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ARTICLE TYPE

Modification of Mg/Al-layered double hydroxide with L-aspartic acid containing dicarboxylic acid and its application in enhancement of thermal stability of chiral poly(amide-imide)

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In this study, Mg/Al-layered double hydroxide (LDH) was intercalated with diacid containing L-aspartic acid in one step using ultrasonic method under green conditions. Organic diacid was used as modifier to enhance their compatibility and led to better dispersion of LDH nanoclay in polymer matrix. An effective intercalation of the examined diacid in LDH was confirmed by increasing in basal spacing of the obtained products in comparison with Mg/Al-CO₃²⁻ LDH precursors using X-ray diffraction. An optically active poly(amide-imide) (PAI) was synthesized via polycondensation of *N,N*-(pyromellitoyl)-bis-phenylalanine diacid with 4,4-diaminodiphenylsulfone in molten tetrabutylammonium bromide. The modified LDH (M-LDH) was used as a filler into the PAI matrix and PAI/M-LDH nanocomposites containing 2, 4 and 8% of M-LDH were fabricated. Thermogravimetric analysis showed improvement in thermal stability and morphology investigations by field emission scanning electron microscopy and transmission electron microscopy indicated that M-LDH is dispersed in the PAI matrix.

1. Introduction

Aspartic acid is an α -amino acid with the chemical formula of HOOCCH(NH₂)CH₂COOH.¹ It was classified as an acidic amino acid and can be used in synthesis of polymers with relatively low molecular weight as well as high molecular weight with polycondensation reaction.² There are two enantiomers of aspartic acid and the name aspartic acid can refer to either enantiomer or a mixture of two of these two forms, one L-aspartic acid, is directly incorporated into the proteins and L-aspartic acid is a chosen amino acid which has been applied to the synthesizing of fresh polymers due to its multifunctionality.³ D-aspartic acid is an internal amino acid, which has been found in nervous and endocrine texture of both invertebrates and vertebrates. D-aspartic acid has a lot of applications in the chicken and rat brain, human and so on.⁴

Layered double hydroxides (LDHs), known as hydrotalcite like compounds, have attracted attention, because of their layered structure and very high anion-exchange capacity.⁵ The structure of these compounds consists of positively charged brucite-like layers with interlayer space containing charge compensating anions and water molecule. The positive charges on the LDH surface are balanced by interlayer anions and water molecules.⁵⁻⁷ The general formula of LDHs is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot yH_2O$, where M^{2+} is a divalent metal ions such as Mg²⁺, Ca²⁺, Fe²⁺, Co²⁺ and M^{3+} is a trivalent ions such as Al³⁺, Fe³⁺, Cr³⁺, Mn³⁺ and

A^{n-} is the exchangeable anion (often carbonate, chloride or nitrate).⁸⁻¹¹ Recently the synthesis, structure and properties of LDHs have been widely studied because of their potential applications in catalysts,¹² drug delivery,¹³ remove harmful oxyanions,¹⁴ adsorption of acid red from dye wastewater,¹⁵ optics,¹⁶ biosensors,¹⁷ synthesis of highly efficient flame retardant nanocomposites (NCs),¹⁸⁻²³ and other areas. LDHs are also naturally abundant, readily synthesized at industrial scale, inexpensive and stable at high temperature (up to 500-600 °C) and pH conditions.²⁴

In the last decade there has been considerable interest in polymer-LDH NCs due to their remarkably enhanced mechanical, thermal, electrical, magnetic and fire retardant properties.²⁵ These enhanced properties are mainly attributed to the dispersion of layered compounds within the polymer matrix. The use of LDHs as nanofillers has some limitations. The high charge density of LDH layers and the high content of anionic compounds and water molecules, result in strong interlayer interactions between the sheets and pronounced hydrophilic properties. Thus, monomer and or polymer cannot easily penetrate within the LDH layers and the homogeneously dispersed of LDH layers within the hydrophobic polymer matrix is difficult. To facilitate the intercalation of LDH within the polymer matrix and to gain a desirable degree of dispersion, the interlayer space should be modified with suitable and capable organic anions.²⁶⁻²⁸ Among

the numerous types of polymer structure, optically active polymers offer a number of advantages in terms of their thermal stability, chemical resistance and efficiency of binding.²⁹ Poly(amide-imide) (PAI) are known to have the property advantages of both polyamides and polyimides such as high strength, good solubility in polar amide-type solvent, hydrogen bonding interaction and extensive chemical resistant, being a promising matrix candidate for hybrid materials.³⁰⁻³²

In this work, Mg/Al-LDH was modified with dicarboxylic acid containing L-aspartic acid and tetrabromophthalic anhydride under ultrasound irradiation as green and safety technique via co-precipitation method in aqueous media. The product (M-LDH) was applied as filler with different percent's (2, 4 and 8 wt %) in the PAI matrix for the preparation of LDH/PAI NCs. Fourier transform infrared (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were used to study the morphological features and the nature of LDH particle dispersion in PAI matrix. The thermal features of the NCs were studied by means of thermogravimetric analysis (TGA) to probe the effects of LDH nanoclay on the thermal stability of the resulting NCs.

2. Experimental section

2.1 Materials

Materials used in the synthesis of LDHs are aluminum nitrate nonahydrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and magnesium nitrate hexahydrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ were purchased from Aldrich Chemical CO. (USA). Tetrabromophthalic anhydride (TBPA), tetrabutylammonium bromide (TBAB), triphenyl phosphite (TPP) and pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) (PMDA) were purchased from Merck Chemical CO. (Germany). Amino acids L-aspartic acid and L-phenylalanine were used without more purification. The other solvents and materials were used as gained without further purification.

2.2 Apparatus

Jasco-680 (Japan) spectrophotometer was used for FT-IR analyses of the synthesized materials. Spectra of solid samples were obtained with KBr disk. The vibration transition frequencies are described in the range of $400\text{--}4000\text{ cm}^{-1}$. The XRD patterns were accumulated by using a Philips Xpert MPD X-ray diffractometer. The diffractograms were measured for 2 θ , in the range of $5\text{--}80^\circ$, using a voltage of 40 kV and Cu K α incident light ($\lambda=1.51418\text{ \AA}$). TGA data were obtained on a STA503 TA apparatus in an argon atmosphere by heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from room temperature to $800\text{ }^\circ\text{C}$. The dispersion morphology of the mixtures was detected using TEM (a Philips CM 120 operated, Netherlands) and FE-SEM (Hitachi, S-4160, Japan). The reaction was happened on a MISONIX ultrasonic liquid processor, XL-2000 series with a wave of frequency $2.25 \times 10^4\text{ Hz}$ and power 100 W.

2.3 Synthesis of biosafe diacid containing aspartic acid

L-aspartic acid containing diacid was synthesized according to the procedure reported by Tagle et al.³³ The mixed solution of 0.50 g (1.0 mmol) of TBPA, 0.15 g (1.1 mmol) of aspartic acid and 8 mL of acetic acid were prepared and 1 mL of pyridine was added into this solution. The mixed solution was stirred at room

temperature for 12 h and then the solution was refluxed at $120\text{ }^\circ\text{C}$ for 12 h. The solvent was removed under reduced pressure and the residue, 50 mL of cold mixture of water and hydrochloric acid (10%) was added. The solution was then stirred for 2 h. A white precipitate was formed, filtered off, and dried to give 0.58 g (89%) of aspartic acid containing diacid. melting point (m.p.) $267\text{--}269\text{ }^\circ\text{C}$, (Literature $265\text{--}267\text{ }^\circ\text{C}$),²⁷ $[\alpha]_{\text{D}}^{17.589}(\text{N,N-dimethylformamide}) = +76\text{ deg}^{-1}\text{g}^{-1}\text{cm}^3$. FT-IR (KBr, cm^{-1}): 3433 (br), 2939 (m), 1779, 1725 (s, br), 1425 (m), 1389 (s), 1342 (s, m), 1292 (s), 1202 (s, w), 1119 (s), 1027 (w), 950 (s, br), 921 (br), 827 (w), 752 (s, m), 669 (s, m), 640 (s, m), 520 (s, w), 421 (s, w).

2.4 Synthesis of M-LDH via ultrasonic method

In this work M-LDH was prepared by the co-precipitation method under ultrasonic irradiation. The mixed solution of 0.50 g (2.0 mmol) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.37 g (1.0 mmol) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (molar ratio 2/1) was prepared in the 20 mL of deionized water (solution A). On the other hand, 0.83 g (1.5 mmol) of L-aspartic based diacid and 0.12 g (3.0 mmol) of NaOH was dissolved in the 20 mL deionized water (solution B). Solution A was added into the solution B and stirred at room temperature for 3h. Then the pH of obtained suspension was adjusted to 10 by adding 1M NaOH. Finally the resulting product was sonicated for 1h and obtained precipitate filtered and washed by deionized water and then was dried at $60\text{ }^\circ\text{C}$ for 24h. The $\text{Mg}/\text{Al}\text{-CO}_3^{2-}$ was synthesized by similar procedure without adding diacid molecule.

2.5 Synthesis of L-phenylalanine containing diacid

N,N-(Pyromellitoyl)-bis-L-phenylalanine monomer was prepared according to earlier study.³⁴

2.6 Synthesis of chiral PAI

PAI was prepared according to the reported procedure in the provirus work.³⁵ An optically active L-phenylalanine containing PAI was prepared by the polycondensation reaction of an equimolar mixture of 0.29 mmol of monomer 3 and 0.29 mmol of 4,4-diaminodiphenyle sulfone (diamine 4) in the 1.16 mmol of molten TBAB. After the reagents dissolved completely, 0.28 mL of TPP was added and the reaction mixture was stirred for 12h at the $120\text{ }^\circ\text{C}$. The viscous and yellow solution was poured into 40 mL of methanol and the precipitate solid was filtered using Whatman filter paper. The inherent viscosity of the resulting polymer was 0.34 dL/g and the yield was 88%. The specific rotation was measured $[\alpha]_{\text{D}}^{25} = -134^\circ$ (at a concentration of 0.5 g/dL in DMF at $25\text{ }^\circ\text{C}$), confirming the optical activity of this polymer.

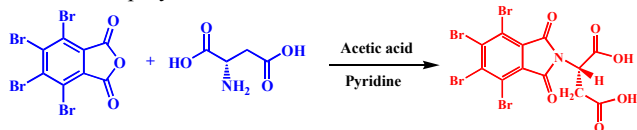
2.7 Synthesis of PAI/M-LDH NCs

Different NC of PAI/M-LDH (2, 4 and 8 wt.%) were prepared by following method. 0.1g of PAI was dispersed in the 8 mL ethanol and a uniform colloidal dispersion was obtained after sonication for 15 min (solution 1). Different percent's of M-LDH were dispersed in 8 mL of ethanol and was sonicated for 30 min (solution 2). Two solutions were mixed together at room temperature and sonicated for 3h. After irradiation, the ethanol was removed and the obtained solid was dried in the room temperature for 24 h.

3. Result and discussions

3.1 Preparation of chiral diacid and M-LDH

L-Aspartic acid containing diacid was synthesized from the reaction of the TBPA and L-aspartic amino acid in refluxed acetic acid at the presence of pyridine as shown in Scheme 1.³³ This diacid was used for organo-modification of Mg/Al-LDH by a simple and green method under ultrasonic irradiation. The schematic of such an adsorption process between chiral diacid and Mg/Al-LDH is shown in Figure 1. The elementary reason for selecting Mg/Al based LDH is their typical metal hydroxide-like chemistry and conventional clay-like layered crystalline structure which makes them appropriate for polymer NCs preparation and can progress their dispersion in polymer matrix. Mg/Al-LDH can't be easily dispersed in polymer matrix; this failure is due to the weak interactions between the polymer and the LDH. In fact, the organic component of the organoclay increases interactions between the polymer and the M-LDH.



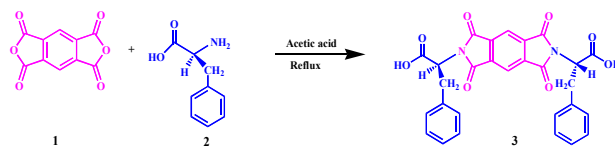
Scheme 1. Preparation of diacid from reaction between TBPA and aspartic acid



Figure 1. Intercalation of diacid in the interlayer of LDH

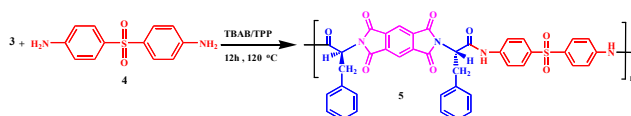
3.2 Synthesis of PAI

From a technological point of view, the use of an organic solvent in big scale preparation is not very friendly and highly polar conventional solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, pyridine, *N*-methylpyrrolidone and chlorinated solvents which are used in polycondensation polymerizations are volatile and most of them are flammable, toxic, quite hazardous and harmful compared to ionic liquids.^{36,37} In this study, molten TBAB ionic liquid was selected because it proved to be the most valuable among those employed. Due to their nonvolatility, ionic liquid have a little effect on the environment and human health and so, they are known as green solvents due to their properties such as chemical stability, low to high viscosity, and high ionic conductivity properties.^{38,39} For the preparation of the polymer, first an optically active and bioactive dicarboxylic acid **3** was synthesized via the reaction of L-phenylalanine and PMDA in refluxing acetic acid solution (Scheme 2). Then PAI **5** was successfully synthesized by the polycondensation reactions of an equimolar mixture of **3** with aromatic diamines **4** in molten TBAB as an ionic liquid media and TPP which acted as activating agent in good yield and moderated inherent viscosity (Scheme 3). The obtained PAI displayed optical rotation, which showed that the polymer is optically active and chirality was introduced into the backbone of the polymer.



Scheme 2. Synthesis of *N,N*-(pyromellitoyl)-bis-L-phenylalanine

monomer



Scheme 3. Synthesis of chiral PAI

3.3 Preparation of PAI/M-LDH NCs

PAI/M-LDH NCs were synthesized by a solution-intercalation method using ultrasound radiation. The organic anions containing the polar groups are intercalated in LDH interlayers and can allow anchoring of the polymeric unit onto LDH. The inorganic nanoparticles (hydroxide nanosheets) are randomly dispersed in the PAI matrix. The adsorption of PAI onto the surfaces of M-LDH was presumed to occur through hydrogen bonding (Figure 2). Although, van der Waals forces between PAI matrix and M-LDH surface would also play an essential role in the overall adsorption process.

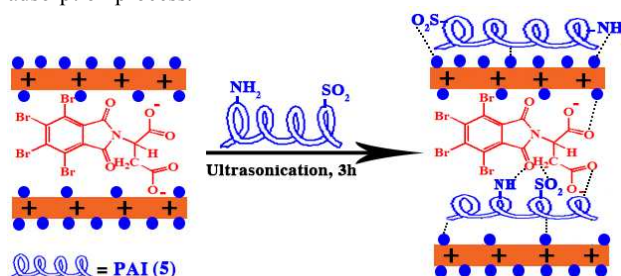


Figure 2. Synthesis of NCs of PAI and M-LDH

3.4.1 FT-IR

FT-IR spectroscopy has been mostly employed to study the structural accommodation of interlayer species and hydrogen bond network in LDH. FT-IR spectra of the LDH- CO_3^{2-} , L-aspartic containing diacid and M-LDH are represented in Figure 3. For LDH- CO_3^{2-} , the broad peak in the 3150-3500 cm^{-1} is ascribed to the water molecules where the hydrogen bonding in the interlayer region between water molecules and the hydroxide sheet is obvious from shoulder at 3050-3100 cm^{-1} . The asymmetric stretching of carbonate in the interlayer space of LDH was shown in the range 1350-1380 cm^{-1} . The strong band at 455 cm^{-1} and the broad one at 651 cm^{-1} are ascribed to the vibrations of metal oxides (Mg-O and Al-O), respectively. The FT-IR spectrum of diacid showed a broad and strong peak at 2350-3650 cm^{-1} , which was assigned to the COOH groups and two absorption bands at 1779 and 1725 cm^{-1} , which are corresponding to the unsymmetrical and symmetrical stretching vibrations of imide C=O group. The adsorption peaks showed at 1389 and 752 cm^{-1} region is related to the presence of the imide heterocycle ring and showed peak in the 1119 cm^{-1} due to the C-Br. FT-IR spectra for M-LDH shows the adsorption peaks at 1775 and 1720 cm^{-1} related to the stretching vibration of C=O, at 1124 cm^{-1} related to the C-Br and 1388 and 752 cm^{-1} can be related to the imide C=O group in comparison with LDH- CO_3^{2-} , which may confirm the presence of diacid in the interlayer of

LDH. Peak due to the carbonate anion (1378 cm^{-1}) is also observed, because the process was applied without N_2 atmosphere and CO_2 can be absorbed from the atmosphere during the process.

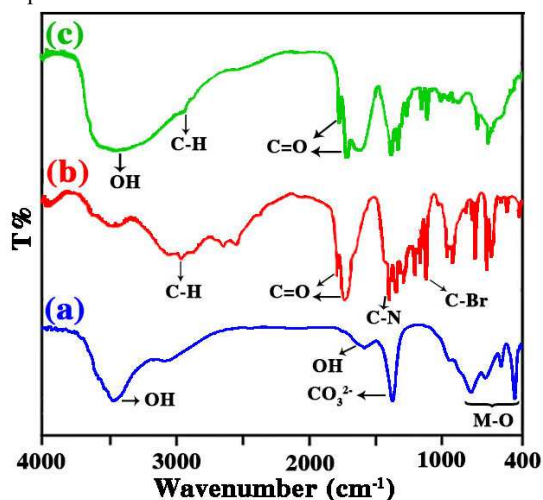


Figure 3. FT-IR spectra of (a) LDH-CO_3^{2-} , (b) diacid and (c) M-LDH

Figure 4 shows the FT-IR spectra of the pure PAI and NCs of PAI with different amount of the M-LDHs. The FT-IR spectrum of PAI showed absorption peaks around 3360 cm^{-1} (N-H), and two overlapped carbonyl (amide and imide's C=O) absorptions at 1779 , 1725 , and 1663 cm^{-1} , respectively. Absorption at 1380 and 727 cm^{-1} indicate the presence of the imide heterocycle in this polymer structure. Absorptions at 1251 and 1150 cm^{-1} are due to the sulfone moiety (SO_2 stretching). The spectra of the prepared NCs clearly exhibit the characteristic absorption peaks corresponding to the polymeric groups, although some peak intensity may be changed. The new peaks showed in the range $400\text{--}600\text{ cm}^{-1}$ are correspond to metal oxide (Mg-O and Al-O) in the NCs spectra. This result in sum confirmed the presence of M-LDH nanoclay in the PAI matrix.

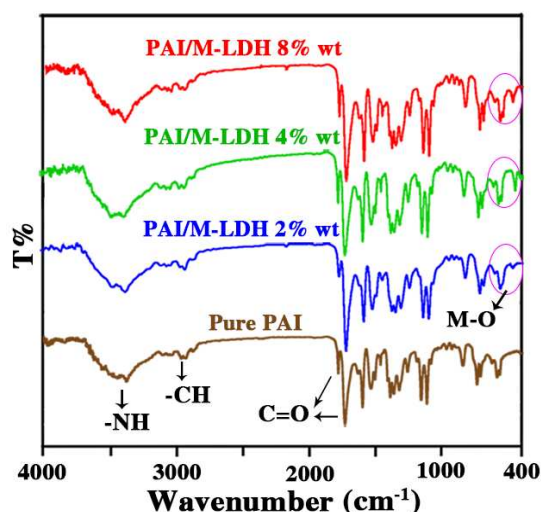
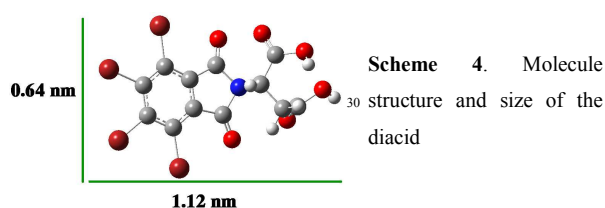


Figure 4. FT-IR spectra of PAI and NCs of PAI with different amount of the M-LDHs

3.4.2 X-ray diffraction

The XRD patterns are very valuable and main analytical technique for the characterization of LDHs and crystalline phases.⁴⁰ It is also used to determine the interlayer spacing and for the determination of the structure of layered samples. The XRD patterns of LDH-CO_3^{2-} , M-LDH, NC4 and 8 wt% were shown in Figure 5. Before organic treatment, the basal spacing of the pure LDH, that is, LDH-CO_3^{2-} is 0.75 nm , which corresponds to the (003) diffraction peak with $2\theta=11.84^\circ$.²⁸ After modified LDH with the diacid molecule, the X-ray reflections have been shifted to a lower angle position. The M-LDH displays a (003) diffraction peak at $2\theta=7.87^\circ$ corresponding to an interlayer distance of 1.12 nm . In conclusion, these increases in the interlayer distances show the intercalation of bigger anionic diacid functionalized between the LDH layers. The size of the guest diacid was estimated and compared to the obtained basal spacing via XRD patterns. Based on previous work, the thickness of LDH-CO_3^{2-} hydroxide sheets is 0.48 nm .¹⁰ The increase of interlayer distance in the M-LDH, calculated from the d003 spacing and thickness of the inorganic layer, is approximately 0.64 nm . This means that the anionic diacid are horizontally oriented in the interlayer space (Figure 1), which are confirmed by the approximate molecule length diacid which were calculated by gauss view (Scheme 4).

For PAI/LDH NCs (4% and 8%), the XRD patterns don't showed any peak for M-LDH in the samples. The only new broad and vast diffraction peak that appeared at $2\theta=17.70^\circ$ related to the PAI polymer matrix. In PAI/clay NCs, complete exfoliation of LDH results in disappearance of the diffraction maxima in their XRD patterns. Moreover, this can also happen due to other reasons, such as extremely low concentration of clay materials in the polymer matrix, crystal defects, etc. The high degree of exfoliation of the LDH clay layers in polymer NCs has also been reported using several studies.^{41,42} However, XRD analysis alone is not adequate for proven of the dispersion in the polymer matrix.

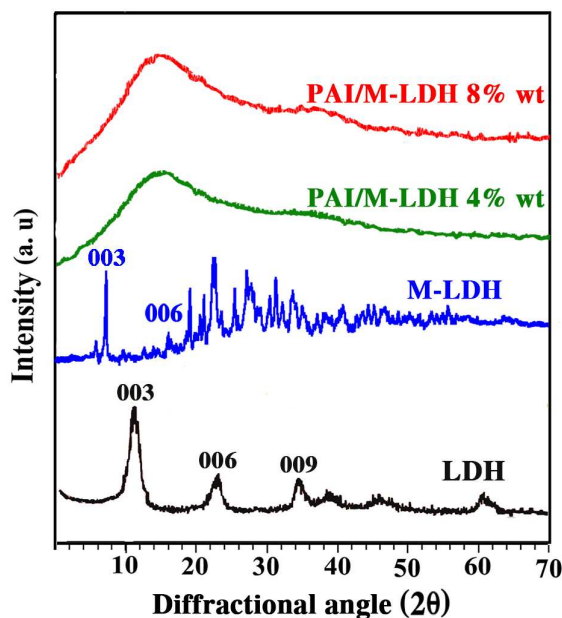


Figure 5. XRD patterns of LDH, M-LDH and NCs of PAI 4 and 8% of the M-LDHs

3.4.3 Thermal analysis

TGA is used to measure variations in the mass of LDH and evaluation of the content of water and anion molecules.³⁰ The TGA curves for LDH and M-LDH are shown in the Figure 6. Three mass-loss steps are noticed for LDH. The weight loss before 200 °C is recognized to the releasing of the physically adsorbed water and water molecules around Mg and Al cations and the about 400 °C removal of water molecules by dehydroxylation process was showed. Third weight loss is related to the removal of the interlayer carbonate anions.¹⁰ For M-LDH the numbers of decomposition stages have enhanced. Diacid modified LDH have similar mass-loss behavior before 400 °C. In comparison to LDH-CO₃²⁻, residual weight percent of the diacid intercalated LDH was decreased. Also the presence of a larger weight loss step within 410-540 °C for LDH-dicarboxylate anion compared to the LDH, confirmed the presence of interlayer surfactant anions in LDH, because the presence of organic groups in the interlayer of M-LDH reduced the thermal stability of the hybrid compounds.¹⁰

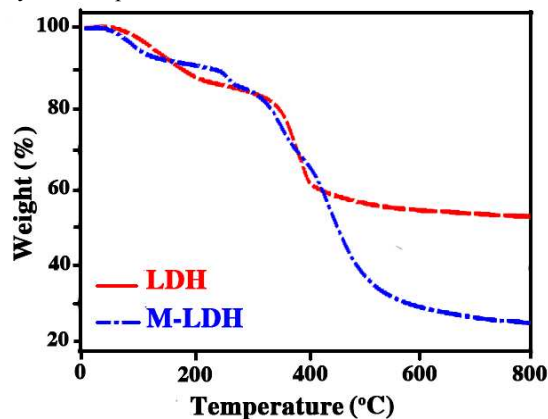


Figure 6. TGA curves for LDH and M-LDH

Figure 7 shows the thermal decomposition of neat PAI and PAI/M-LDH NCs with different contents of M-LDH and resulting TGA data are summarized in Table 1. The thermal stability of the PAI and PAI/M-LDH NCs was studied on the basis of 5 and 10% weight losses (T_5 and T_{10} , respectively) of the samples and the char yield (residue weight at 800 °C). The initial decomposition temperatures of the NCs with different M-LDH percent (2, 4 and 8 %) were over 315°C, which can be related to the decomposition of pristine polymer matrix.³⁵ According to the Table 1, T_5 , T_{10} and char yield for NCs with different M-LDH content are higher than of pure PAI. It is clear that the PAI/M-LDH materials improved thermal properties due to the incorporation of M-LDH. The improvement of thermal property of PAI/M-LDH NCs can be attributed to the homogeneous dispersion of M-LDH nanoclay in polymer matrix and the strong hydrogen bonding between O-H groups on the surface of M-LDH and nitrogen atoms or carbonyl group of PAI matrix. Char yield can be applied as a crucial factor for estimating limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftzyer equation.⁴³

$$LOI = 17.5 + 0.4 CR$$

Where CR = char yield. According to this equation, LOI values calculated based on their CR at 800 °C were higher than 30, showing that such macromolecules can be classified as self-extinguishing polymers.

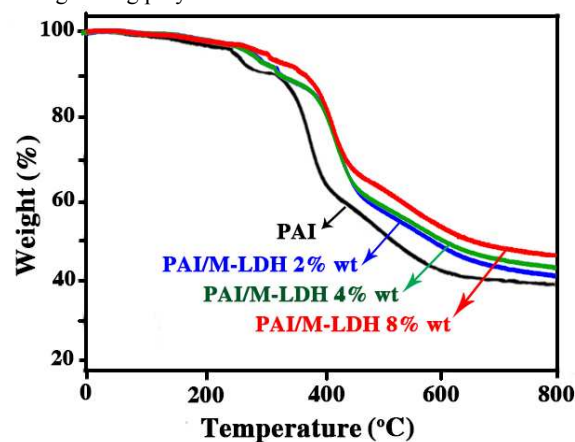


Figure 7. TGA curve of PAI and NCs of PAI with different amount of the M-LDHs

Table 1. The data obtained from TGA thermogram of PAI and PAI/M-LDH NCs

Sample	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield (%) ^b	LOI
PAI	289	349	39.00	33.10
PAI/M-LDH 2%	316	379	41.23	33.99
PAI/M-LDH 4%	342	382	42.42	34.46
PAI/M-LDH 8%	342	400	46.46	36.08

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

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

3.4.4 Morphological analysis by electron microscopy

FE-SEM and TEM provide beneficial and crucial images of textural and crystal morphologies of LDH intercalated materials. LDH generally shows a hexagonal platelet morphology.²⁷ The FE-SEM images of LDH-CO₃²⁻ and M-LDH with different magnification are showed in the Figure 8. The LDH displayed the nature of LDH particles, which roughly contained of plate-like shapes with lateral dimensions and thickness ranging over few nanometer (Figures 8a and 8b). The FE-SEM images for M-LDH showed formation of plate-like nanoparticles with regular shape, as commonly observed for the typical organic anionic intercalated LDH compounds. The layer nanoparticles have a diameter over a few hundred nanometers and a thickness over several tens of nanometers (Figures 8c and 8d).

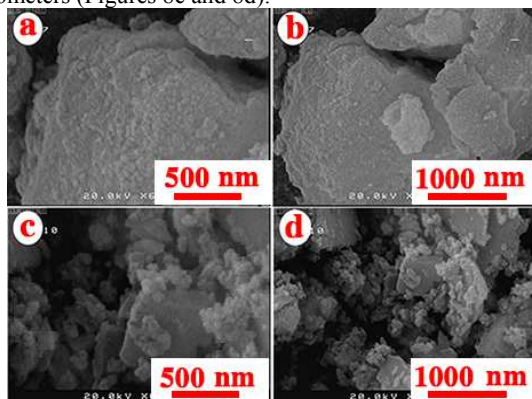


Figure 8. FE-SEM images of (a, b) LDH-CO₃²⁻ and (c, d) M-LDH

The FE-SEM micrograph for neat PAI and NCs with different percent represent in the Figure 9. The morphology of neat PAI seems to be smooth relatively (Figures 9a and 9b). After modification of PAI with M-LDH the surface morphology of the NCs is changed and the micrograph showed uniform distribution and excellent dispersion of M-LDH into the PAI matrix (Figures 9c-9f). These observations are perhaps a result of modification of LDH with diacid. TEM shows a real image of nanoclay platelets to allow identification of internal morphology and hybrid structure of NCs. In Figures 10a and 10b, TEM images of LDH-CO₃²⁻ showed and the synthesized LDH-CO₃²⁻ are smooth, well-shaped in a hexagonal form, crystalline and don't showed any aggregated platelets. After modification of LDH with L-aspartic containing diacid, the expected plate-like nature of the crystallites and hexagonal structure is clearly apparent and there are no signs of aggregation visible in the micrographs (Figures 10c and 10d). Figures 10e and 10f shows the TEM images of PAI/M-LDH NCs with 8 wt% of M-LDH. The TEM image showed that the LDHs are dispersed throughout the polymer matrix. The layers are well shown in this image and the thickness and lateral sizes of the LDH layers can be calculated as being about nanometric size.

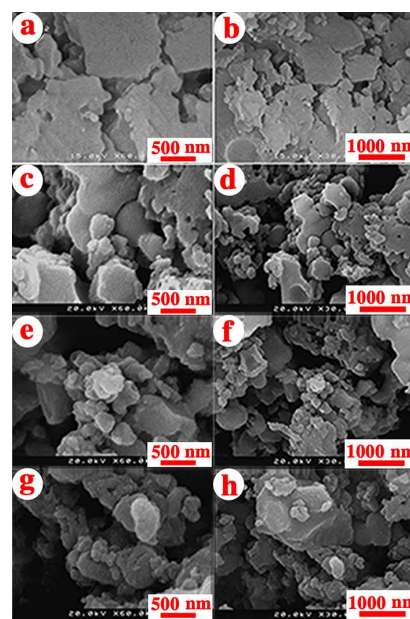


Figure 9. FE-SEM images of (a, b) PAI (c, d) PAI/M-LDH NC 2% (e, f) PAI/M-LDH NC 4% and (g, h) PAI/M-LDH NC 8%

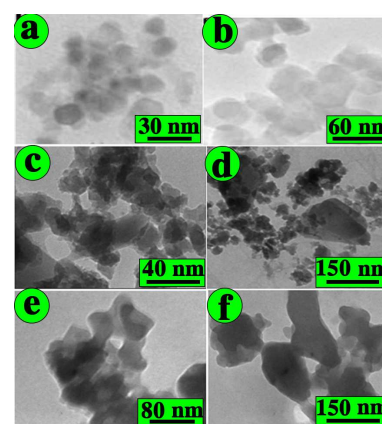


Fig. 10. TEM images of LDH-CO₃²⁻ (a, b), M-LDH (c, d) and PAI/M-LDH NC 8% (e, f)

4. Conclusions

LDH was modified with diacid containing TBPA and aspartic acid by co-precipitation method through applying the ultrasonic irradiation as green, easy and safety tool. The increase in basal spacing of M-LDH in comparison to the LDH, showed by XRD analyses, indicated an intercalation of bigger organic anions into the LDH interlayer space. Polycondensation reaction of chiral diacid with sulfonated diamine furnished a chiral PAI, due to L-phenylalanine amino acid in the polymer structure. LDH nanoclay modified with organic diacid as a bifunctional coupling agent was used to enhance the compatibility between PAI matrix and LDHs. The morphology and textural of NCs was study by FE-SEM and TEM techniques and the results showed well dispersed and formation of intercalated and or exfoliated modified LDH platelets in the PAI matrix. Thermal properties increase for NCs in the presence of M-LDH due to the hydrogen bonding between the M-LDH nanoclay and the PAI matrix.

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Notes and references

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