrotopic hydrogens that were bonded to the neighboring carbon of chiral center appeared in the range of 3.20–3.47 ppm as two discrete multiplets peaks. The aforementioned results show that PAI was synthesised successfully.

In the FT-IR spectra of the diamine 1, the absorption of amine NH_2 and NH BI bonds appeared around 3,394 and 3,323 cm⁻¹ and the peak at 1,627 cm⁻¹ confirms that the presence of NH deformation provided the successful formation of this compound. Two absorption bands at 1,577 and 1,484 cm⁻¹ were characteristic peaks for aromatic rings. The BI group also gave bands at 1,484 cm⁻¹ (inplane deformation of the BI ring), 1,590 cm⁻¹ (ring vibration of conjugation between fused benzene and imidazole rings) and a shoulder at 1,630 cm⁻¹ (C–N stretching).

In the FT-IR spectrum of the chiral PAI, the absorption bands for the imide ring were observed around $1,722 \text{ cm}^{-1}$, which is indicative of the asymmetrical and symmetrical C=O stretching vibration, and at 1,375, 1,064, and 731 cm^{-1} due to imide ring deformation. The NH stretching band of the amide and BI groups was observed around $3,320 \text{ cm}^{-1}$, and the C=O stretching band of amide group at $1,669 \text{ cm}^{-1}$ (Fig. 2b).

In the FT-IR spectrum of Cloisite Na⁺, the absorption bands of about $3,100-3,700 \text{ cm}^{-1}$ are due to O–H stretching and stretching band of hydrogen-bonded water. A weak broad peak at 1639 cm^{-1} is related to H–O–H bending region. The characteristic peaks at 1,115 and $1,042 \text{ cm}^{-1}$ were due to the out-of-plane Si–O stretching and in-plane Si–O stretching for layered silicates, respectively. Other characteristic vibration peaks at 524 and



Fig. 2 FT-IR spectra of the OC, neat PAI and different BNCs

468 cm⁻¹ are for bending vibration of Si–O and Al–O, respectively. Upon intercalation of L-tyrosine amino acids into the clay gallery for modification of layer silicates, the absorption peaks were observed with origins being from amino acid molecules. For example, in OC spectrum, shoulder in the range of 2,500–3,700 cm⁻¹ is related to OH stretching of the –COOH group (Fig. 2a). The peak at 2,960 is attributed to C–H stretching vibration aliphatic hydrocarbon of phenylalanine and around 1,700 cm⁻¹ it is related to the carbonyl group of the amino acid (Mallakpour and Dinari 2012b).

In the BNC 5, 10 and BNC 15 %, the presence of a peak at 1,048 cm⁻¹ is corresponding to the Si–O and peaks at 400–600 cm⁻¹ for Al–O and Mg–O indicate the incorporation of OC in the PAI matrix (Fig. 2). By comparison of these spectra, it can be concluded that the BNCs not only have characteristic neat PAI bands, but also have characteristic peak for OC. These data, in summary, confirm the formation of the BNCs.

X-ray diffraction

The most common technique used to analyze the OC and polymer/clay nanocomposites is XRD, which measures the interlayer *d*-spacing. The XRD patterns of the OC and PAI/OC BNCs containing different amounts of OC (2, 5, 10 and 15 wt %.) are shown in Fig. 3. Pristine Cloisite Na⁺ has an XRD peak at $2\theta = 7.56^{\circ}$ that was caused by the diffraction of the (001) crystal surface of layered silicates, equaling a *d*-spacing of 1.17 nm. In the XRD pattern of OC, the *d*-spacing of OC was 13.8 nm based on Bragg's Law $(n\lambda = 2d \sin \theta)$. The presence of 2, 5, 10 and 15 wt % of OC in the PAI matrix resulted in a shift of this diffraction

peak toward smaller angle. The peak that was observed in OC at $2\theta = 6.40^{\circ}$ corresponded to the basal spacing of OC and disappeared in the BNCs 2 and 5 %, suggesting the disorder and loss of structure regularity of the clay layers. Thus, the clay tactoids are considered to be exfoliated and the 0.96-nm thick clay layers are dispersed at the molecular level into PAI. When the OC content was increased to 10 and 15 wt %, the samples showed a small diffraction peak at $2\theta = 2.20^{\circ}$, equaling a *d*-spacing of 4.01 nm, respectively, as opposed to the diffraction peak at $2\theta = 6.40^{\circ}$ (d = 1.38 nm) for the OC. This implies that there is a small amount of OC that cannot be exfoliated in PAI and exists in the form of an intercalated layer structure. The peak value indicates the possible presence of PAI molecules outside the MMT layers that squeezed the clay layers during the solvent removal process and caused a reduction in the spacing between the layers (Wang et al. 2004). These XRD results imply that the OCs are well dispersed or exfoliated in the PAI polymer matrix. However, further evidence should be found using TEM to reveal the exact microstructures of the BNCs.

Morphology studies

FE-SEM

FE-SEM micrographs of fracture surfaces of PAI with different OC contents (0, 5, 10 and 15 wt %) are shown in Fig. 4. The micrographs of the PAI hybrids from 5 and 10 wt % OC contents showed dispersed platelet orientation morphology and the wave patterns appeared to be uniformly distributed over the fracture surface. When the OC content was increased to 15 wt %, besides intercalation and exfoliation, partially agglomerated OC particles were also observed in the PAI matrix. Therefore, at low OC contents (below 10 wt %), the OC particles may be



Fig. 3 XRD of OC and different BNCs

dispersed in the polymer matrix without appreciable agglomeration of particles (Fig. 4).

TEM

More direct evidence for the formation of a true nanoscaled composite was provided by using TEM analysis. Figure 5a, b shows the TEM micrographs of the PAI/OC BNC 5 and 15 % in which the brighter region represents the polymer matrix while the dark narrow stripes represent the stacked and intercalated stacked nanoparticles. The micrograph 5a exhibits well-dispersed individual OC layers, which are apparent as dark lines, for the BNC 5 %. Compared to this result, the 15 wt % OC hybrid shows more banded or aggregated lines in Fig. 5b. Owing to the potential for interaction between the free carboxylic acid and hydroxyl groups of the tyrosine modified OC with amide, imide and BI groups of PAI, the TEM micrographs of BNC 5 % reveal wellexfoliated structures. This suggests that a greater interaction force between PAI and organic modifiers is required for the formation of exfoliated structures. Both exfoliated silicate lamellae and intercalated stacks are visible, consistent with the XRD and FE-SEM results. The majority of the particles observed were exfoliated silicate-lamella stacks.

Thermal properties

The TGA curves for thermal degradation of neat PAI and PAI/OC BNCs are shown in Fig. 6. It shows that a loss of mass in the BNC materials occurred above 450 °C. The 5 and 10 % weight loss temperatures of the BNCs were higher than those of the pristine PAI (Table 1). The higher thermal stability of BNCs was attributed to the formation of char-like material as a result of the decomposition of OC. This material acted both as a barrier to mass transport of the decomposed products to the surface of the decomposing polymer and a thermal barrier to prevent additional exposure of the polymer to the flame.

The percent char yield at 800 °C was increased with an increase of OC content in the BNCs, which indicated that the dispersion of OC in the PAI matrix was uniform. Char yield can be applied as a decisive factor for estimating limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation (1976).

$$LOI = 17.5 + 0.4 CR$$

Where CR = char yieldThe BNC 5, 10 and 15 % have LOI values in the range of 42–46 %, as calculated from their char yield at 800 °C. On the basis of LOI values, all BNCs can be classified as self-extinguishing materials (Table 1). From these data, it is clear that neat PAI and its BNCs are thermally stable owing to the existence of various linkages such as imide and BI groups in polymer backbones.



Fig. 4 FE-SEM micrographs of pure PAI (a), BNC 5 % (b), BNC 10 % (c) and BNC 15 % (d)



Fig. 5 TEM images of BNC 5 % (a) and BNC 15 % (b)



Fig. 6 TGA thermograms of PAI and different BNCs

Table 1 Thermal properties of the PAI and different BNCs

Samples	Decomposition temperature (°C)		Char yield (%) ^b	LOI ^c
_	T_5^a	T_{10}^{a}		
PAI	418	451	54	39.1
BNC 5 %	449	478	58	40.7
BNC 10 %	472	492	61	41.9
BNC 15 %	484	506	63	42.7

 a Temperature at which 5 and 10 % weight loss was recorded by TGA at heating rate of 10 $^\circ C\ min^{-1}$ in a N_2 atmosphere

 $^{\rm b}$ Weight percent of the material left undecomposed after TGA at maximum temperature 800 °C in a N_2 atmosphere

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

Conclusions

In this study, a method for achieving a homogeneous dispersion of exfoliated layered silicates as nanometer-thick layers in a polymer matrix was developed. This involved the use of an organic molecule with different polar groups as the matrix to aid in the dispersion of the layered silicate inclusions. A specially designed reactive swelling agent (protonated L-tyrosine amino acid) containing three functional groups was used for the modification of Cloisite Na⁺ during ion exchange reaction. A novel end-capped organosoluble PAI containing L-phenylalanine and BI pendant group was synthesised via direct polycondensation in green media. Near complete dispersion of exfoliated layered silicates was observed in FE-SEM and TEM micrographs, as confirmed by XRD. Dispersed OC platelets into PAI matrix were found to increase the thermal stability, as in the enhancement of thermal decomposition temperature and char yield of PAI/OC BNCs based on the TGA studies. Overall, these results show that the addition of a small amount of reactive OC is sufficient to improve the properties of a chiral PAI. The presence of amino acids as a biodegradable segment in both novel organo-modified nanoclay and optically active PAI makes the obtained BNCs materials more susceptible for better bio-degradation process. These findings are important and relevant to the preparation of low-cost and bio-degradable chiral OCs and related BNCs for industrial applications.

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