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Insertion of novel optically active poly(amide-imide) chains containing pyromellitoyl-bis-L-phenylalanine linkages into the nanolayered silicates modified with L-tyrosine through solution intercalation

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ABSTRACT

In the present investigation, for the first time, functional optically active poly(amide-imide) (PAI)/ organonanosilica bionanocomposite films were successfully fabricated through solution intercalation technique. At the start, Cloisite Na⁺ and protonated form of L-tyrosine amino acid were used for the preparation of the novel chiral organoclay via ion-exchange reaction. Then, PAI containing phenylalanine amino acid was synthesized via solution polycondensation of N,N'-(pyromellitoyl)-bis-phenylalanine diacid chloride (5) with 4,4'-diaminodiphenylsulfone (6). This polymer was end-capped with amine end groups near the completion of the reaction to interact chemically with organoclay. Finally, PAI/organ-nanosilica bionanocomposites films containing 5, 10 and 15% of organoclay were prepared via solution intercalation method through blending of organoclay with the PAI solution. The nanostructures and properties of the PAI/organoclay hybrids were investigated using Fourier transform infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and thermogravimetry analysis (TGA) techniques. XRD, FE-SEM and TEM results revealed the formation of exfoliated and intercalated organoclay platelets in the PAI matrix. TGA results indicated that the addition of organoclay into the PAI matrix increases in the thermal decomposition temperatures of the resulted bionanocomposites. The transparency of the nanocomposite films decreased gradually by the addition of organoclay, and the films became semitransparent as well as brittle at high loading of organoclay. Mechanical data indicated improvement in the tensile strength and modulus with organoclay loading. The film containing a 10 wt.%. of organoclay had a tensile strength of the order of 85.24 MPa relative to the 67.52 MPa of the pure PAI.

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1. Introduction

Nanocomposites are an important class of new generation materials, which typically reveal properties superior to those of their individual components. To optimize the concert properties of these materials, the dispersion of inorganic domain in the organic matrix at nanolevel is enviable [1]. Nanocomposites based on organic polymers and inorganic nanoclay minerals consisting of silicate layers are amongst the most promising composite systems [2–5]. The uniform dispersion of silicate layers is usually desirable for maximum reinforcement of the materials [6]. Nanoclays have several advantages over conventional microsized clays in polymer composites: good mechanical and gas barrier properties, thermal stability and conductivity properties without significant reduction in other relevant properties, including toughness. An additional benefit is the transparency because of their low filler loading, for the reason that the clay content is below a critical loading level [7]. Incorporation of layered silicate into the polymeric matrix provides several improvements in the physical and mechanical properties, such as Young's modulus, yield stress, heat deflection temperature, permeability, and flammability. The superior mechanical properties of the polymer/clay nanocomposites are achieved not only through the molecular-level dispersion of the aluminosilicate layers but also through the strong interactions between the polymer matrix and the clay layers [4,8].



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The incompatibility between organophilic polymer and the hydrophilic layered silicates has been resolved through surface modification of the nanoclays. This can be carried out via an ionexchange reaction of the surface sodium ions with organics producing organically modified layered silicates. The replacement of inorganic exchange cations by organic onium ions on surface of clay not only serves to match the clay surface polarity with the polarity of the polymer but also expands the interlayers of clay, thus facilitating the penetration of polymer precursors or preformed polymer. Depending on the charge density of nanoclay and the onium ion surfactant, different arrangements of the onium ions are possible [9]. The organomodification of clay is an important step in the preparation of polymer/clay nanocomposites. This is usually done by ion-exchange reactions between alkaline cations situated inside clay galleries and organic cationic surfactant molecules, such as ammonium and phosphonium cations [10,11].

Chiral phenomenons play vital roles in nature. Amino acids are among the simplest chiral biomolecules that contain intramolecular hydrogen bonds and they serve as building blocks of more complex peptides and proteins. Most of the naturally occurring compounds for instance nucleic acids, proteins, and polysaccharides are chiral and optically active. Some of them show characteristic functionalities such as molecular recognition ability and catalytic activity, due to their specific chiral structure as represented by genes and proteins. Amino acid based synthetic materials are also expected to show biocompatibility and biodegradability similar to those of polypeptides [12,13]. The use of amino acid compounds in the hybrid materials increases the biocompatibility of such system and allows interactions with biological systems [14,15]. In another hand, peptide-based systems have been found to show nanoscale ordering into stable hierarchical superstructures administered by the formation of secondary structures in the peptide segments. Positively charged amino acids have a similarity in chemical structure with conventional modifiers with alkylammonium cations. When compared with chemically synthesized modifier, amino acid biosurfactants have the important advantage of biodegradability, low toxicity and various possible structures [16].

In addition, the synthesis of macromolecules containing amino acids is a subject of much interest. Because amino acids are naturally occurring compounds, synthetic poly(α -amino acids)s and their copolymers would likely be biodegradable, biocompatible, and nontoxic [17–19]. Moreover, amino acid based chiral copolymers can incorporate crystallinity with the ability to form higher ordered structures that exhibit improved solubility. Synthetic macromolecules containing amino acids are potentially biodegradable because of the incorporation of amino acids, which can be targeted for cleavage by enzymes such as proteases [20–22].

Poly(amide-imide)s (PAI)s contains both amide and heterocycle imide structures along the main chain of the polymer backbone are a kind of thermoplastic resin, have good high-temperature resistance, outstanding mechanical properties, excellent oxidative stability and hydrogen bonding interaction, being a promising matrix candidate for hybrid materials [23–27]. They have been widely used with electronic materials, adhesives, composite materials, fiber, and film material. Comparing with the polyimide and polyamide, the PAI own the better process ability and heat resistant properties [3,26–30].

In the present study, for the first time, we wish to report the synthesis and characterization of new optically active PAI/organoclay bionanocomposites films (BNCF)s which were prepared by solution intercalation method through blending of organoclay with the PAI solution for full dispersion of organoclay throughout the matrix. Cloisite Na⁺ and ammonium salt of L-tyrosine amino acid were used for the preparation of the novel chiral organoclay by a cation-exchange method in a green and environmentally friendly process. The optically active PAI chains was produced by reacting of *N*,*N*'-(pyromellitoyl)-bis-phenylalanine diacid chloride **5** with 4,4'-diaminodiphenylsulfone **6** in *N*,*N*-dimethyl acetamide (DMAc). The amide chains were selectively end-capped with amine end groups near the completion of the reaction to interact chemically with modified organoclay. As a result, chemically combined and thermally stable BNCFs were produced with permanent intercalating effect. The organoclay and thin BNCFs obtained by evaporation of the solvent were subjected for Fourier transfer infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetry analysis (TGA) techniques and mechanical properties. The morphology of the obtained materials was examined by scanning electron microscopy (SEM), field emission scanning electron microscopy (TEM) techniques.

2. Experimental

2.1. Materials

The source clay, sodium montmorillonite (Cloisite Na⁺), was purchased from Southern Clay Products, Gonzales, Texas (USA). The cation-exchange capacity (CEC) of Cloisite Na⁺ is 92.6 meq/100 g as reported by suppliers. This compound was used without any further purification. Pyromellitic dianhydride (benzene-1,2,4,5tetracarboxylic dianhydride) (1) (from Merck Chemical CO., Germany) was purified with acetic anhydride in boiling acetic acid. 4,4'-Diaminodiphenylsulfone (**6**) was used as obtained without further purification. DMAc was dried over BaO, and then distilled in vacuum. L-Tyrosine, L-phenylalanine, triethylamine (TEA) and hydrochloric acid (HCl) were purchased from Merck Chemical Co. (Germany) and were used as obtained without further purification.

2.2. Equipments

FT-IR spectra of the hybrid films were recorded with a Jasco-680 (Japan) spectrometer at a resolution of 4 cm^{-1} and they were scanned at wavenumber range of 400–4000 cm⁻¹. Vibration bands were reported as wavenumber (cm⁻¹). Thin films of BNCFs were made by evaporating solvent at 80 °C and used for FT-IR analysis. FT-IR spectra of Cloisite Na⁺, organoclay and PAI were also collected by making their pellets in KBr as a medium. The band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on Bruker Avance 400 MHz spectrometer operating polymer solution in DMSO-d₆. The Proton resonances were designated as singlet (s) and multiplet (m). 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). TGA is performed with a STA503 win TA at a heating rate of 10 °C/ min from 25 °C to 800 °C under nitrogen atmosphere. XRD patterns were recorded using $CuK\alpha$ radiation on a Bruker, D8ADVANCE, (Germany) diffractometer operating at current of 100 mA and a voltage of 45 kV. The diffractograms were measured for 2θ , in the range of 1.2–10°, using CuK α incident beam ($\lambda = 1.51418$ Å). And Bragg's law $n\lambda = 2d \sin\theta$ was used to compute the *d*-spacing. The dispersion morphology of the nanoparticles on PAI matrix was observed using SEM (XL30, Philips) and FE-SEM (HITACHI S-4160). TEM images were obtained using a Philips CM 120 microscope with an accelerating voltage of 100 kV. The BNC films were first microtomed into 60 nm ultra thin sections with a diamond knife using Leica Ultracut UCT ultramicrotome. Tensile properties of the BNC films were measured according to DIN procedure 53455 having



Scheme 1. Spatial array of the intercalated protonated L-tyrosine amino acid ions in Cloisite Na⁺.

a crosshead speed of 5 mm min^{-1} using Testometric Universal Testing Machine M350/500.

2.3. Synthesis of organoclay

The organo-modified bionanoclay was prepared by a cationexchange method, which is a displacement of the sodium cations of Cloisite Na⁺ with the positively charged L-tyrosine amino acid. The equation for calculating the intercalating amino acid used for a cationic-exchange reaction is expressed as follows:

$$\frac{92.6}{100} \times Y \times 1.5 = \left(\frac{X}{\text{MW of interclated amino acid}}\right) \times 1 \times 1000$$

where 92.6/100 represents the CEC value per 100 g of Cloisite Na⁺ nanoclay; 1.5 (>1) indicates the excess amount of intercalating agent used; Y is the amount of nanoclay and X and MW represent the amount and molecular weight of intercalating amino acid, respectively. Typically, 2 g of Cloisite Na⁺ was mechanically stirred with 100 mL of deionized water at 80 °C for 3 h to swell the layered silicates. The aqueous solutions of the tyrosine amino acid was prepared separately by dissolving amino acid (1.5 times the CEC of clay) in 50 mL of distilled water at 80 following by addition of stoichiometric amount of concentrated HCl to the solution. Then the dispersed clay solution was added to the solution of the

protonated form of L-tyrosine amino acid and the mixture was stirred at 60 °C for 6 h under mechanically stirred. The precipitates of novel modified clay were isolated by suction-filtration using Whatman filter paper, placed in a 250-mL beaker again and washed with 200 mL hot water. This process was repeated three times to ensure the removal of excess ammonium salt of amino acid. The final product obtained by filtration was dried under vacuum at 60 °C for 8 h. The dried cake was ground and screened with a 325mesh sieve to obtain the organoclay.

2.4. Monomer synthesis

N,*N*'-(Pyromellitoyl)-bis-L-phenylalanine diacid chloride **5** was prepared by procedure reported elsewhere [31].

2.5. Synthesis of PAI and amine end-capped PAI

An optically active PAI was synthesized by the solution polymerization of diacid chloride **5** and aromatic diamine **6** at low temperature. The measured amount of diamine **6** (0.36 mmol) was placed in the flask followed by the addition of DMAc as a solvent under an inert atmosphere. After complete mixing, stoichiometric amount of diacid chloride **5** (0.36 mmol) was added again under anhydrous conditions. To remove HCl from the PAI solution, after



Scheme 2. Synthesis of chiral monomer 5.





Scheme 3. Preparation of optically active amine end-capped PAI.

the reagents dissolved completely, stoichiometric amount of TEA was added with constant stirring for 2 h. The polymerization reaction after initial mixing of monomers was allowed to come to ambient temperature after 1 h. While reaction between diamine and diacid chloride is extremely fast, however, further 24 h were given to the reaction mixture for its completion. The reaction mixture was highly viscous and golden in color. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80 °C for 6 h under vacuum to yield 0.246 g (85%) of the solid PAI **7**, and the specific rotation was measured ($[\alpha]_D^{25} = -134$, measured at a concentration of 0.5 g/dL in DMF at 25 °C).

Amine end-capped PAI chains was produced by adding excess (1%) amount of diamine **6** near the end of the polymerization reaction.

Yellow solid; FT-IR (KBr): 3483(sh), 3367 (br), 3101 (w), 3029 (w), 2929 (w), 1776 (m), 1725 (s), 1590 (s), 1525 (m), 1455 (m), 1381 (m, br), 1354 (m, br), 1316 (m, br), 1250 (m), 1180 (sh), 1150 (m), 1105 (m), 956 (w), 917 (w), 835 (m), 727 (m, br), 700 (m, br), 613 (w), 579 (m, br) cm⁻¹.

¹H NMR (400 MHz, DMSO- d_6 , δ, ppm): 3.5 (m, 2H, CH₂), 5.2 (s, br, 1H, chiral center hydrogen), 7.1–7.3 (m, Ar–H), 7.7 (s, 2H,), 7.8 (s, 2H,), 8.2 (s, 2H, Ar–H), 10.3 (s, amide hydrogen) ppm.

Elemental analysis: calcd. for (C₄₀H₃₀N₄O₈S): C, 66.11%; H, 4.16%; N, 7.71%; S, 4.41%. Found: C, 65.88%; H, 4.44%; N, 7.93%; S, 4.60%.

2.6. Preparation of the PAI/organoclay BNCFs

The novel BNCFs were prepared by mixing the appropriate amounts of the PAI and organoclay in DMAc as a solvent in a flask for a particular concentration. The solution was agitated to high speed stirring at 80 $^{\circ}$ C for 2 h and then at 40 $^{\circ}$ C for 20 h for uniform

dispersion of organoclay platelets in the polymer matrix. Various compositions (2, 5, 10 and 15 wt.%) of organoclay were prepared by mixing various amounts of organoclay to the PAI solution. Thin BNCFs of uniform thickness were obtained by pouring the hybrid solutions into glass dishes, followed by solvent evaporation at high temperature. These films were further dried at 80 °C under reduced pressure to a constant weight.

3. Results and discussion

3.1. Preparation of chiral organoclay

In this study, positively charged of L-tyrosine amino acid is chosen to replace the chemically synthesized surfactant for modification of Cloisite Na⁺. During this reaction, the Cloisite Na⁺ changes from hydrophilic to organophilic and the interlayer space of organoclay was increased. These phenomena causes enlarge in the *d*-spacing which facilitates the entry of the host polymer molecules into the organoclay gallery for further applications. Scheme 1 illustrates the schematic of such an adsorption process. This scheme only provides to accentuate the route of adsorption and does not present information on the arranging in which the adsorbent molecules are present along with ammonium ions ionically bound on the surface.

3.2. Synthesis of aromatic polymer

At first, an optically active monomer **5** was synthesized according to the reported procedure as show in Scheme 2 starting from pyromellitic dianhydride and L-phenylalanine amino acid. Then an optically active PAI **7** was synthesized by the step-growth polymerization reactions of an equimolar mixture of monomer **5**



Scheme 4. Preparation of chiral PAI/organoclay BNCs.

with aromatic diamine **6** in dry DMAc (Scheme 3). The inherent viscosity of the synthesized PAI was 0.37 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 specific rotation of this polymer is $[\alpha]_D^{25} = -134(0.05 \text{ g in 10 mL of DMF})$. The structure of this polymer was confirmed as PAI using FT-IR spectroscopy, ¹H NMR and elemental analysis techniques.

3.3. Preparation of the PAI/organoclay BNCFs

The affinity between polymer matrix and organoclay is one of the most important factors in achieving good exfoliation; to a certain extent the affinity can be enhanced by optimizing the structure of the organoclay for a given polymer matrix. Novel optically active PAI/organoclay BNCFs containing 2, 5, 10 and 15% of organoclay were successfully fabricated using functionalized organoclay (COOH and OH) and amine end-capped PAI chains in dry DMAc through solution intercalation technique (Scheme 4). 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 physical, morphological, and mechanical property enhancements in the resulting BNCFs.

3.4. Characterizations methods

3.4.1. FT-IR spectra

Any changes in the structure of the organoclay and BNCFs will be observed through changes in the FT-IR spectra. The representative FT-IR spectra of the unmodified clay (Cloisite Na⁺), organoclay, bulk PAI and PAI/organoclay BNCs materials are shown in Fig. 1. Thin films of PAI and BNCs were made by evaporating solvent at 80 °C and used for FT-IR analysis. Fig. 1a and b shows the FT-IR spectra of Cloisite Na⁺ and organoclay, respectively. In the spectrum of Cloisite Na⁺ the absorption band at 3626 cm⁻¹ is due to -OH stretching of Al–OH and Si–OH. The broad band at 3440 cm⁻¹ results from the –OH stretching vibration of interlayer water. The characteristic peaks at 1637 and 1040 cm⁻¹ is due to interlayer water deformation vibrations and Si–O stretching, respectively. The infrared spectrum of the Cloisite Na⁺ also show bands in the 400–600 cm⁻¹ regions that are attributed to Si–O and Al–O bending vibration. The spectrum of organoclay is dominated by the bands of the Cloisite Na⁺, but the presence of the amino acid is also seen. The peaks at $1650-1400 \text{ cm}^{-1}$ of the intercalated materials and comparison with the same wavenumber interval of the amino acid and that of the nanoclay reveal that organic cations are in the interlayer of Cloisite Na⁺ or on its outer surface. Bands in the 3500-2500 cm⁻¹ region of tyrosine are mostly observable in the spectrum of the organoclay. The protonated amino acid ions should be largely among the layers since after intercalation the materials were intensively washed, thus excess of organic cation were removed. Bands at 2918 and 1682 cm⁻¹ are attributed to C-H stretching vibration of CH₂ aliphatic and C=C aromatic segment. respectively for the interlayered L-tyrosine amino acid. Bands of carboxylic OH and the phenolic OH vibrations of tyrosine were observed in both hybrid materials virtually unchanged just as the C=O stretching mode and the OH groups of Cloisite Na⁺ were consumed.

The FT-IR spectra of PAI (Fig. 1c) showed absorptions around 3360 cm⁻¹ (N–H), 3100 cm⁻¹ (aromatic C–H stretching), 2930 cm⁻¹ and 2857 cm⁻¹ (CH₂ stretching) and two overlapped



Fig. 1. FT-IR spectra of (a) Cloisite Na $^+$, (b) organoclay, (c) PAI, (d) BNC5%, (e) BNC10% and (f) BNC15%.



Fig. 2. XRD patterns of (a) Cloisite Na $^+$, (b) organoclay, (c) BNC2%, (d) BNC5%, (e) BNC10% and (f) BNC15%.

carbonyl (amide and imide's C==O) absorptions at 1776, 1725, and 1663 cm⁻¹ respectively. Absorption at 1380 and 727 cm⁻¹ was showed the presence of the imide heterocycle in this polymer. Absorptions at 1251 and 1150 cm⁻¹ showed due to the sulfone

Table 1

Basal spacing of Cloisite Na⁺, organoclay and PAI/organoclay BNCFs.

| Sample | 2	heta (°) | d (001) Spacing (nm) |
|--------------------------|------------|----------------------|
| Cloisite Na ⁺ | 7.56 | 1.17 |
| Organoclay | 6.4 | 1.38 |
| BNCF2% | 4.62 | 1.91 |
| BNCF5% | 4.62 | 1.91 |
| BNCF10% | 4.70 | 1.88 |
| BNCF15% | 4.96 | 1.78 |
| | | |

moiety (SO₂ stretching). These FT-IR data confirm the formation of the aromatic PAI.

Fig. 1d—f also shows the FT-IR spectra of PAI/organoclay BNCFs containing 5, 10 and 15% of organoclays, respectively. As the loading of organoclay is increased, the intensities of organoclay bands become more pronounced. From these Figs, it can be concluded that the BNCFs not only have characteristic neat PAI bands, but also have characteristic pick for organoclay.

3.4.2. ¹H NMR spectra

¹H NMR data of neat PAI is described in experimental section. In the ¹H NMR spectrum of PAI, appearances of the N–H protons of amide group at 10.30 ppm indicate the presence of amide group in the polymer chain. The absorption of aromatic protons appeared in the range of 7.1–7.3 ppm and the peak at 8.20 ppm was assigned to pyrimillitimide ring protons. The proton of the chiral center appeared as multiplets in the range of 5.26–5.34 ppm. The absorption of the diastrotopic hydrogens bonded to neighbor carbon of chiral center appeared in the range of 3.40–3.59 ppm as



Fig. 3. SEM micrographs of (a-c) Cloisite Na⁺, (d-f) organoclay and (g-i) pure PAI.



Fig. 4. FE-SEM images of (a-c) organoclay, (d-f) pure PAI and (g-i) BNC10%.

two discrete multiplets peaks. The aforementioned results show that PAI was synthesized successfully.

3.4.3. XRD patterns

The most conventional technique used to analyze the organoclay and polymer/clay nanocomposites is XRD, which measure the interlayer *d*-spacing. The layers were propped open upon swelling in water and the basal distances became higher after the ionexchange process by the protonated amino acids compare to the original clay. Fig. 2(a-e) shows XRD patterns of Cloisite Na⁺, organoclay and different BNCs (BNC2%, BNC5%, BNC10% and BNC15%) and the result are summarized in Table 1. The *d*-spacing of pristine Cloisite Na⁺ is 1.17 nm calculated from the peak position $2\theta = 7.56^{\circ}$ using Bragg's equation. After the ion-exchange reaction with ammonium salt of L-tyrosine amino acid, peak of the organoclay shifted to a new position at $2\theta = 6.40^{\circ}$ (d = 1.38 nm). An increase of the interlayer distance, leads to a shift of the diffraction peak toward lower angles and confirmed that intercalation and surface modification of Cloisite Na⁺ had taken place. This means that the basic structures of the Cloisite Na⁺ is kept, the layers only propped open, and the basal distances increased significantly, providing evidence that intercalation has occurred. The presence of 2, 5, 10 and 15 wt% of organoclay in the PAI matrix resulted in a shift of this diffraction peak towards smaller angle $2\theta = 4.62 - 4.98^{\circ}$. It corresponds to a *d* spacing of 1.78–1.91 nm, suggesting a degree of intercalation of PAI into the organoclay galleries.

3.4.4. SEM and FE-SEM

The morphological images of the Cloisite Na⁺, organoclay and pure PAI were studied by SEM and FE-SEM. The morphology of Cloisite Na⁺ before and after modification is shown in Fig. 3a–f. The Cloisite Na⁺ shows massive, aggregated morphology and in some instances, there are some bulky flakes (Fig. 3a–c). Figs. 3d–3f show the morphology of modified organoclay with tyrosine amino acid. Organoclay has more fragments of smaller size and they are formed with irregular shapes. The SEM images of pure PAI show the flakelike structure and the high yield of organoclay (10%) that have the smoother morphology than organoclay (Fig. 3g–i). Fig. 4a–i also, shows the FE-SEM of organoclay, pure PAI and PAI/organoclay (10%), respectively. The results demonstrate that organoclay is homogeneously dispersed in PAI matrix.

3.4.5. TEM

TEM is supplementary utilized as an effective means of developing insights into the internal structure and spatial distribution of the various components, through direct visualization [4,32,33]. Structure of the organo-modified clay was directly investigated by means of TEM. It has been reported that the layer-structure images of untreated Cloisite Na⁺ can not be observed with TEM [34]. Unlike unmodified Cloisite Na⁺, nanoclay modified with protonated form of the tyrosine amino acid show clear layer structures (Fig. 5a and b). Intercalated structures with higher interfacial distance are observed. In some places, there are some curved layers for modified



Fig. 5. TEM micrograph of (a-c) organoclay and (d-f) BNC10%.

nanoclay. Nevertheless, some bundles aggregates can be highlighted in certain regions.

Fig. 5c and d also shows the typical TEM image of the 10 wt.% BNCF in which the brighter region represents the polymer matrix while the dark narrow stripes represent the stacked and intercalated stacked nanoparticles. TEM study of the BNC structure revealed a coexistence of exfoliated and intercalated organoclay layers. TEM observations have been complete by XRD analysis, which gives information on the interlayer distance of the aluminosilicate platelets. The nanoclay sheets were appraised to be about 1 nm thick and an average length of about 100 nm. It is referred to intercalated layers structures where the inorganic layers maintain the parallel registry of pristine silicates and are separated by ultra thin (1.3–5 nm) PAI films. Because of the periodic parallel assembly of the silicates, the intercalated structures give rise to XRD peaks. In addition, it is referred to exfoliated layers structures where the layers are much further apart (5 nm), and in general both the layer registry and the parallel stacking are lost [35]. This TEM photograph demonstrates that most of the organoclay layers were intercalated and dispersed homogeneously into the PAI matrix.

3.4.6. Thermal analysis

The TGA curves for Cloisite Na⁺ and organoclay are shown in Fig. 6. According to these data, decomposition of Cloisite Na⁺ occurs in two steps: the mass loss before 100 °C was attributed to the desorption of water from the interlayer space, since, the maximum decomposition starts at around 660 °C due to dehydroxylation of the layers and proceeds till around 700 °C [36]. In comparison with Cloisite Na⁺, organoclay have lower mass loss before 100 °C, implying less free water in the modified Cloisite Na⁺. In addition, the presence of organic cations increases the number of decomposition steps. Previous studies [34,37,38] showed that the decomposition of an organoclay takes place in four steps: (1) water desorption, (2) dehydration, (3) surfactant decomposition and loss and (4) dehydroxylation of the organoclay. In addition, there are

three different molecular environments for the surfactant in the organoclay: surfactant cations intercalated into the clay interlayers through cation exchange and bound to surface sites via electrostatic interaction; surfactant physically adsorbed on the external surface of the clay; and surfactant molecules located within the clay interlayer [34]. Therefore, the decomposition temperatures for surfactants with different molecular environments will be different from each other. Cloisite Na⁺ does not undergo thermally induced changes in the temperature range of 100–610 °C, therefore the mass loss in this temperature range should be attributed to the decomposition and/or evaporation of the tyrosine amino acid ions.

The TGA curves of PAI and PAI/organoclay BNCFs are shown in Fig. 7 and the resulting TGA data are summarized in Table 2 that including temperatures at which 5% (T_5), 10% (T_{10}) degradation occur and char yield at 800 °C. The initial decomposition temperatures of the nanocomposites with different organoclay contents (5, 10 and 15%) are about 300 °C. These values are related to the decomposition of pristine polymer matrix. The char yields at 800 °C



Fig. 6. TGA thermograms of Cloisite Na⁺ and organoclay.



Fig. 7. TGA thermograms (a) neat PAI, (b) BNC5% (c) BNC10% and (d) BNC15%.

of the nanocomposites with different organoclay content are higher than that of pure PAI. Char yield can be applied as decisive factor for estimated limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation [39].

 $LOI\,=\,17.5+0.4\,CR$

Where CR = char yield.

The BNCF5%, BNCF10% and BNCF15% have LOI values around 35 which were calculated from their char yield at 800 °C. On the basis of LOI values, all BNCFs can be classified as self-extinguishing nanocomposites (Table 2). This enhancement in the char formation is ascribed to the high heat resistance exerted by the organoclay, because the organoclay have high thermal stability, so the incorporation of organoclay can improve the thermal decomposition rate of the nanocomposites, although the initial decomposition temperature does not increase.

3.4.7. Optical clarity of the BNCFs

Even though layered silicates are microns in lateral size, they are just 1 nm thick. Thus, when single layers are dispersed in a polymer matrix, the resulting nanocomposite is optically clear in visible light. Owing to the nanoscale distribution of organo-nanoclay in the PAI matrix, optical transparency remains high at different organo-nanoclay contents. Fig. 8(a-e) shows the UV-visible transmission spectra of pure PAI and BNC materials with 2, 5, 10 and 15 wt % of organoclay. These films had a thickness of \sim 50–55 μ m. The spectra of BNCF2% and BNCF5% in the visible regions (400–700 nm) were slightly affected by the presence of the clay and retained the high transparency, indicating that exfoliated BNC materials might exist at low clay contents. Furthermore, BNCF10% and BNCF15% had a lower transparency than BNCF2% and BNCF5% resulting from agglomeration of the clay particles. The translucency of the BNCF comes from the nanoscale dispersion of the organoclay particles in the matrix polymer.

| Table | 2 |
|-------|---|
|-------|---|

Thermal properties of the PAI and different BNCFs.

| Polymer | Decomposition temperature (°C) | | Char yield (%) ^b | LOI ^c |
|---------|-----------------------------------|------------------------------|-----------------------------|------------------|
| | T ₅ ^a | T ₁₀ ^a | | |
| PAI | 281 | 298 | 43 | 34.7 |
| BNC5% | 296 | 307 | 49 | 37.1 |
| BNC10% | 305 | 318 | 51 | 38.0 |
| BNC15% | 317 | 348 | 55 | 39.5 |

 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.

 b Weight percent of the material left undecomposed after TGA at maximum temperature 800 $^{\circ}\text{C}$ in a N_{2} atmosphere.

 $^{\rm c}\,$ Limiting Oxygen Index (LOI) evaluating at char yield at 800 $^\circ\text{C}$



Fig. 8. UV-vis transmission spectra of (a) neat PAI, (b) BNC2%, (c) BNC5%, (d) BNC10% and (e) BNC15%.

3.4.8. Mechanical properties

The stress-strain curves of pure PAI and BNC materials with 5.10 and 15 wt. % organoclav are shown in Fig. 9. The BNCs were found to be stiffer than the neat polymer and the elastic modulus increased with increasing organoclay. The maximum modulus value was observed with 10 wt. % organoclay in the polymer matrix, providing more stiffness to the materials, since stiffness is a function of the aspect ratio. A decreased attraction between the silicate layers caused larger interlayer spacing between the silicate layers and more exfoliated nanolayers with a high aspect ratio. Another reason for the enhancements in the tensile modulus of BNCs is the strong interaction between the matrix and silicate layer via formation of hydrogen and chemical bonding. The extent of the improvement of modulus depends directly upon the average length of the dispersed clay particles and hence the aspect ratio and excellent enhancement in the modulus is attributed to the uniformly dispersed silicate layers [4]. The results also indicated significant increase in tensile strength of the BNC materials, relative to that of the neat PAI. The incorporation of organoclay into the polymer reinforced the polymer, giving the observed increase in this important property. The intimate blending of the two phases, presumably with the covalent bonding between them, provides a combination of some of the best properties of the two components [6]. The maximum stress at break (ultimate strength) was found to increase initially with increase in organoclay content, and at 10 wt% organoclay showed a maximum value of 85.24 MPa (relative to the 67.52 MPa of the neat PAI) representing significant enhancement in tensile strength. Further addition of organoclay decreased the strength because of increasing brittleness.



Fig. 9. Stress versus strain curves of pure PAI and different BNC films.

At high clay loading, silicate layers may stack together in the form of tactoids and the intergallery space does not increase much so that more chains can travel into the space between the layers. These large size particles then deteriorated the properties of the composites. Further addition of organoclay decreased the strength because of increasing brittleness [9]. The above results on mechanical properties suggested considerable reinforcement, presumably from the bonding between the PAI chains and the organoclay. However, the higher the molecular weight of the polymer, the fewer the end groups available for bonding to the ceramic phase. Perhaps, organoclay platelets in excess of those linkable to PAI chains contribute obviously to the final brittleness that was observed.

4. Conclusions

One successful approach to the synthesis of nanocomposites is the dispersion or break-down of inorganic nanoclay minerals consisting of layered silicates into nanoscale building blocks in the polymer matrices. The selection of modifier is important because it can enlarge the nanoclay galleries as well as improve the compatibility between nanoclay and the polymer. Organoclay when added to the PAI matrix reinforces materials with improved compatibility between the two phases. In this investigation, the incompatibility between organophilic polymer and the hydrophilic layered silicates was resolved through surface modification of the Clouisite Na⁺ nanoclay. In view of that, at first, Cloisite Na⁺ and protonated form of L-tyrosine amino acid was used for preparation of the novel chiral organoclav via ionexchange reaction. Then, novel optically active PAI containing phenylalanine amino acid was synthesized via solution polycondensation of N,N'-(pyromellitoyl)-bis-phenylalanine diacid chloride with 4,4'-diaminodiphenylsulfone in DMAc and then it was selectively end-capped with amine end groups near the completion of the reaction to interact chemically with modified organoclay. Finally, novel PAI/organ-nanosilica BNCFs with different compositions of the organoclay were prepared via solution intercalation method. The nanostructure and properties of the synthesized organoclay and PAI/organoclay hybrids were investigated using different techniques. XRD, FE-SEM and TEM results revealed the formation of intercalated and exfoliated organoclay platelets in the PAI matrix. Thermal stability of BNCFs increased compared with pristine PAI by increasing organoclay content. Tensile strength and modulus improved for BNCFs with optimum organoclay content (10 wt.%). Enhancement in the mechanical properties results from the fine dispersion of the nanoclay particularly up to 10 wt. % in BNC materials.

The presence of amino acids as a biodegradable segment in both novel organo-modified nanoclay and optically active PAI, make the obtained BNCs materials more susceptible for better biodegradation process. These findings are important and relevant to the preparation of low-cost, biodegradable and biocompatible chiral organoclay and novel BNCs for industrial applications.

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