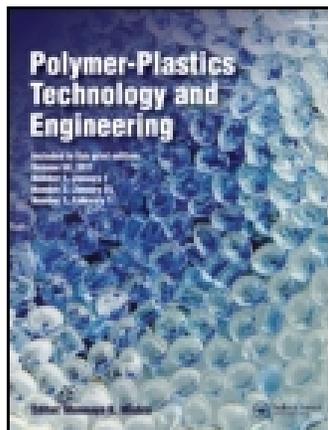


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Shadpour Mallakpour<sup>a b</sup> & Mohammad Dinari<sup>a b</sup>

<sup>a</sup> Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, Islamic Republic of Iran

<sup>b</sup> Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan, Islamic Republic of Iran

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# Structural Characterization and Thermal Properties of Chiral Poly(amide-imide)/Modified MgAl Layered Double Hydroxide Nanocomposites Prepared via Solution Intercalation

Shadpour Mallakpour<sup>1,2</sup> and Mohammad Dinari<sup>1,2</sup>

<sup>1</sup>Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, Islamic Republic of Iran

<sup>2</sup>Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan, Islamic Republic of Iran

Intercalated poly(amide-imide) (PAI)/modified layered double hydroxide (LDH) nanocomposites (NCs) were synthesized by the solution intercalation method. Modified LDH was synthesized from the co-precipitation reaction of the  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and *N,N'*-(pyromellitoyl)-bis-valine under ultrasound irradiation. An optically active amino acid containing PAI was synthesized by direct polymerization reaction of chiral diacid and 3,5-diamino-*N*-(thiazole-2-yl)benzamide under green condition. The synthesized materials were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA), field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) techniques. TEM and FE-SEM analysis confirmed that modified LDH was dispersed within the polymer matrix in intercalated and exfoliated forms.

**Keywords** Layered double hydroxides; Nanocomposite; Poly(amide-imide); (S)-Valine amino acid; X-ray diffraction

## INTRODUCTION

Inorganic/polymer nanocomposites (NCs) are a class of composites in which the inorganic phase dimensions are in the order of nanometers. These NCs contain only a few percent of well-dispersed inorganic components of nanometer size in an organic polymer, and exhibit better properties than pure polymers<sup>[1–6]</sup>. The most part of previous studies has been focused on NCs based on clay and layered silicates because the starting clay materials are easily available and their intercalation chemistry has been studied for a long time<sup>[7–11]</sup>.

Address correspondence to Shadpour Mallakpour, Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Islamic Republic of Iran. E-mail: mallak@cc.iut.ac.ir, mallak777@yahoo.com, mallakpour84@alumni.ufl.edu

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Recently, polymer/layered double hydroxide (LDH) NCs have been studied extensively for their remarkable improvement in the mechanical properties, thermal stability, reduced gas permeability, and flame retardancy compared with virgin polymers and traditional organic–inorganic composites<sup>[12–17]</sup>. This is mainly due to the effective dispersion of LDH layers of nanometer thickness with the aspect ratios of about 30–100 within the polymer matrix<sup>[18]</sup>.

The LDHs can be represented by the ideal formula  $[\text{M}_{1-x}^{2+} \text{M}_x^{3+}(\text{OH})_2][(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}]$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  represent di- and trivalent metal ions within the brucite-like layers respectively, and  $\text{A}^{n-}$  is an interlayer anion<sup>[19–22]</sup>. The use of LDH as nanofillers is met with some limitations. The high charge density of LDH layers and the high content of anionic species and water molecules result in strong interlayer electrostatic interactions between the sheets and pronounced hydrophilic properties. So, monomer or polymer cannot easily penetrate within LDH layers nor can LDH layers be easily homogeneously dispersed within hydrophobic polymer matrix.

To ease the intercalation of LDH within the polymer matrix and to achieve a good degree of dispersion, the interlayer space should be modified with suitable, usually organic, anions with intention of increasing both the interlayer distance and the hydrophobicity of LDH layers. The anions are typically intercalated into LDH interlayers by three experimental approaches. The first is the co-precipitation method, which requires the addition of an M2/M3 metal salt solution to a base solution of the desired anions<sup>[23–27]</sup>. The second is the direct ion exchange method, in which LDHs are stirred in a solution of desired anions of a suitable concentration<sup>[27–29]</sup>. The third is the rehydration method in which calcined LDH is added to solutions of desired anions<sup>[30–32]</sup>.

Poly(amide-imide)s (PAIs) are a class of high performance polymeric materials with good compromise between thermal stability and processability. They possess desirable characteristic for a variety of applications as they retain good mechanical properties at high temperature by comparable properties with aromatic polyamides and polyimides<sup>[33–37]</sup>. PAIs containing L-amino acid linkages can be a good qualification for these purposes because of their important properties such as thermo stable, mechanical strength, good chemical resistance, and high biodegradability. In addition presence of L-amino acids into PAIs backbones causes to have chiral property<sup>[38,39]</sup>. Recently molten tetrabutyl ammonium bromide (TBAB) was used as a green solvent for the preparation of PAIs<sup>[40]</sup>. Ionic liquids (ILs) are frequently considered as green solvents due to their small vapor pressure and other properties, such as excellent ability to dissolve organic compounds, salts and metals, facile recyclabilities non-flammability and high temperature stability<sup>[41–43]</sup>.

In this study, novel NCs of high performance PAI with thiazole side chain and different amount of modified LDH with chiral dicarboxylic acid (2, 4 and 8%) were synthesized for the first time. An optically active amino acid containing diacid was synthesized in high yield from the reaction of pyromellitic dianhydride with L-valine amino acid and then it was used for organo-modification of chiral LDH as well as for preparation of thermally stable PAI. Modified-LDH was synthesized by ultrasonic technique in a short time. High performance and optically active PAI was synthesized by the direct polymerization reaction of 3,5-diamino-*N*-(thiazole-2-yl)benzamide and amino acid containing diacid in green media by using TBAB as molten IL. Different NCs of PAI and modified-LDH were prepared through solution intercalation technique. The structure and morphology of the novel materials was confirmed via different techniques.

## EXPERIMENTAL

### Materials

All chemicals with analytical reagent were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck (Darmstadt, Germany). Aluminum nitrate nonahydrate [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ], magnesium nitrate hexahydrate [ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], pyromellitic dianhydride (PMDA), sodium hydroxide (NaOH), 2-aminothiazole, 3,5-dinitrobenzoylchloride, propylene oxide, acetone, hydrazine monohydrate,  $\text{FeCl}_3$ , L-valine amino acid, glacial acetic acid, TBAB and triphenyl phosphite (TPP) were used as received without further purification. *N,N*-Dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) as solvent were distilled over barium oxide under reduced pressure before use.

### Ultrasonic Assistance Synthesis of $\text{MgAl} - \text{CO}_3^{2-}$ and Chiral LDH-Diacid

The reaction was occurred on a MISONIX ultrasonic liquid processor, XL-2000 series with a wave of frequency  $2.25 \times 10^4$  Hz and power 100 W.

Synthesis of LDH –  $\text{CO}_3^{2-}$  was carried out via a similar procedure as our earlier report<sup>[44]</sup>. For chiral modified LDH; at first, *N,N*-(pyromellitoyl)-bis-L-valine diacid was synthesized according to our previous study<sup>[45]</sup>. Intercalation of dicarboxylate anions into LDH was carried out as follows; solution A was prepared by dissolving  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 50 mL of deionized water (Mg/Al molar ratio of 2:1) and solution B was prepared by dissolving NaOH (0.02 mol) and *N,N*-(pyromellitoyl)-bis-L-valine (0.02 mol) in 20 mL of deionized water. Then, solution A was dripped into solution B and stirred at R.T for 1 h. Then the pH of resulting suspension was adjusted to pH = 9.0 by adding 1 M NaOH solution. The mixed solution was covered with a stopper and transferred immediately into an ultrasound tool and was sonicated for 1 h. The obtained precipitate was filtered and washed by deionized water and then was dried at 60°C for 24 h.

### Synthesis of Diamine with Thiazole Side Group

3,5-Diamino-*N*-(thiazole-2-yl)benzamide was synthesized according to our previous study<sup>[46]</sup>.

### Synthesis of Optically Active and High Performance PAI

The PAI was prepared by the following general procedure: A mixture of chiral diacid *N,N*-(pyromellitoyl)-bis-L-valine (0.20 g,  $4.8 \times 10^{-4}$  mol), 3,5-diamino-*N*-(thiazole-2-yl)benzamide (0.10 g,  $4.8 \times 10^{-4}$  mol) and TBAB (0.58 g,  $1.8 \times 10^{-3}$  mol) was ground until a powder was formed. After the mixture was completely ground, it was transferred into a 25 mL, round-bottom flask and then 0.28 mL ( $8.9 \times 10^{-4}$  mol) of TPP was added to the mixture, which was heated until a homogeneous solution was formed. Then, the solution was stirred for 12 h at 120°C, and the viscous solution was precipitated in 10 mL of methanol. The white solid was filtered off and dried to give 0.26 g (89%) of PAI. The specific rotation and inherent viscosity of the synthesized PAI were  $[\alpha]_D^{25} = -26.16^\circ$  and 0.47 dL/g, respectively (measured at a concentration of 0.5 g dL<sup>-1</sup> in DMF at 25°C).

FT-IR (KBr, cm<sup>-1</sup>): 3,500 (m, br), 3105 (w), 2910 (w), 1780 (m), 1,723 (s), 1620 (m), 1522 (s), 1455 (s), 1382 (s), 1348 (s), 1317 (s), 980 (s), 965 (m), 804 (m), 756 (m), 720 (m), 680 (m), 550 (m). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): 1.03 (d, 12H, CH<sub>3</sub>, distorted), 2.80 (m, 2H, CH), 4.64-4.65 (d, 2H, CH, *J* = 3.6 Hz), 6.94 (s, 1H, Ar-H), 7.49 (s, 2H, Ar-H), 7.89-7.91 (d, 1H, Ar-H, *J* = 6.4 Hz), 8.09-8.11 (d, 1H, Ar-H, *J* = 8.4), 8.34 (s, 2H, Ar-H), 10.27 (s, 2H, NH), 12.67 (s, 1H, NH).

### Preparation of the PAI/Modified-LDH NCs

NC materials were prepared by mixing the appropriate amounts of the optically active PAI and chiral modified LDH in DMAc as a solvent in a flask for a particular concentration. NC were prepared by mixing different amounts of modified LDH (2, 4 and 8 wt.%) to the PAI solution. The solution was agitated to high speed stirring at 80°C for 2 h, at 60°C for 2 h and then at 40°C for 20 h for uniform dispersion of modified LDH in the PAI matrix. NC 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 under reduced pressure to a constant weight.

### Characterization Techniques

Fourier transformed infrared (FT-IR) spectra for pristine LDH and other samples were recorded for wave numbers 4000–400 cm<sup>-1</sup> using a Jasco-680 FT-IR spectrometer (Japan). The powdered samples were mixed with KBr and pressed in the form of pellets for the measurement. Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).

Specific rotation was measured with a Jasco (Osaka, Japan) P-1030 polarimeter at the concentration of 0.5 g dL<sup>-1</sup> at 25°C. The inherent viscosities of the polymer was determined with a Cannon-Fenske Routine Viscometer (Germany).

X-ray diffraction analysis (XRD) over  $2\theta = 1.8$  to  $70^\circ$ , in steps of  $0.02^\circ$  was carried out using a X-ray diffractometer (Bruker, D8 Avance, Germany) with Cu-K $\alpha$  radiation ( $\lambda = 0.154$  nm, monochromatization by primary graphite crystal) generated at 100 mA and 45 kV. XRD curves were interpreted with respect to the position of the basal reflection (003), which depends on the distance between two adjacent metal hydroxide sheets in the LDH lattice. The  $d$ -spacing of the sample was analyzed by using Bragg's equation ( $n\lambda = 2d \sin \theta$ ), where  $n$  is an integer,  $\lambda$  is the wavelength,  $\theta$  is the glancing angle of incidence, and  $d$  is the interplanar spacing of the crystal.

Thermogravimetric analysis (TGA) data for samples were taken on a STA503 TA instrument (USA) in a nitrogen atmosphere at a rate of 10°C/min from ambient temperature to 800°C at nitrogen atmosphere.

The morphology of the LDH and NCs was examined by field emission scanning electron microscopy [FE-SEM, (HITACHI, S-4160, Japan)]. The powdered sample was dispersed in H<sub>2</sub>O, and then the sediment was dried at room temperature before gold coating.

The dispersion of the nanoclay within the medium has been controlled by transmission electron microscopy [TEM, (Philips, CM120, Netherlands)] using an accelerator voltage of 100 kV. For TEM sample preparation, NC was suspended in water and a small drop of it was deposited

and dried on a carbon coated copper grid. The inorganic components appear black/grey colored on the micrographs.

## RESULTS AND DISCUSSION

### Synthesis of Modified-LDH and Preparation of PAI/Modified-LDH NCs

In recent years, polymer/LDH NCs have attracted considerable interest in the field of material chemistry. However, LDH layers possess a high charge density ( $\sim 300$  mequiv/100 g) thus strong interlayer electrostatic interaction makes the exfoliation of LDH much more unfavorable. In addition, pristine LDH is not suitable for the penetration of giant polymer chains or chain segments into their gallery space unless its interlayer distance is significantly increased. Accordingly, the intercalation of LDH involves organic modification of LDH to expand the basal spacing and/or ionogenic modification of the polymer to graft anions onto the polymers or monomers. In this study an optically active diacid was synthesized from the reaction of PMDA and valine amino acid (Scheme 1).

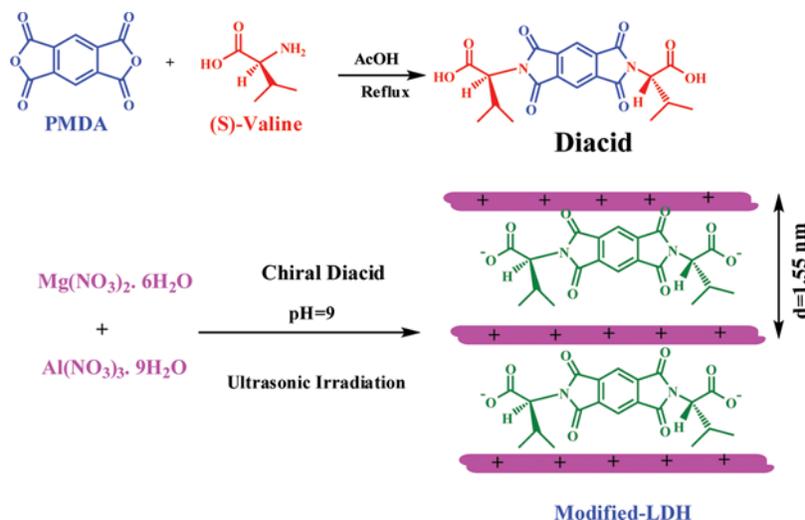
This compound exhibited specific rotations ( $[\alpha]_D^{25} = -67.2^\circ$ ; measured at a concentration of 0.5 g/dL in DMF at 25°C). It was used for preparation of novel modified-LDH via one pot co-precipitation reaction using ultrasonic wave for the first time. The obtained modified-LDH is organophilic and the interlayer space of this compound is increased (Scheme 1). These phenomena causes enlarge in the  $d$ -spacing which facilitates the entry of the host polymer molecules between the layered of modified LDH for further applications of this compound in the synthesis of LDH/polymer NCs.

Molten TBAB was used as solvent for the production of the organo-soluble and thermally stable PAI by the direct polymerization reaction of diacid and diamine with thiazole side chain (Scheme 2). The chiral polymer was synthesized under conventional heating in the presence of TBAB and TPP, and it took 12 h at 120°C for the completion of the reaction and the inherent viscosity of this PAI was 0.47 dL/g. The incorporation of a chiral unit into the polymer backbone was obtained by measuring the specific rotations of  $[\alpha]_D^{25} = -26.16$  (0.05 g in 10 mL of DMF). Chemical structure and purity of this polymer was confirmed in our previous study<sup>[46]</sup>.

### Characterization

#### FT-IR Study

The LDH-CO<sub>3</sub> and diacid modified-LDH were confirmed by examination of the FT-IR spectra shown in Figure 1. The spectra of both materials show very broad bands centered at above 3500 cm<sup>-1</sup>, relating to the  $\nu(\text{OH})$  stretching vibration of hydroxyl groups of the host layers and to the interlayer and physically absorbed water molecules<sup>[47]</sup>. For LDH-CO<sub>3</sub><sup>2-</sup>, free CO<sub>3</sub><sup>2-</sup> anions that



SCH. 1. Synthesis of bioactive diacid and preparation of chiral MLDH.

there are in solution show three different FT-IR vibration modes: at  $880\text{ cm}^{-1}$  (bending non-planar mode),  $1415\text{ cm}^{-1}$  (the asymmetric stretching mode) and  $680\text{ cm}^{-1}$  (the bending angular mode). The bending vibration of the interlayer  $H_2O$  is also reflected in the broad bands around  $1590\text{ cm}^{-1}$  and bands due to  $MgAl-OH$  translation modes are recorded below  $600\text{ cm}^{-1}$  (Fig. 1)<sup>[47]</sup>.

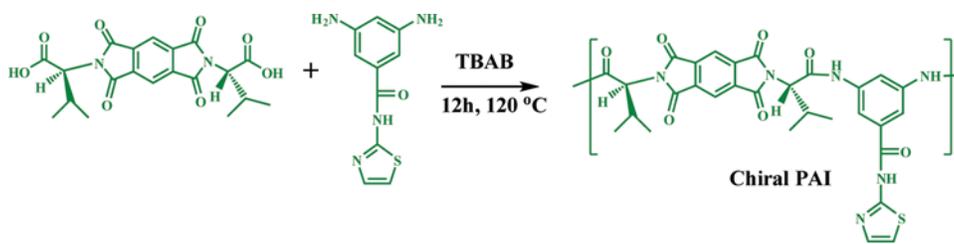
The FT-IR spectra of modified-LDH show two types of bands: one corresponding to the anionic species intercalated and other corresponding to the host LDH materials (Fig. 1). The absorption bands at  $2930\text{--}3100\text{ cm}^{-1}$  correspond to the  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  (C-H) modes of  $CH_2$  group in the chiral dicarboxylate molecules. The other dicarboxylate bands originated from various functional groups are also found at  $1740\text{--}1700\text{ cm}^{-1}$  (C=O),  $1300\text{--}1000\text{ cm}^{-1}$  (C-O), and  $1600\text{--}1475\text{ cm}^{-1}$  (conjugate C=C). This result indicates the presence of the diacid in the interlayer space of LDH.

Figure 2 shows the FT-IR spectra of the neat PAI and NC of the PAI with 2, 4, and 8% of modified-LDH. The FT-IR spectra of pure PAI showed absorptions around  $3360\text{ cm}^{-1}$  (N-H),  $3100\text{ cm}^{-1}$  (aromatic C-H stretching),  $2930\text{ cm}^{-1}$  and  $2857\text{ cm}^{-1}$  ( $CH_2$  stretching) and two overlapped carbonyl (amide and imide's C=O) absorptions at  $1776$ ,  $1725$ , and  $1663\text{ cm}^{-1}$ , respectively. Absorption at

$1380$  and  $727\text{ cm}^{-1}$  showed the presence of the imide heterocycle in this polymer. Compared with pure PAI, a new broad absorption band below  $600\text{ cm}^{-1}$  can be found in the FT-IR spectra of PAI/modified-LDH NCs, which increases with increasing modified-LDH contents and can be ascribed to the vibration of M-O-M groups. From these figures, it can be concluded that the resulting NC materials not only have characteristic neat PAI bands, but also have characteristic peaks for modified-LDH (Fig. 2).

#### X-Ray Diffraction

The powder XRD patterns for the materials prepared are in Figure 3. For  $LDH-CO_3^{2-}$ , a serial of sharp peaks are observed. The gallery spacing between LDH platelets related to the peak of (003) plane (characteristic peak at  $2\theta = 11.84$ ) is calculated as around  $0.79\text{ nm}$  by Bragg equation. Other peaks at relatively high  $2\theta$  value are indexed to non-basal (006), (009), (110), and (113) reflections<sup>[48]</sup>. As expected, the position of the basal reflections of modified sample is shifted to higher  $d$  value indicating the expansion in the interlayer distance (Fig. 3). The modified sample does not show a distinct reflection at  $d = 0.76\text{ nm}$ . The XRD patterns of the modified LDH showed the expanding LDH structure with a sharp (003) spacing of  $1.55\text{ nm}$  in



SCH. 2. Preparation of chiral PAI with thiazole pendant group.

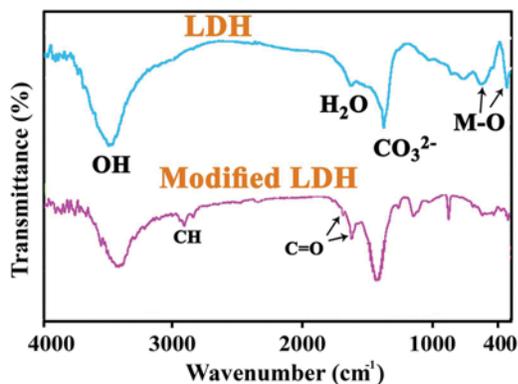


FIG. 1. FT-IR spectra of the LDH and modified-LDH.

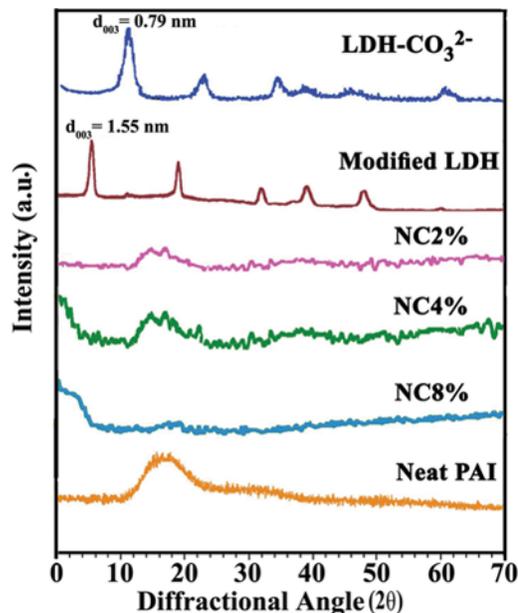


FIG. 3. XRD patterns of the different samples.

Figure 4. This value indicates that an expansion of the inter-layer spacing, compared to the LDH-CO<sub>3</sub> ( $d_{003} = 0.79$  nm) may be caused by the chiral diacid intercalation into LDH by co-precipitation method.

The XRD patterns of pure PAI and NCs o PAI with modified-LDH (2, 4 and 8%) are shown in Figure 3. In the XRD pattern of the neat PAI, no sharp diffraction peaks was observed and this indicated that this polymer is amorphous. For NCs, the disappearance of the diffraction peaks corresponding to the LDH was observed. The disappearance of LDH peaks in the NCs may be as a result of the partial exfoliated structure, in which the gallery height of intercalated layers is large enough and the layer correlation is not detected by XRD (Fig. 3). Although XRD provides a partial picture about distribution of nanofiller and disappearance of the peak corresponding to  $d$ -spacings does not always confirm the exfoliated NCs, a complete characterization of NC morphology requires microscopic investigation.

*FE-SEM*

The FE-SEM micrograph of LDH-CO<sub>3</sub> and modified-LDH are shown in Figure 4. The FE-SEM image of pure LDH reveals the nature of LDH particles, which roughly consists of plate-like shape stacked on top of each other (Figs. 4a and 4b). The FE-SEM images of the modified-LDH are similar to the unmodified LDH and the particle sizes of the nanolayers are between 20–50 nm (Figs. 4c and 4d).

The surface morphology of the PAI/modified-LDH NCs was also investigated by FE-SEM technique as shown

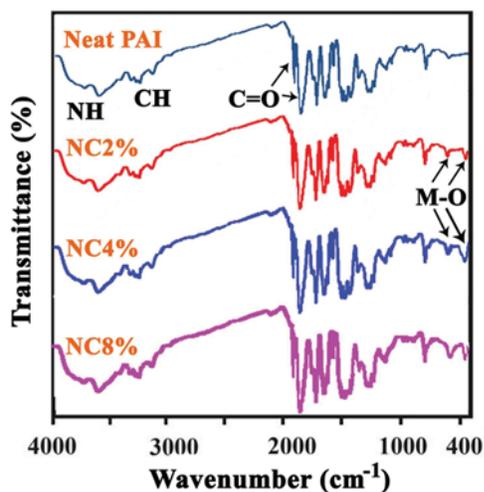


FIG. 2. FT-IR spectra of the neat PAI and different NCs.

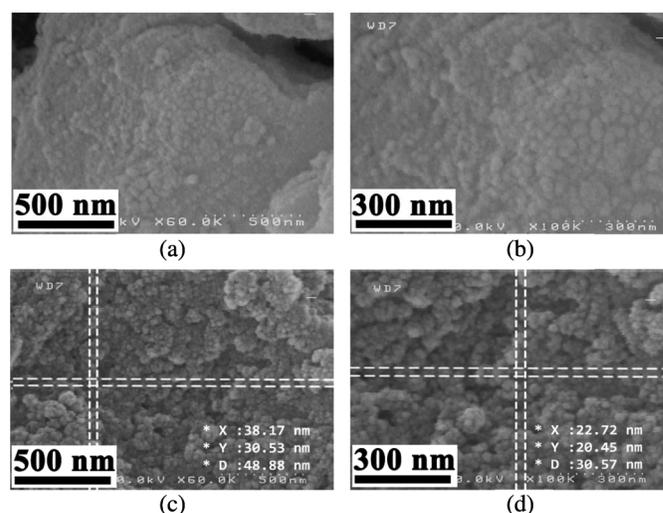


FIG. 4. FE-SEM photographs of neat LDH (a, b) and modified LDH (c, d).

in Figure 5. According to these images, in NC4%, the LDH nanosheets have a better dispersion in comparison with NC with high amount of modified-LDH (8%).

### TEM

The most direct measure of the dispersion of these Mg/Al nanolayers in PAI matrix is typically TEM micrographs of the PAI/modified LDH NCs. Typical TEM images of modified-LDH and NC of PAI and 4wt% of modified-LDH are shown in Figures 6a–6d. In the TEM micrograph of the modified-LDH, the platelets have a hexagonal shape with rounded corners. There are no signs of aggregation visible in the micrographs (Figs. 6a and 6b). TEM images of the NC4% show that the modified-LDHs were dispersed in the polymer matrix by intercalated and exfoliated states (Figs. 6c and 6d). These results of TEM are consistent with the XRD.

### Thermal Degradation Characteristics

The thermal behavior of the LDH-CO<sub>3</sub> and modified-LDH was examined by TGA technique and the curves are shown in Figure 7. For the LDH-CO<sub>3</sub> the TGA curve shows three weight loss steps which relate to the desorption of absorbed water at around 104°C, the dehydroxylation of the brucite-like layer at around 230°C as well as the decomposition of carbonate ions at around 350–400°C (Fig. 7). The organic modification of the LDH changes its the thermal decomposition behavior in comparison to the unmodified sample<sup>[29,44]</sup>.

As can be seen in Figure 7, the numbers of decomposition stages have increased for modified-LDH. Also degradation of interlayer diacid anion took place before de-hydroxylation process in the case of modified LDHs and so showed less thermal stability than the original

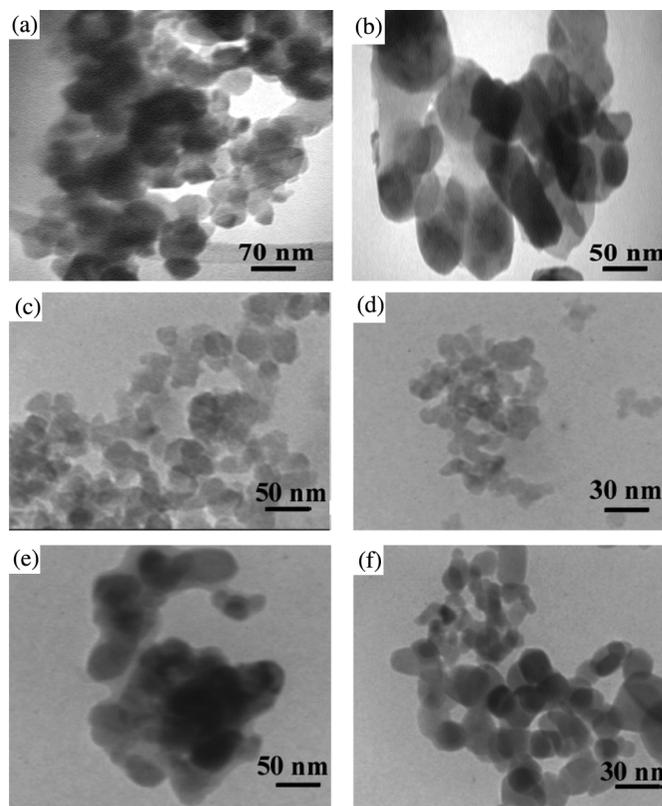


FIG. 6. TEM micrographs of modified LDH (a and b) and NC4% (c and d).

LDH. The presence of a larger weight loss step within 370–560°C for LDH-dicarboxylate anions compared to the LDH confirmed the presence of interlayer surfactant anions in LDH.

The thermo-stability of the pure amino acid containing PAI and the NCs of PAI and different amount of modified-LDH (2, 4, and 8%) were evaluated by TGA under nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>, and

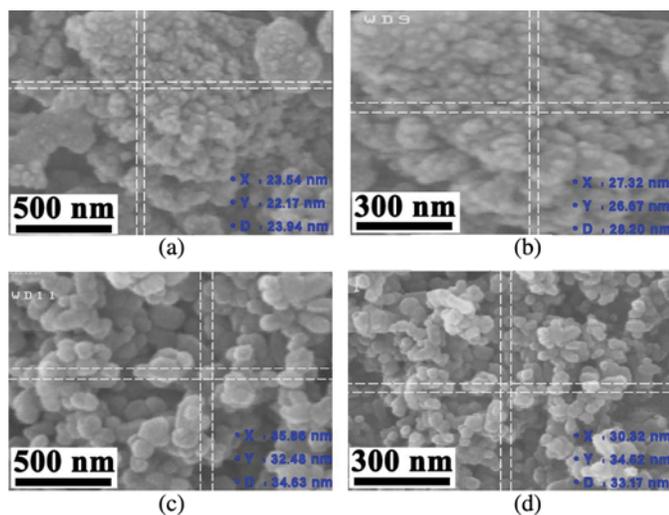


FIG. 5. FE-SEM photographs of NC4% (a, b), and NC8% (c, d).

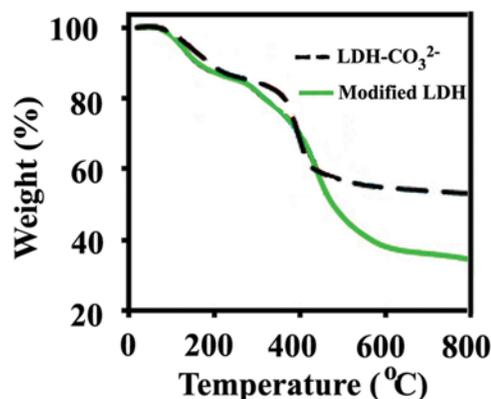


FIG. 7. TGA thermograms of LDH and modified LDH with chiral dicarboxylate.

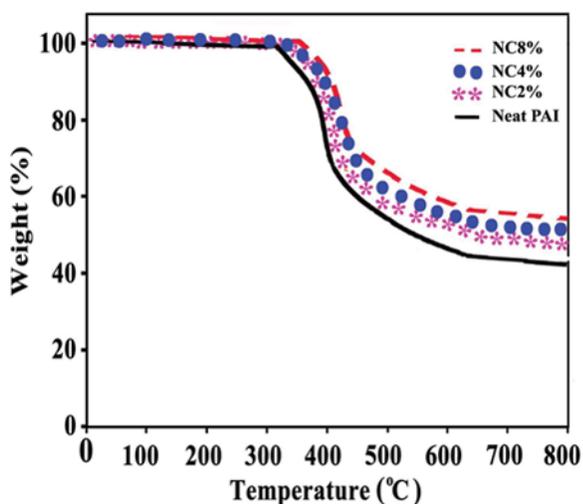


FIG. 8. TGA thermograms of PAI and different PAI/modified-LDH NCs.

the corresponding weight loss temperatures of 5% and 10% ( $T_{5\%}$  and  $T_{10\%}$ ) were all determined from original TGA curves. Typical TGA curves of representative samples are shown in Figure 8. In addition, the results obtained from these analyses are completely tabulated in Table 1. Single-step degradation was observed in all samples.

The onset of decomposition temperature of the NCs was higher than that of pure PAI, shifting toward higher temperatures as the amount of modified-LDH was increased. The marginal increase in thermal stability of PAI matrix upon incorporation of modified-LDH could be attributed to the higher thermal conductivity of modified-LDH that facilitated heat dissipation within the composites, hence preventing the accumulation of heat at certain points for degradation. The end temperature of decomposition was also retarded with increasing modified-LDH content.

The masses remaining at 800°C were almost entirely due to the remaining modified-LDH, consistent with initial

TABLE 1  
Thermal properties of the PAI and different BNCs

Sample	Decomposition temperature (°C)		Char yield (%) <sup>b</sup>
	$T_{5\%}^a$	$T_{10\%}^a$	
PAI	346	374	43
NC2%	358	388	47
NC4%	361	397	50
NC8%	365	406	53

<sup>a</sup>Temperature at which 5 and 10% weight loss was recorded by TGA at heating rate of 10°C min<sup>-1</sup> in a N<sub>2</sub> atmosphere.

<sup>b</sup>Weight percent of the material left undecomposed after TGA at maximum temperature 800°C in a N<sub>2</sub> atmosphere.

modified-LDH loading. The weight percent remaining after major degradation at 800°C was higher for composites rather than neat PAI. This indicated that modified-LDH reduced the degradation of PAI at high temperature as the effect was clearly seen in the curves. Therefore, it could be demonstrated that a small amount of modified-LDH acted as effective thermal degradation resistant reinforcement in the PAI matrix, increasing the thermal stability of the PAI/ modified-LDH NCs [29].

## CONCLUSIONS

The very exciting recent progress in intercalation reactions of LDHs shows that this area of existing solid state chemistry has a very promising future. Especially, the continuing work on the intercalation of biologically active guests has great potential. In the work, a new organic-inorganic hybrid material has been prepared in a simple, low cost, efficient, and environmentally-friendly method by one-pot co-precipitation reaction of the Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and bioactive *N,N'*-(pyromellitoyl)-bis-L-valine under ultrasonic irradiation in aqueous media.

The modified Mg-Al LDH shows an increase in inter-layer distance as compared to the unmodified LDH by XRD. Chiral amino acid containing high performance PAI with thiazole side chain was prepared in molten TBAB as a green solvent. Then different NCs of PAI and modified-LDH were prepared by a solution-intercalation method. XRD and FT-IR results pointed to the incorporation of the modified-LDH within the PAI matrix. FE-SEM and TEM analysis demonstrate that the exfoliated and partially exfoliated NCs are formed. Thermal stability of the PAI/ modified-LDH NCs is increased by about 4–10°C compared with neat PAI.

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## REFERENCES

- Okada, A.; Usuki, A. The chemistry of polymer-clay hybrids. *Mater. Sci. Eng. C* **1995**, *3*, 109–115.
- Kickelbick, G. Concepts for the incorporation of inorganic building blocks into organic polymers on a nano scale. *Prog. Polym. Sci.* **2003**, *2*, 2883–2885.
- Dou, Y.; Lin, K.; Chang, J. Polymer nanocomposites with controllable distribution and arrangement of inorganic nanocomponents. *Nanoscale* **2011**, *3*, 1508–1511.
- Naffakh, M.; Diez-Pascual, A.M.; Marco, C.; Ellis, G.J.; Gómez-Fatou, M.A. Opportunities and challenges in the use of inorganic

- fullerene-like nanoparticles to produce advanced polymer nanocomposites. *Prog. Polym. Sci.* **2013**, *38*, 1163–1231.
5. Mallakpour, S.; Dinari, M. Novel nanocomposites based on reactive organoclay of L-tyrosine and amine end-capped poly(amide-imide): Synthesis and characterization. *Appl. Clay Sci.* **2013**, *75–76*, 67–73.
  6. Das, T.K.; Prusty, S. Graphene-based polymer composites and their applications. *Polym. Plast. Technol. Eng.* **2012**, *51*, 319–331.
  7. Harrats, C.; Groeninckx, G. Features, questions and future challenges in layered silicates clay nanocomposites with semicrystalline polymer matrices. *Macromol. Rapid Comm.* **2008**, *29*, 14–26.
  8. Esteki, B.; Garmabi, H.; Saeb, M.R.; Hoffmann, T. The crystallinity behavior of polyethylene/clay nanocomposites under the influence of water-assisted melt blending. *Polym. Plast. Technol. Eng.* **2013**, *52*, 1626–1636.
  9. Kiliaris, P.; Papaspyrides, C.D. Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. *Prog. Polym. Sci.* **2010**, *35*, 902–958.
  10. Mohd, F.A.R.; Hazizan, M.A.; Sharif, J.M. Influence of organo-clay on mechanical and thermal properties of OMuscovite/PP layered silicate nanocomposite. *Adv. Mater. Res.* **2012**, *364*, 174–180.
  11. Zubitur, M.; Mugica, A.; Areizaga, J.; Cortázar, M. Morphology and thermal properties relationship in poly(p-dioxanone)/layered double hydroxides nanocomposites. *Coll. Polym. Sci.* **2010**, *288*, 809–818.
  12. Leroux, F.; Besse, J.P. Layered double hydroxide/polymer nanocomposites. *Interf. Sci. Technol.* **2004**, *1*, 459–495.
  13. Yang, J.; Chen, F.; Ye, Y.; Fei, Z.; Zhong, M. Preparation and characterization of polystyrene (PS)/layered double hydroxides (LDHs) composite by a heterocoagulation method. *Coll. Polym. Sci.* **2010**, *288*, 809–818.
  14. Qiu, L.; Qu, B. Polymer-layered double hydroxide nanocomposites by emulsion and suspension polymerization. *RSC Nanosci. Nanotechnol.* **2010**, *2010*, 32–63.
  15. Feng, Y.; Tang, P.; Xi, J.; Jiang, Y.; Li, D. Layered double hydroxides as flame retardant and thermal stabilizer for polymers. *Recent Patents Nanotechnol.* **2012**, *6*, 231–237.
  16. Gaume, J.; Therias, S.; Leroux, F.; Rivaton, A.; Gardette, J.L. Exfoliated polymer nanocomposites by in situ coprecipitation of layered double hydroxides in a polymer matrix. *J. Appl. Polym. Sci.* **2013**, *123*, 1345–1349.
  17. Kuila, T.; Srivastava, S.K.; Bhowmick, A.K. Rubber/LDH nanocomposites by solution blending. *J. Appl. Polym. Sci.* **2009**, *111*, 635–641.
  18. Forano, C.; Hibino, T.; Leroux, F.; Taviot-Guého, C. Layered Double Hydroxides. In: Bergaya, F.; Theng, B.K.G.; Lagaly, G., eds. *Developments in Clay Science*, Vol. 1, Elsevier: Amsterdam, The Netherlands, Chapter 13.1, pp. 1021–1095, 2006.
  19. Kakati, K.; Pugazhenth, G.; Iyer, P.K. Effect of organomodified Ni-Al layered double hydroxide (OLDH) on the properties of polypropylene (PP)/LDH nanocomposites. *Int. J. Polym. Mater. Polym. Biomater.* **2012**, *61*, 931–948.
  20. Jiao, F.P.; Chen, X.Q.; Fu, Z.D.; Hu, Y.H.; Wang, Y.H. Intercalation of Mg–Al layered double hydroxides by (+)-dibenzoyl-D-tartaric acid: Preparation and characterization. *J. Mol. Struct.* **2009**, *921*, 328–332.
  21. Wang, Q.; Ohare, D. Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. *Chem. Rev.* **2012**, *112*, 4124–4155.
  22. Zumreoglu-Karan, B.; Ay, A.N. Layered double hydroxides—Multifunctional nanomaterials. *Chem. Papers* **2012**, *66*, 1–10.
  23. Mahkam, M.; Davatgar, M.; Rezvani, Z.; Nejati, K. Preparation of pH-sensitive polymers/layered double hydroxide hybrid beads for controlled release of insulin. *Int. J. Polym. Mater. Polym. Biomater.* **2013**, *62*, 57–60.
  24. Hibino, T. Delamination of layered double hydroxide containing amino acids. *Chem. Mater.* **2004**, *16*, 5482–5488.
  25. Kameda, T.; Takeuchi, H.; Yoshioka, T. Hybrid inorganic/organic composites of Mg–Al layered double hydroxides intercalated with citrate, malate, and tartrate prepared by co-precipitation. *Mater. Res. Bull.* **2009**, *44*, 840–845.
  26. Shen, Y.; Liu, D.; Fan, L.; Li, S.; Gao, L. Simultaneous incorporation of palladium and zirconium ions in Mg–Al layered double hydroxides by co-precipitation. *Appl. Clay Sci.* **2011**, *54*, 179–183.
  27. Lee, J.; Rhee, S.; Jung, D.Y. Orientation-controlled assembly and solvothermal ion-exchange of layered double hydroxide nanocrystals. *Chem. Comm.* **2003**, *9*, 2740–2741.
  28. Aisawa, S.; Ohnuma, Y.; Hirose, K.; Takahashi, S.; Hirahara, H.; Narita, E. Intercalation of nucleotides into layered double hydroxides by ion-exchange reaction. *Appl. Clay Sci.* **2005**, *28*, 137–145.
  29. Mallakpour, S.; Dinari, M. Facile synthesis of nanocomposite materials by intercalating an optically active poly(amide-imide) enclosing (L)-isoleucine moieties and azobenzene side groups into a chiral layered double hydroxide. *Polymer* **2013**, *54*, 2907–2916.
  30. Sasaki, S.; Yokohama, Y.; Aisawa, S.; Hirahara, H.; Narita, E. Intercalation of natural cyclodextrins into layered double hydroxide by calcination-rehydration reaction. *Chem. Lett.* **2005**, *34*, 1192–1193.
  31. Pfeiffer, H.; Lima, E.; Lara, V.; Valente, J.S. Thermokinetic study of the rehydration process of a calcined MgAl-layered double hydroxide. *Langmuir* **2010**, *26*, 4074–4079.
  32. Pfeiffer, H.; Martínez-Delacruz, L.; Lima, E.; Flores, J.; Vera, M.A.; Valente, J.S. Influence of Mg/Al ratio on the thermokinetic rehydration of calcined Mg–Al layered double hydroxides. *J. Phy. Chem. C* **2010**, *114*, 8485–8492.
  33. Liaw, D.; Liaw, B. Synthesis and characterization of new polyamide-imides containing pendent adamantyl groups. *Polymer* **2001**, *42*, 839–845.
  34. Thiruvasagam, P.; Venkatesan, D. Synthesis of diimide-diacid monomers and poly(amideimide)s: Effects of flexible linkages and pendant hexafluoroisopropylidene unit on processability, thermal stability and electrical properties. *Polym. Plast. Technol. Eng.* **2012**, *51*, 1133–1140.
  35. Shockravi, A.; Abouzari-Lotf, E.; Javadi, A.; Atabaki, F. Preparation and properties of new ortho-linked polyamide-imides bearing ether, sulfur, and trifluoromethyl linkages. *Eur. Polym. J.* **2009**, *45*, 1599–1606.
  36. Mallakpour, S.; Dinari, M. Chiral poly(amide-imide)/organoclay nanocomposites derived from pyromellitoyl-bis-L-isoleucine and benzimidazole containing diamine: Synthesis, nanostructure, and properties. *Coll. Polym. Sci.* **2012**, *290*, 81–90.
  37. Diahm, S.; Locatelli, M. Dielectric properties of polyamide-imide. *J. Phy. D.* **2013**, *46*, 1–8.
  38. Mallakpour, S.; Asadi, P.; Sabzalian, M.R. Synthesis of biodegradable chiral poly(ester-imide)s derived from valine-, leucine and tyrosine-containing monomers. *Amino Acids* **2011**, *41*, 1215–1222.
  39. Mallakpour, S.; Dinari, M. Novel nanostructure amino acid-based poly(amide-imide)s enclosing benzimidazole pendant group in green medium: Fabrication and characterization. *Amino Acids* **2012**, *43*, 1605–1613.
  40. Mallakpour, S.; Barati, A. Optically active poly(amide-imide)/TiO<sub>2</sub> bionanocomposites containing L-isoleucine amino acid moieties: Synthesis, nanostructure and properties. *Polym. Plast. Technol. Eng.* **2013**, *52*, 997–1006.
  41. Lu, J.; Yan, F.; Texter, J. Advanced applications of ionic liquids in polymer science. *Prog. Polym. Sci.* **2009**, *34*, 431–448.
  42. Mallakpour, S.; Dinari, M. Ionic Liquids as Green Solvents: Progress and Prospects. In: Mohammad, A.; Inamuddin, A., eds. *Green Solvents II: Properties and Applications of Ionic Liquids*, Springer: The Netherlands, pp. 1–32, 2012.
  43. Smith, T.W.; Zhao, M.; Yang, F.; Smith, D.; Cebe, P. Imidazole polymers derived from ionic liquid 4-vinylimidazolium monomers:

- Their synthesis and thermal and dielectric properties. *Macromolecules* **2013**, *46*, 1133–1143.
44. Mallakpour, S.; Dinari, M.; Behronvand, V. Ultrasonic-assisted synthesis and characterization of layered double hydroxides intercalated with bioactive N,N-(pyromellitoyl)-bis-L-a-amino acids. *RSC Adv.* **2013**, *3*, 23303–23308.
45. Mallakpour, S.; Dinari, M. Progress in synthetic polymers based on natural amino acids. *J. Macromol. Sci. Pt. A* **2011**, *48*, 644–679.
46. Mallakpour, S.; Ahmadizadegan, H. Poly(amide-imide)s obtained from 3,5-diamino-N-(thiazol-2-yl)-benzamide and dicarboxylic acids containing various amino acid units: Production, characterization and morphological investigation. *High Perform. Polym.* **2013**, *25*, 156–164.
47. Kloprogge, J.T.; Frost, R.L. Fourier transform infrared and Raman spectroscopic study of the local structure of Mg-, Ni-, and Co-hydroxalclites. *J. Solid State Chem.* **1999**, *146*, 506–515.
48. Zhang, F.H.; Sun, M.; Xu, S.L.L.; Zhao, L.L.; Zhang, B.W. Fabrication of oriented layered double hydroxide films by spin coating and their use in corrosion protection. *Chem. Eng. J.* **2008**, *141*, 362–367.