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PREPARATION AND CHARACTERIZATION OF MAGNESIUM/ALUMINIUM LAYERED DOUBLE HYDROXIDE AS FILLER IN LOW-DENSITY POLYETHYLENE COMPOSITE

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Abstract: Polymer had been widely used in industries nowadays. However, the properties of the polymer itself are limited to a particular application. This study describes synthetic clay, layered double hydroxide (LDH), as a filler in low-density polyethylene (LDPE) composite. LDHs of magnesium/aluminium-dodecyl sulfate (Mg/Al-DS) and its grafted with triethoxymethylsilane (TEMS), (TEMS-g-Mg/Al-DS) were synthesized through co-precipitation and salinization reaction methods. The presence of alkyl group, v(C-H) in both LDH had confirmed through Fourier transform infrared (FTIR). The appearance of peaks in FTIR spectra within the absorbance range of 2800 – 2930 cm^{-1} indicates a successful surface modification of LDH, supported by the changes of interlayer spacing and the presence of carbon from X-ray diffractogram and CHNS elemental analysis, respectively. The synthesized LDH was mixed with LDPE via melt intercalation method. The LDH modification resulted in higher interaction and compatibility between the LDPE matrix and LDH by the formation exfoliated type of nanocomposites, as suggested by XRD analysis.

Keywords: Layered double hydroxide, co-precipitation method, triethoxymethylsilane; nanocomposites, salinization.

Introduction

Polymers are broadly used materials that can be found most in our daily life, and it is essential because of their various applications in science, technology, and industries (Namazi, 2017). A specific polymer property for new applications is more easily produced by compounding commercially available polymer rather than synthesizing a new polymer. A study on reinforcing filler such as clay has attracted scientists worldwide to tailor the properties of polymer for a specific application.

Layered double hydroxide (LDH) is a synthetic clay that can be an alternative to natural clay such as montmorillonite (MMT) as filler in polymer nanocomposites. MMT, which is known as 2:1 types of clay minerals commonly utilized by polymer technologists to improve the properties of a polymer. However, MMT's chemical compositions differ depending on the location it is obtained, which may affect the final properties of polymer composites. LDH advantages such as manageable chemical composition and charged layers and ion exchange capacity can improve with surfactants to be compatibilized with organic polymer (Eili *et al.,* 2012). With latest understanding of the fundamental about LDH, this layered material, which commonly consists of approximately 10um-size multilayer stack (Gianellis, 1996), can be separated into individual nano-layer, hence increasing the surface area for interaction with polymer matrixes. The introduction of nanoparticle in polymer composites increased in terms of optical (Loste *et al.,* 2019), thermal (Kurt and Koca, 2015), mechanical (Bek & Jeon, 2010) and permeability (Ramesh and Punithamoorthy, 2019) properties that must give a variety of applications in many fields.

However, LDH is hydrophilic and not compatible with an organic polymer resulted in the phase-separated and agglomeration of clay platelets or known as conventional polymer-clay composites. By introducing a functionalized organic surface modification via physical and chemical reaction onto LDH, the compatibility between the polymer and LDH can be improved

(Zhang *et al.,* 2016). The compatibility between polymer and LDH resulted in LDH-functionalized layer stacks separated and distributed into individual layer throughout the organic polymer matrix.

Previous literature shows that a small organoclay loading (1–5 %wt) in polymers provides substantial benefits in composites' properties. The tensile, flexural, and thermal properties are improved by 30–40 % with the presence of organoclay in the composite compared to the pristine polymer (Shunmugasamy *et al*., 2015). However, at higher organoclay loading can lead to a reversal of the trends and reduce the mechanical properties of nanocomposites due to entrapment of air porosity and agglomeration of the clay (Bee *et al.,* 2017).

In this work, we study the compatibility of Mg/Al layered double hydroxide with LDPE by benchmarking the types of composites obtained when introducing LDH into the LDPE matrix.

Materials and Methods

Materials

Metal salts, magnesium nitrate hexahydrate, $Mg(NO_3)_2.6H_2O$ and aluminium nitrate nonahydrate $Al(NO_3)_3.9H_2O$, and chemicals, sodium dodecyl sulfate (SDS), low-density polyethylene, and sodium hydroxide purchased from Sigma-Aldrich (M) Sdn. Bhd. Moreover, distilled water utilized throughout the experiments. All LDHs prepared via a co-precipitation method.

Synthesis of Mg/Al –Dodecylsulphate LDH

Mother liquor solution was prepared by mixing, magnesium nitrate hexahydrate and aluminium nitrate nonahydrate with a metal molar ratio of 3:1 in 90 mL distilled water. 50 mL 0.50 M sodium dodecyl sulphate solution then added to the mother liquor solution. 2.0M sodium hydroxide solution added dropwise until pH 10 obtained. The mixture was aged at 80˚C in an oil bath for 12 hours and afterwards, the resultant slurry was filtered, washed with distilled water, and dried in an oven. This mono functionalized LDH was labelled as Mg/Al-DS LDH.

Grafting triethoxymethylsilane (TEMS) onto Mg/Al-DS LDH

Salinization of LDH conducted using TEMS via a sialylation reaction with the hydroxyl group in LDH. A similar procedure was adopted to synthesize Mg/Al –DS LDH with the addition of 50 mL TEMS solution into the mother liquor before titration with sodium hydroxide. This twice-functionalized LDH was labelled as TEMS-g-Mg/Al-DS LDH.

Preparation of LDPE/LDH nanocomposites

Low-density polyethylene (LDPE) composites with various LDH loads (1-5wt%) were prepared via melt intercalation using a Haake internal mixer, at 180°C, screw speed of 60 rpm with residence time of 10 minutes.

Materials Characterization

The orientation of the LDH layer in composites based on diffraction of d003 plane using X-ray diffractometer, Rigaku Mini Flex II using CuKa radiation at wavelength 0.154 nm. The scanning rate used in this study was 2° min^{-1}. The interactions of the clay minerals with inorganic or organic compounds were determined using Perkin Elmer spectrum 100 within the wavelength range 400-4000 cm^{-1}. The sample was prepared using KBr pressed pellet technique. LECO CHNS-932 Elemental analyser provides the quantitative analysis of carbon presence in LDH. Composite specimens for XRD analysis were prepared using Haake Minijet injection moulding.

Results and Discussion

FTIR Analysis

Figure 1 shows FTIR spectra of synthesized LDHs. The LDHs displayed similar features due to water and hydroxyl vibration modes from 4000 to 1600 cm^{-1}. The hydroxyl stretching gives strong and broad absorption bands at 3437 and 3458 cm^{-1} and deformation vibration of the interlayer water at 1637 and 1639 cm^{-1} for Mg/Al-DS and TEMS-g-Mg/Al-DS LDH, respectively. The broadness of the hydroxyl stretch region attributed to the presence of hydrogen-bonded hydroxyl groups. For TEMS-g-Mg/Al-DS LDH, the broad peak of OH is shifted from 3458 to lower wavenumber which is 3437 compared to Mg/Al-DS LDH which means that grafted LDH with TEMS and the modification with SDS give significant influence to the shifting of wavenumber (Tao *et al.,* 2009).

The presence of the alkyl group from DS structure represent by the C-H aliphatic stretching vibration implied by the observation of the triplet band at 2800-3000 cm^{-1}. Weak peaks at 1467 and 1468 for the bending mode of CH$_2$ group of DS. S-O and S=O stretching modes of dodecyl sulphate at 1216 and 1217. The absorption peak at 1383 cm^{-1} indicated the presence of nitrate anion in the interlayer gallery of LDH, which co-existed with DS anion.

The grafted TEMS onto LDH brings a vibration of Si-O-M (M = Mg & Al) at 1016 cm which appeared in TEMS-g-Mg/Al-DS LDH spectrum. This finding agrees with XRD results, and elemental analysis supported the successful TEMS grafted onto LDH layers.

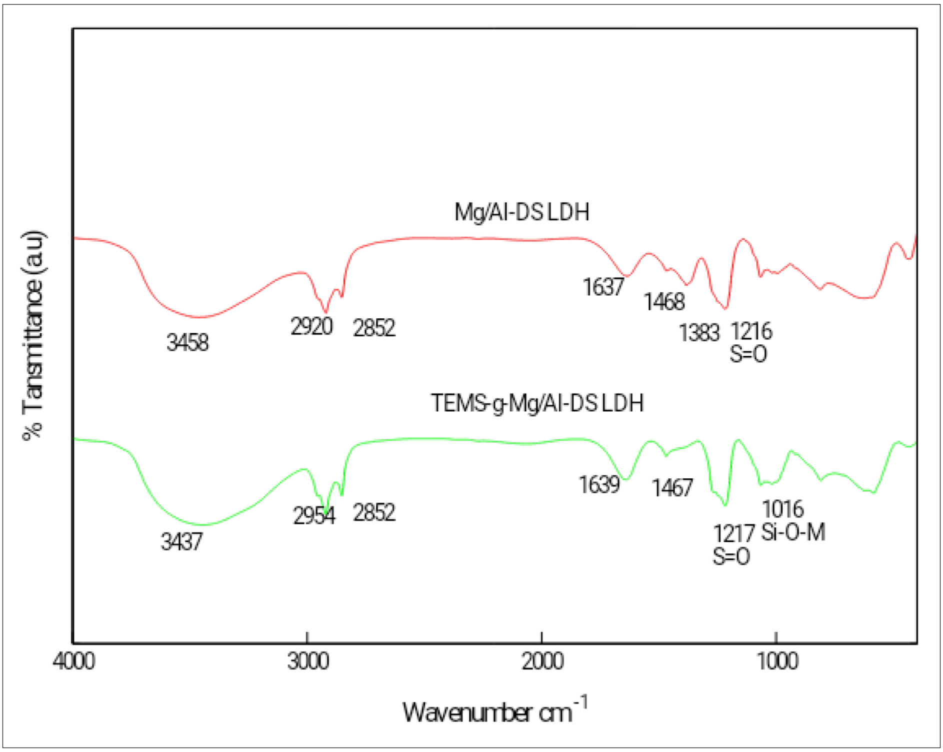

Figure 1: FTIR spectra of LDHs

Elemental Analyses

Based on the percentage of carbon, there are 229 mmol DS anion presence in 100g Mg/Al-DS LDH. However, the presence of DS content decreases from 33% to 32% after the grafting of TEMS onto LDH suggested the grafting TEMS altered the charge of the LDH. The presence of 1% nitrogen in Mg/Al-DS LDH and 4% in TEMS-g-Mg/Al-DS LDH suggested the nitrate anion co-exist as the interlayer anion in LDHs as supported by FTIR.

PXRD Results

From X-ray diffractograms of LDHs (Figure 2), the d_{003} diffraction plane peaks of Mg/Al-DS LDH and TEMS-g-Mg/Al–DS LDH, were 2.63 and 3.24 nm, respectively. The higher value of interlayer spacing for TEMS-g-Mg/Al–DS LDH possibly due to the grafting of TEMS onto interlayer of LDH (Bee *et al.,* 2017).

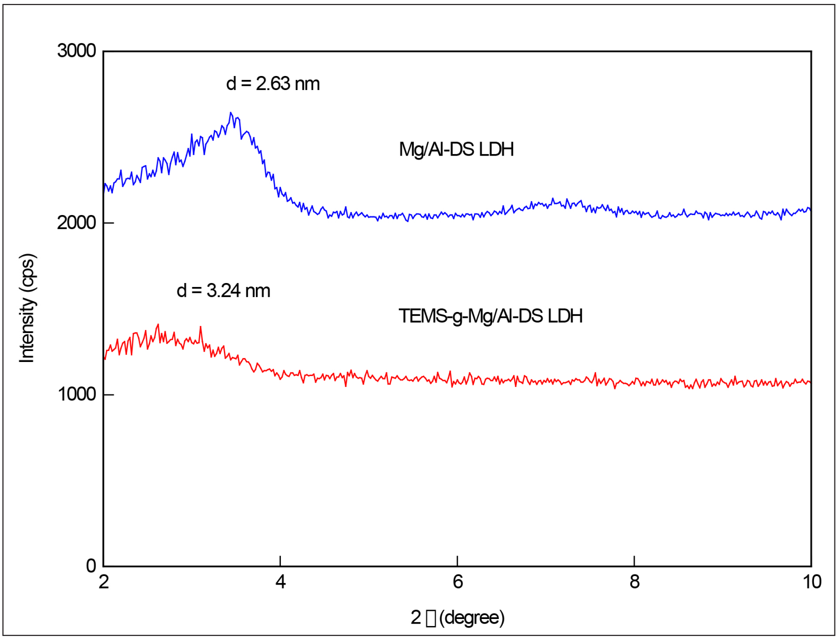

Figure 2: X-Ray diffractograms of LDHs

Surface morphology of LDPE composites

After the LDHs were melt blended with LDPE, the dispersion level of LDH layer into the LDPE matrix were studied. The basal spacing from the diffraction d_{003} plane of LDH was used for comparison. The surface interaction is the primary factor affecting the composite properties. Maximum degree of dispersion and interaction occurred when LDH layers exfoliated or delaminated in the polymer matrix. Intercalated types of nanocomposite have less surface interaction with the platelet structure remains with a higher interlayer spacing due to the insertion of polymer in the interlayer of LDH (Suresh *et al.,* 2016). The conventional composite is considered to have the lowest interaction due to only the outer layered surface of LDH interacting with polymer matrices.

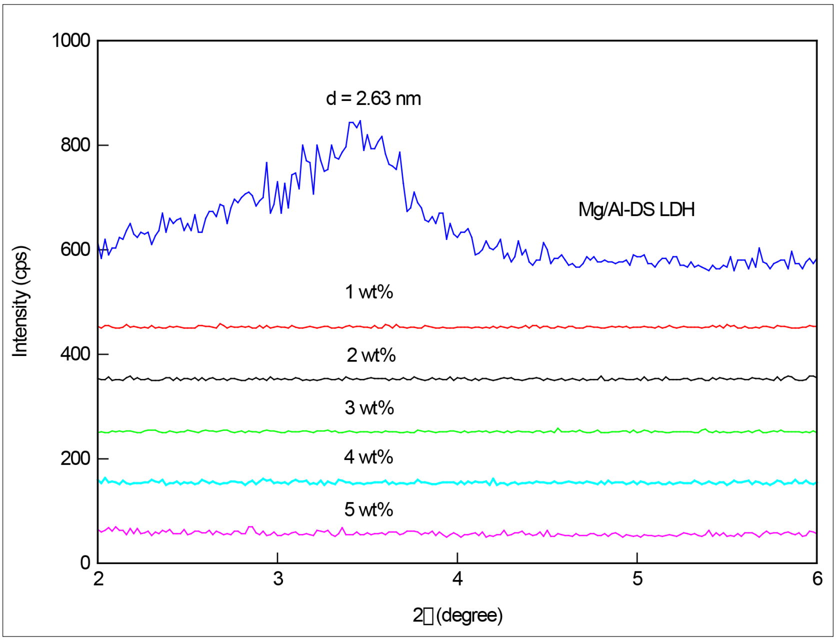

Figure 3: X-ray diffractograms of Mg/Al-DS LDH and its composites at a different weight percent.

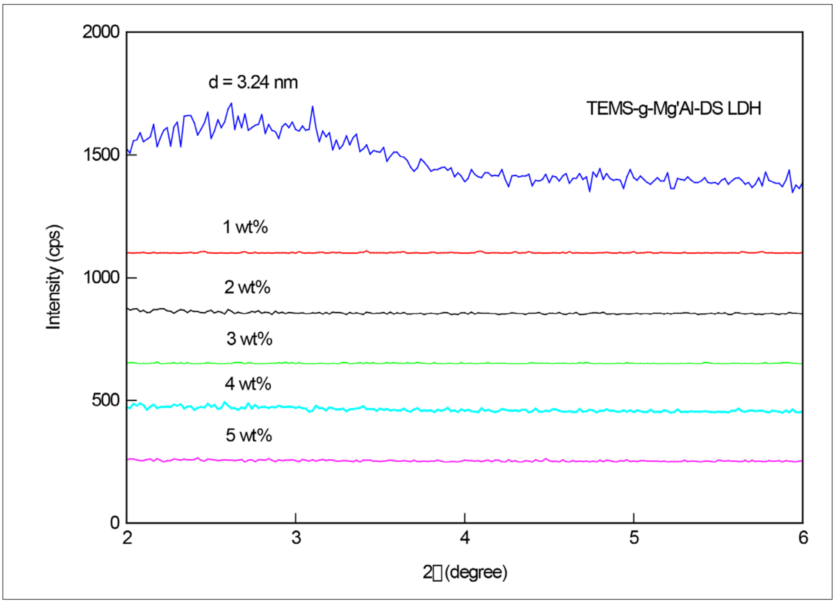

Figure 4: X-ray diffractograms of TEMS-g-Mg/Al-DS LDH and its composites at a different weight percent.

Figures 3 and 4 show the X-ray diffractograms of composites after LDHs mixed with LDPE. The diffraction d_{003} plane of the LDH layer for both composites disappeared, indicated the highest degree of layered hydroxide interaction with LDPE, which caused the loose interaction among layered hydroxide layers due to the presence of LDPE matrix between the LDH layers. The presence of organic surfactant (dodecyl sulphate) in both LDH had increased its hydrophobicity. The less abundant hydroxyl groups on the TEMS-g-Mg/Al-DS surfaces after the grafting reaction took place improves the compatibility with LDPE. As there was no d_{003} diffraction plane indicate the layers of LDH are not in a structured stack for 1 - 5 wt. %, this suggested the formation of exfoliated composites (Suresh *et al.,* 2016).

Conclusion

Organo layered double hydroxide of Mg/Al-DS system was successfully synthesized and grafted with TEMS. Mono and twice- functionalized LDHs have potential as reinforcing filler for LDPE by forming composites with the highest degree of interaction between galleries of LDH and intercalation of LDPE into it. Exfoliated nanocomposites expected to have an improvement in properties.

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