

## PREPARATION AND CHARACTERIZATION OF SODIUM LAURYL ETHER SULPHATE MODIFIED LAYERED DOUBLE HYDROXIDES

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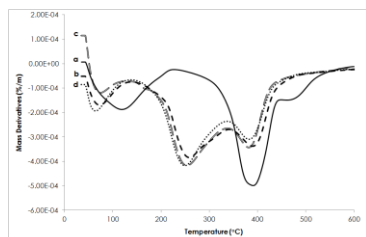
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### Graphical abstract



### Abstract

Layered double hydroxides (LDHs) has attracted much attention of many industrialists as well as academicians as these materials can be used as catalysts, adsorbents, anion exchangers, stabilizers and fillers for polymers. The materials which consist of divalent and trivalent cations, and anions are nontoxic and easy to prepare. In addition, the exchangeability of their anions makes them easy to be modified to increase their hydrophobicity property through anion exchange process using long chain surfactant anions. In this study, sodium lauryl ether sulphate (SLES) modified LDHs was prepared by co precipitation of LDHs and followed SLES ions modification via ion exchange process. Intercalations of the anions into the LDHs layers were confirmed by X-ray diffraction analysis. The presence of functional groups before and after modification was studied by FTIR spectrometry. Thermalgravitmeric analysis also was carried out to determine the amount of surfactant intercalated into LDHs.

**Keywords:** Co-precipitation, layered double hydroxides, sodium lauryl ether sulphate

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## 1.0 INTRODUCTION

Layered silicates are very attractive alternative materials as nanofillers for altering properties of many polymers. Montmorillonite (MMT) has been studied as filler for polymers for many years and successfully blended into some polymers, resulting in increased tensile properties and thermal stability [1-4]. LDHs is an anionic clay which consists of positively charged

metal hydroxide sheets with exchangeable anions and water molecules.

Its general formula is  $[M_{1-x}^{2+} + M_x^{3+}(\text{OH})_2]_x + A^{n-}_{x/n} \cdot m\text{H}_2\text{O}$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations, and  $A^{n-}$  is an exchangeable anion. Recently, LDHs has received a lot of attention since these materials have several advantages such as ease of synthesis, non toxic and well-defined alternatives to MMTs [5-8]. Furthermore, LDHs has also a great potential in industries uses such as catalysts, ion-exchangers, sorbents and antacids [9-10].

Modification of LDHs materials is almost a requirement prior to fabrication of LDHs-polymer composites. This process facilitates the intercalation of anion chains, resulting in enhanced hydrophobicity property of the LDHs hence makes it easier to mix with polymers [13]. Mahboobeh et al (2010) successful intercalated stearate ions into LDHs layers and used the product in poly(lactic acid) modification [14]. They found that blending a small amount of it into this polymer improved significantly the polymer's flexibility without affecting its tensile strength. In the present work, SLES, an anionic surfactant is used in the modification of LDHs. The properties of the surfactant-modified LDHs were then characterized by X-ray diffraction (XRD) technique, thermogravimetric analysis (TGA) and Fourier Transform Infrared (FTIR) spectrophotometry.

## 2.0 METHODOLOGY

### 2.1 Materials

Magnesium nitrate hexahydrate, aluminium nitrate nonahydrate and sodium hydroxides (supplied by Merck, Germany) were used as received.

### 2.2 Synthesis of LDHs

LDHs was synthesized as follows: sodium hydroxides solution (1M) was first slowly added into a 500 mL solution containing 38.44 g of magnesium nitrate hexahydrate and 18.76 g of aluminium nitrate nonahydrate until pH 9 was obtained. The solution was then shaken at 100 rpm, 70°C for 24 hours. Finally, the LDHs obtained was filtered, washed with deionized water twice and dried at 60°C for 24 hours.

### 2.3 Preparation of SLES modified by LDHs

One gram of LDHs was stirred in 500 mL SLES solution at 75°C for 24 hours. The SLES solution was prepared by dissolving 1 g of surfactant in deionized water at 50°C and 500 rpm. The solid was then filtered, washed with deionized water and dried in an oven at 60°C for 24 hours. Two other weights (2g and 3g) of the surfactants were used to prepare the SLES solutions for study the effect of LDHs-SLES ratio in the modification.

### 2.4 X-ray Diffraction Analysis

X-ray diffraction (XRD) analysis of the composites was carried out using a Shimadzu's XRD 6000 Diffractometer. The instrument was operated at 30 kV/30 mA and produced Cu- K $\alpha$  radiation ( $\lambda = 0.15405$  nm). Powder samples were scanned at a rate 0.2° 2 $\theta$ /min in a range from 2 to 35°. The intensity

of diffracted X-ray was recorded as the sample and detector were rotated with their respective angle.

### 2.5 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was conducted to identify the functional groups of the composites using Perkin Elmer System FTI 1650 Spectrum BX Spectrometer at room temperature. The sample which was mixed with KBr powder and grounded until a well mixed powder was obtained, was then pressed into a disk. The FTIR spectrum of the sample from the average of 16 scans was recorded in the range from 400 to 4000 cm<sup>-1</sup>.

### 2.6 Thermogravimetry Analysis

Samples were heated from ambient temperature to 350°C at a heating rate of 10°C/min under nitrogen atmosphere by TA Instruments Q 500 TGA Instrument. The weight loss of samples were recorded and plotted as a function of temperature.

## 3.0 RESULTS AND DISCUSSION

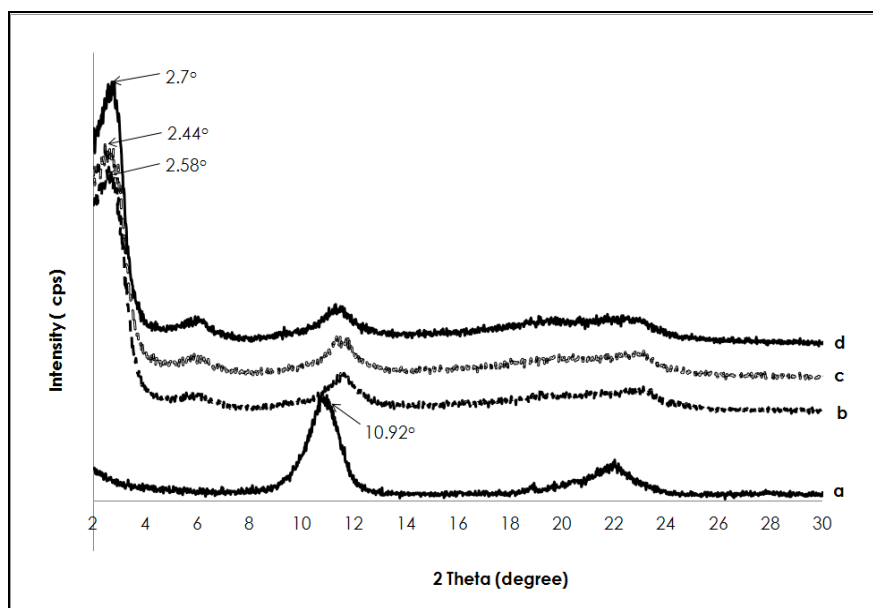
### 3.1 XRD Analysis

Figure 1 shows the x-ray diffraction patterns of pristine LDHs and SLES-LDHs of various weight ratios of LDHs and surfactant. The LDHs-SLES weight ratios used for the LDHs modification are 1:1, 1:2 and 1:3 respectively. The XRD patterns for pristine and SLES modified LDHs show that they are crystals of well layered structure.

The interlayer spacings were calculated using Bragg's equation which is  $n\lambda = 2d \sin \theta$ , where  $n$  is 1,  $\lambda$  is the wavelength of Cu-K $\alpha$  radiation,  $d$  is interlayer spacing of the LDHs and  $\theta$  is the diffraction angle and the results are shown in Table 1. The increase in the interlayer spacing indicates that the surfactant anions has successfully replaced some of the simple anions present in the LDHs interlayers. Similar effect was reported when stearic acid was used as the modifier [14]. Insignificant change of the spacings for various SLES concentrations suggests that 1g of SLES is sufficient to modify the LDHs. Hence, SLES-LDHs produced from the modification with SLES:LDHs weight ratio of 1:1 was chosen for further investigation.

**Table 1** Interlayer Spacing of LDHs and SLES modified LDHs

Sample	Weight Ratios/ SLES:LDH	2 $\theta$ / degree	Interlayer spacing/ Å
Pristine LDHs	-	10.92	8.10
SLES-LDH1	1:1	2.58	34.23
SLES-LDH2	2:1	2.44	32.71
SLES-LDH3	3:1	2.70	36.16

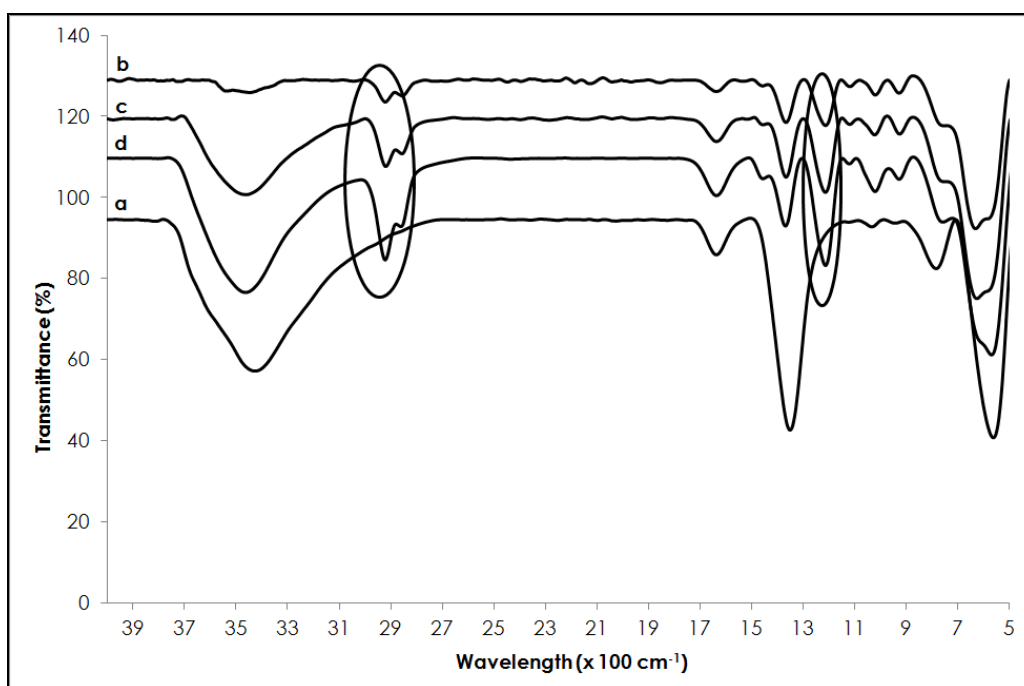


**Figure 1** XRD patterns for pristine and modified LDHs  
(a) pristine LDH, (b) SLES-LDH1 (1:1), (c) SLES-LDH2 (2:1) and (d) SLES-LDH3 (3:1)

### 3.2 FTIR Analysis

FTIR spectra of pristine and modified LDHs are shown in Figure 2. The broad peak at  $3439\text{ cm}^{-1}$  is due to O-H stretch from the LDHs and water (H-OH). The existence of  $\text{NO}_3^-$  anions in the pristine LDHs structure is indicated by a sharp peak at  $1357\text{ cm}^{-1}$  meanwhile wavelength range from  $800\text{--}500\text{ cm}^{-1}$  is due to M-O (where  $M=\text{Mg}$  or  $\text{Al}$ ) lattice vibrations [14]. Three

peaks that are appeared in the modified LDHs spectra, which do not exist in the pristine LDHs spectrum, are of surfactant anion peaks. The bands are attributed to surfactants anion of long alkyl (CH,  $\text{CH}_2$  and  $\text{CH}_3$ ) group around  $2900\text{ to }2950\text{ cm}^{-1}$  and  $\text{SO}_3^-$  group at around  $1200\text{ to }1250\text{ cm}^{-1}$ . This observation is in agreement with the XRD results that suggest that the surfactant anions are intercalated in the LDHs.

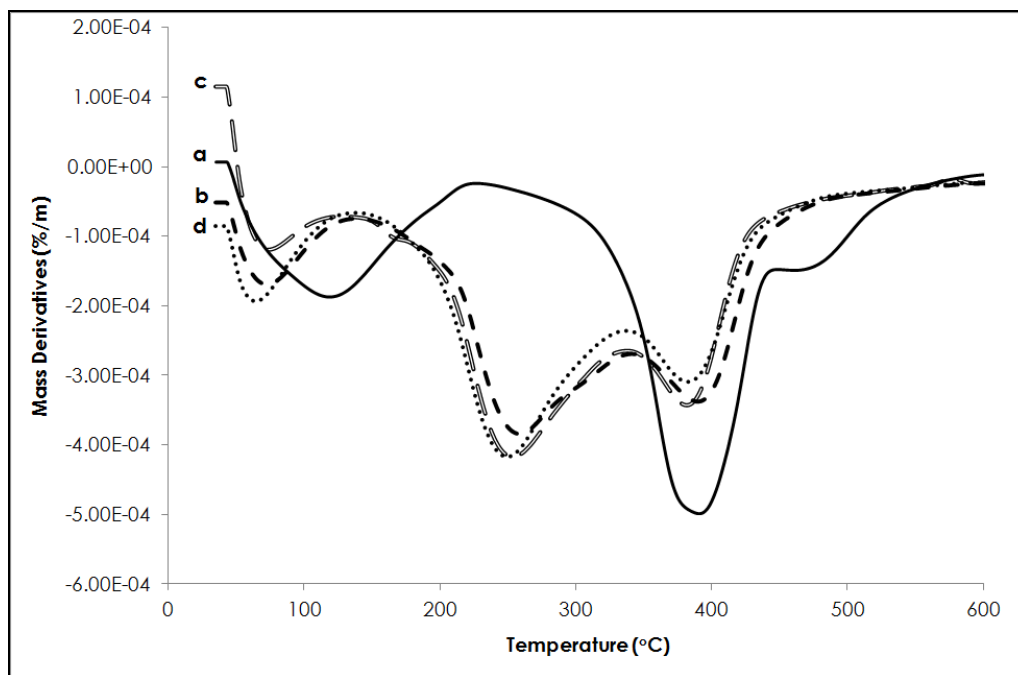


**Figure 2** FTIR spectra for pristine and modified LDHs  
(a) pristine LDH, (b) SLES-LDH1 (1:1), (c) SLES-LDH2 (2:1) and (d) SLES-LDH3 (3:1)

### 3.3 Thermogravimetry Analysis

Figure 3 shows the thermograms of pristine and SLES modified LDHs. SLES modified LDHs curves show that SLES in LDHs decomposes at around 240°C. The percentages of the intercalated SLES in the SLES

modified LDHs are given in Table 2. It shows that the amount of intercalated surfactant in all the LDHs samples is around 28% which also indicates, as mentioned above, 2 g/L of SLES concentration, is sufficient to effectively modify the LDHs.



**Figure 3** DTG Thermogram of pristine LDH and modified LDHs  
(a) pristine LDH, (b) SLES-LDH1 (1:1), (c) SLES-LDH2 (2:1) and (d) SLES-LDH3 (3:1)

**Table 2** Percentage of SLES intercalation into LDHs

Sample	Weight ratio (SLES:LDHs)	% of surfactant
SLES-LDH1	1:1	28.11
SLES-LDH2	2:1	28.41
SLES-LDH3	3:1	28.80

### 4.0 CONCLUSION

LDHs, that was prepared by co-precipitation method, was successfully modified by SLES. The optimum concentration of the SLES solution used for the modification was 2g/L with the amount of surfactant intercalated was around 28%. As the result of the modification, the interlayer distance of the LDHs increased from 8.10Å to around 34 Å.

### Acknowledgement

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### References

- [1] Rees, J. R., Burden, C. S. and Fogg, A. M. 2015. New layered double hydroxides by prepared by the intercalation of gibbsite. *Journal of Solid State Chemistry*. 224: 36-39.
- [2] Ray, S. S. and Bousmina, M. 2005. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. *Progress in Material Science*. 50(8): 962-1079.
- [3] Ray, S. S., Maiti, P., Okamoto, M., Yamada, K. and Ueda, K. 2002. New polylactide/layered silicate nanocomposites. 1. Preparation, characterization, and properties. *Macromolecules*. 35(8):3104-3110
- [4] Singh S. and Ray, S. S. 2007. Polylactide based nanostructured biomaterials and their applications. *Journal of Nanoscience and Nanotechnology*. 7(8): 2596-2615
- [5] Dagnon, K. L., Ambadapadi, S., Shaito, A., Ogbomo, S. M., DeLeon, V., Golden, T. D. and et al. 2009. Poly(L-lactic acid) nanocomposites with layered double hydroxides functionalized with ibuprofen. *Journal of Applied Polymer Science*. 113(3): 1905-1915.
- [6] Chiang, M. F. and Wu, T. M. 2010. Synthesis and characterization of biodegradable poly (L-

- lactide)/layered double hydroxide nanocomposites. *Composites Science and Technology*. 70(1):110-115.
- [7] Pan, P. J. Zhu, B., Dong, T. and Inoue, Y. 2008. Poly(L-lactide)/layered double hydroxides nanocomposites: preparation and crystallization behavior. *Journal of Polymer Science Part B - Polymer Physics*. 46(20): 2222-2233.
- [8] Du L. C. and Qu, B. J. 2006. Preparation of LLDPE/MgAl-LDH exfoliation nanocomposites with enhanced thermal properties by melt intercalation. *Chinese Journal of Chemistry*. 24(10): 1342-1345.
- [9] Cavani, F., Trifir'ò, F. and Vaccari, A. 1991. Hydrotalcite-type anionic clays: preparation, properties and applications. *Catalysis Today*. 11(2): 173-301.
- [10] Reichle, W. T. 1986. Anionic Clay Minerals. *Chem. Tech*. 16(1): 58-63
- [11] Hochstetter, C. 1842. Untersuchung über die Zusammensetzung einiger Mineralien. *Journal für praktische Chemie*. 27: 375-378.
- [12] Feitknecht W. and Gerber, M. 1942. Zur Kenntnis der Doppelhydroxyde und basischen Doppelsalze III. über magnesium-aluminium-doppelhydroxyd. *Helvetica Chimica Acta*. 25(1): 131-137.
- [13] Maiti, M., Bhattacharya, M. and Bhowmick, A. K. 2008. Elastomer nanocomposites. *Rubber Chemistry and Technology*. 81(3): 384-469.
- [14] Mahboobeh, E., Yunus, W. M. Z. W., Hussein, Z., Ahmad, M. and Ibrahim, N. A. 2010. Flexibility Improvement of Poly(Lactic Acid) by Stearate-Modified Layered Double Hydroxide. *Journal of Applied Polymer Science*. 118(2): 1077- 1083.