

PREPARATION AND PROPERTIES OF NATURAL RUBBER/ LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

MOHD AIDIL ADHHA ABDULLAH*¹, MANSOR HJ AHMAD², WAN MD ZIN WAN YUNUS², MOHAMAD ZAKI AB RAHMAN², MOHD ZOBIR HUSSEIN² AND KHAIRUL ZAMAN HJ MOHD DAHLAN³

¹Department of Chemical Sciences, Faculty of Science and Technology, Universiti Malaysia Terengganu (UMT), 21030 Kuala Terengganu, MALAYSIA. ²Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, UPM Serdang, 43400 Selangor, MALAYSIA ³Nuclear Agency Malaysia, Bangi, 44300 Kajang, Selangor, MALAYSIA.

*Corresponding author: aidil@umt.edu.my

Abstract: Nanocomposites of natural rubber (NR)/organo ZnAl layered double hydroxide (ZnAl LDH-DS) were successfully synthesized and characterized. A hydrophilic Zn-Al layered double hydroxide (ZnAl LDH-NO₃⁻) was converted into the organophilic form by replacing the nitrate ion in between the ZnAl LDH-NO₃⁻ with dodecylsulfate ion (DS) to form ZnAl LDH-DS. The melt intercalation technique followed by vulcanization process was adopted to synthesize the nanocomposites of NR/ZnAl LDH-DS. Intercalation of DS ion into the interlayer of ZnAl LDH-NO₃⁻ increased the surface area and the porosity of the LDH. X-Ray diffractogram of the organophilic ZnAl LDH-DS shows that the basal spacing of the ZnAl LDH-NO₃⁻ expands from 0.89 to 2.53 nm due to the accommodation of DS ion in the intergallery. After the compounding process with the NR, the basal spacing of ZnAl LDH-DS in the composites is increased to 3.90 and 3.27 nm when the ZnAl LDH-DS contents were 1 and 15 phr, respectively. Transmission electron microscope image revealed that the ZnAl LDH-DS was distributed in the NR matrix in such a way of exfoliated and different grade of intercalated. The tensile strength values of NR/ ZnAl LDH-DS (nanocomposites) were found to be higher than that of the NR/ZnAl LDH-NO₃⁻ (macrocomposites).

KEYWORDS: Nanocomposites; Layered Double Hydroxide; Natural Rubber; Intercalate

Introduction

In recent years, organic-inorganic nanocomposites have attracted great interest from researchers, since they frequently exhibit unexpected hybrid properties synergistically derived from these two components. One of the most promising composite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of a layered structure, which belongs to the general family of 2:1 layered silicates. The generic term “layered silicates” refers to natural clays but also to synthesize layered silicates such as magadiite, laponite and fluorohectorite. Both natural clays and synthetic layered silicates have been successfully used in the synthesis of polymer nanocomposites (Leroux *et al.*, 2005).

Layered Double Hydroxides (LDHs) are a kind of layered material that consists of positively charged layers and the interlayer exchangeable anions. Their general composition can be represented as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O]^{x-}$, where M^{II} = divalent cations (Ca²⁺, Mg²⁺, Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Mn²⁺, but also the monovalent cation Li⁺); M^{III} = trivalent cations (Al³⁺, Cr³⁺, Fe³⁺, Co³⁺, Mn³⁺), and A = interlayer anions (Cl⁻, NO₃⁻, ClO₄⁻, CO₃²⁻, SO₄²⁻) (Meyn *et al.*, 1990, and Kopka *et al.*, 1988). The anions and water molecules intercalated into LDH interlayers can be replaced with other organic anions and polar molecules. When exchanging interlayer anions with organic anions, the interlayer spacing of LDHs increases, which is dependent on the nature, size and

geometrical structure of the intercalated species. The replacement of inorganic anions with organic species such as long chain surfactants yields modified organo-LDHs with hydrophobic surface properties.

The inorganic and organic phases are quite incompatible, resulting in phase separation. Thus, interfacial adhesion is introduced between the inorganic and organic components to minimize the degree of phase separation (Chen and Iroh, 1999 and Mascia and Kioul, 1995). Generally, the existence of interfacial bonding, especially covalent bonding, between the inorganic and organic phases dramatically improves the mechanical properties such as modulus, tensile strength, hardness, fatigue, cracking, and resistance to corrosion (Jang, 1992, Sohn, 1985 and Tien and Wei, 2001). Therefore, the surface of the inorganic components is organo-modified before the inorganics/polymer nanocomposites are prepared to enhance the compatibility between the inorganic and organic phases. Furthermore, the organo-modification makes the inorganic components more hydrophobic (Tyan *et al.*, 1999), enabling it to disperse in a polar solvent or polymer matrix.

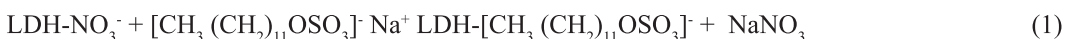
In the past decade, the concept of “nano reinforcement” with layered silicates has become very popular. Research was focused on the development of other reinforcing agent to replace the carbon black in the rubber compound. The reinforcing effect of layered silicates in *cis* 1,4 polyisoprene and epoxidized natural rubber (ENR) showed that the organic modification of the clay filler facilitated the intercalation of the non-polar elastomer into the clay galleries (Vu *et al.*, 2001). In the scope of this study, we will focus on the use of a layered double hydroxide as a reinforcing agent for natural rubber. The synthesized hydrophilic ZnAl-LDH was converted into organophilic form through ion exchanged process before mixing with the natural rubber (NR). The physico-chemical properties of the LDH and reinforcing effects of LDH at macro or nanoscale on the tensile properties of the NR/ZnAl LDH-DS composites are studied.

Experimental

SMR CV 60 grade natural rubber (NR) used for this study was supplied by the Lembaga Getah Malaysia (LGM), Malaysia. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was obtained from Fluka, and, aluminium nitrate nanohydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium dodecylsulphate (SDS) and sodium hydroxide were used as supplied by BDH. All other ingredients used were of commercial grade. Decarbonated deionised water, boiled and purged with nitrogen gas to remove CO_2 , was used throughout this work.

Preparation of ZnAl-LDH- NO_3^- and ZnAl-LDH-DS

ZnAl-LDH- NO_3^- was prepared via co-precipitation method in which Zn/Al molar ratio was fixed at 3. A mixed aqueous solution or mother liquor of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was prepared at $\text{pH } 7.50 \pm 0.05$ by drop-wise addition of an aqueous NaOH solution (2.0 M) with vigorous stirring. The titration of NaOH was performed under a constant flow of nitrogen gas in order to avoid or at least minimize contamination by atmospheric CO_2 . The precipitate was stirred continually for an hour with occasional adjustment of pH. The precipitate was then aged at 70°C for 18h, washed and dried in an oven at 70°C , and ground into fine powder and kept in a sample bottle for further use and characterization. The organically modified ZnAl-LDH-DS was synthesized by an ion exchange reaction between as a synthesised ZnAl-LDH- NO_3^- and anionic surfactant as shown in Eq (1).



The synthesised ZnAl-LDH-NO_3^- was added to 0.1 mole dm^{-3} sodium dodecylsulphate (SDS) solutions with a solid/solution ratio of $1 \text{ g per } 50 \text{ cm}^3$. The suspension was shaken at low speed in oil bath for 16h, filtrated and the supernatant solution decanted. The solid material was washed three times using distilled water and oven dried at 65°C . Deionised water that was boiled and purge with nitrogen (N_2) gas were used through out the process.

Preparation of natural rubber / ZnAl-LDH composites

The mixing study was carried out using an internal mixer Polydrive Thermo Haake Rheomix 600p. The ZnAl-LDH-DS (act as a filler) and NR were prepared to produce composites with different composition, consisting filler loading between 1,3,5,7,10 and 15 phr. Mixing was carried out at a mixing temperature of 60°C with a rotor speed of 80 rpm and for a period of 5 min. The resulting blends were then mixed with sulfur and CBS in the internal mixer at a temperature of 40°C .

The resulting blends were then mixed with sulfur and CBS in the internal mixer at a temperature of 40°C . The composites were then compression molded in an electrical heated hydraulic press, Hsin-Chi LM-50 into 1 mm thickness sheets under a pressure 100 kgcm^{-2} at 150°C by using the respective cure times, t_{95} which was determined by using a Mosanto Rheometer, model MDR 2000. All the recipe of the blends is given in the Table 1. For comparison, a similar procedure was applied to prepare composites of NR/ZnAl LDH- NO_3^- .

Table 1: Formulation for vulcanization of composite

Ingredients	phr ^a
Natural rubber	100.0
LDH	1.0/ 3.0/ 5.0/ 7.0/ 10.0/15.0
Zinc Oxide	5.0
Stearic acid	2.0
Process oil	5.0
CBS*	1.5
Sulfur	1.5

^aParts per hundred of rubber

* N- Cyclohexyl-2-benzothiazyl sulfenamide

Characterizations and measurements

The X-ray diffraction patterns were recorded on Shimadzu XRD6000 X-ray Diffractometer, using CuK_α radiation at wavelength $\lambda=0.154 \text{ nm}$. Scanning rate used in this study was 2° min^{-1} . The FTIR spectra were collected by a Perkin-Elmer FT-IR 1650 spectrophotometer within the wavelength range of $4000 - 4000 \text{ cm}^{-1}$. The samples were mixed ($\sim 1.0\%$) with dried KBr and pressed into a pellet. Carbon, hydrogen and nitrogen analyses were carried out with LECO CHNS-932 Elemental Analyzer. The specific surface area and pore size distribution were determined by nitrogen adsorption-desorption isotherms. This analysis was carried out at liquid nitrogen temperature, 77K by using a Micromeritics ASAP 2000. Specific total surface area was calculated using the Brunauer Emmet and Teller (BET) equation. The surface morphology of the LDHs was observed with the scanning electron microscope JEOL JSM-6360LA (SEM). The dispersion of LDH was studied by Energy Filtering Transmission Electron Microscope (EFTEM), LEO 912 AB with an acceleration voltage of 120KeV . The specimens were prepared using a Reichert Jung Ultracut E cryo-ultramicrotome. Thin sections of about 100 nm were cut with a glass knife at -120°C . The tensile properties were measured using an Instron-4302 Universal testing machine at a crosshead speed of 500 mm/min following standard method (ASTM D412-92). The samples were cut into dumbbell shapes using a

dumbbell cutter. All tensile tests were performed at room temperature on five samples or more, and the average values will be given by the software.

Results and Discussion

X-Ray diffraction measurement

The X-ray diffractograms for the LDH samples containing nitrate and DS anion as an interlayer species are shown in Figure 1 (a) and (b), respectively. The XRD patterns for the LDH samples were indexed based on the hexagonal unit cell. The peak which occurs at approximately 10.1° 2θ angle (d spacing 0.89 nm) for ZnAl LDH- NO_3^- was attributed to the reflections from the 003 family of the crystallographic plane. This plane is spaced one-thirds of the unit cell distance apart and corresponds to the interlayer repeat distance. The d spacing (d_{003}) can be termed the interlayer spacing and includes a contribution from the metal hydroxide sheet and the gallery region that contains the intercalated anions. This gallery region between adjacent metal hydroxide layers may also be referred to as the interlayer distance or the gallery height. DS insertion into the LDH gallery resulted in an expansion of the basal spacing from 0.89 nm for ZnAl LDH- NO_3^- to 2.53 nm for ZnAl LDH-DS, suggesting that the DS had been intercalated into the LDH interlayer galleries after the ion exchanged process. The intercalation of anionic surfactant of sodium dodecylsulfate into ZnAl LDH interlayer altered the surface properties from hydrophilic to hydrophobic (Tyan *et al.*, 1999). Furthermore, a larger space between the ZnAl LDH nanolayers will promote the intercalation of NR, leading to easy exfoliation or intercalation of the stacking ZnAl LDH nanolayers in NR matrix to form NR/LDHs nanocomposites.

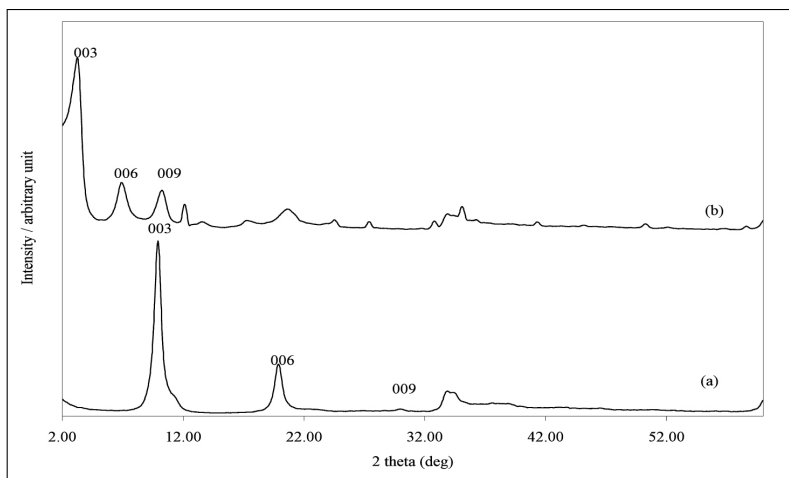


Figure 1: XRD diffractograms of ZnAl LDH- NO_3^- (a) and ZnAl LDH-DS (b)

FTIR Analyses

FTIR spectra for the samples ZnAl LDH- NO_3^- and ZnAl LDH-DS are shown in the Figure 2. All samples displayed similar features due to water and hydroxyl vibration modes in the region between $4000\text{--}1600\text{ cm}^{-1}$. A very strong and broad absorption band at approximately 3462 cm^{-1} was caused by OH stretching. The broadness of the hydroxyl stretch region attributed to the presence of hydrogen bonded hydroxyl groups. The absorption band at 1630 cm^{-1} is attributed to deformation vibrations

of the interlayer water. Two other peaks at 626 cm^{-1} and 426 cm^{-1} can be attributed to the Al–OH and Zn–Al–OH bending vibration, respectively (Mascia and Kioul, 1995).

A strong absorption peak at 1384 cm^{-1} for ZnAl LDH- NO_3^- can be attributed to the presence of the nitrate group located in the intergallery. However, the absence of this peak for ZnAl LDH-DS revealed that all the nitrate anions were completely exchanged with DS anions. The presence of the methyl group from DS anion can be seen from the CH stretching vibration implied by the observation of the triplet band at $2800\text{--}3000\text{ cm}^{-1}$. The peak at 1460 cm^{-1} indicates the CH_2 plane scissoring; and absorption by sulfonate salt can be observed at 1080 cm^{-1} . These show that the FTIR spectrum of ZnAl LDH-DS resembles a mixture of DS and ZnAl LDH- NO_3^- which confirmed the intercalation of DS.

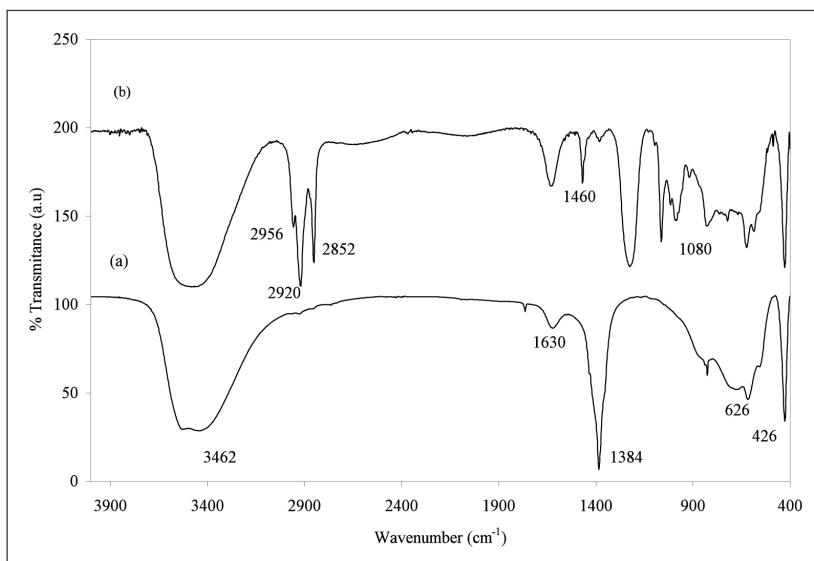


Figure 2: FTIR spectra of (a) ZnAl LDH- NO_3^- and (b) ZnAl LDH-DS

CHNS Elemental Analyses

CHNS analysis of LDH revealed that the percentage of carbon and sulfur contents increased from 0.502 to 17.97% and from 0.592 to 4.018%, respectively after ion exchange took place. The increase of the carbon and sulfur content confirmed the presence of the DS ion in the modified ZnAl LDH-DS. Quantitative calculation of DS presents in this organo LDH was made based on sulfur content, and it is found that there were 107 mmol DS ions intercalated into 100 g of the LDH.

Surface Properties

The surface area of the filler played a major role in the interaction between the polymer and the filler. The surface characteristic of the LDH was studied by using the adsorption isotherm. The BET surface area and BJH desorption average pore diameter are summarized in Table 2.

Table 2: Surface properties of LDH

Materials	Basal spacing (nm)	BET surface area (m^2g^{-1})	BJH desorption average pore diameter (nm)
Zn-Al LDH- NO_3^-	0.89	5.073	18.520
Zn-Al LDH- DS	2.51	10.271	15.971

Figure 3 shows adsorption-desorption isotherms for LDH. It clearly indicates that both ZnAl LDH- NO_3^- and ZnAl LDH-DS exhibit Type IV isotherm, attributed to the mesoporous-type of adsorbent (2.0-50 nm) with H3 loop, associated with aggregates of plate-like particles giving rise to slit-shaped pores. SEM micrographs for ZnAl LDH- NO_3^- and ZnAl LDH-DS are given in Figures 4 (a) and (b), which confirm the formation of plate-like structure.

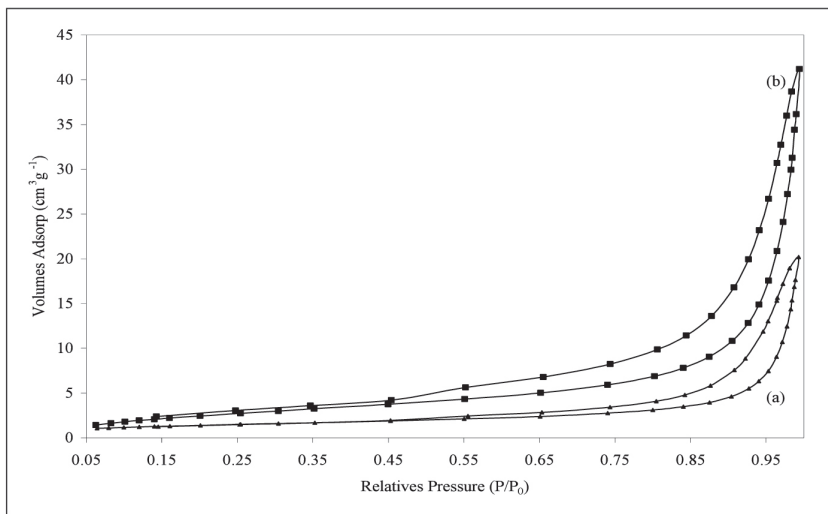


Figure 3: Adsorption-desorption isotherms for ZnAl LDH- NO_3^- (a) and ZnAl LDH-DS (b)

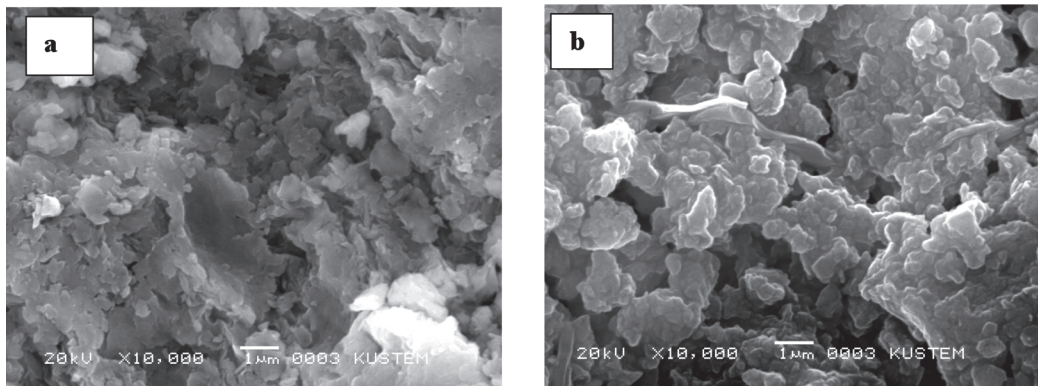


Figure 4: Electron micrographs for ZnAl LDH- NO_3^- (a) and ZnAl LDH-DS (b) at magnification of 10,000X

Analyses of composites

Determination of the structure in nanocomposites requires the measurements of d-spacing from X-ray diffraction. In an immiscible mixture, the d-spacing should be virtually identical with that of the original clay while, if an intercalated nanocomposite is formed, the d-spacing must increase (Yahaya *et al.*, 2003).

Figure 5 shows the XRD patterns for ZnAl LDH-NO₃⁻(a) and its composites with NR at 7 phr of ZnAl LDH-NO₃⁻ (b). The d₀₀₃ peak which indicates the interlayer spacing for the layers shows a clear peak at the same position. The calculated results of interlayer spacing based on Bragg's Law are given in the Table 3. The interlayer spacing for the composites is around 0.89 nm for all the LDH content. This indicates no intercalation of NR into the intergallery of ZnAl LDH-NO₃⁻ took place. When the polymer is unable to intercalate between the silicate sheets, a phase separated composites is obtained, whose properties stay in the same range as traditional microcomposites (Zhu *et al.*, 2002). Since ZnAl LDH-NO₃⁻ is hydrophilic, it is impossible for an organic polymer such as NR to enter the gallery space, leading to the formation of macrocomposites. Figures 6 (a) and (b) show the TEM images of the NR/ ZnAl LDH-NO₃⁻ composite filled with 7 phr of ZnAl LDH-NO₃⁻ loading. It shows that the LDH dispersed in NR matrix in the form of large particles. The morphology is in agreement with XRD results which show the formation of conventional composites (macrocomposites).

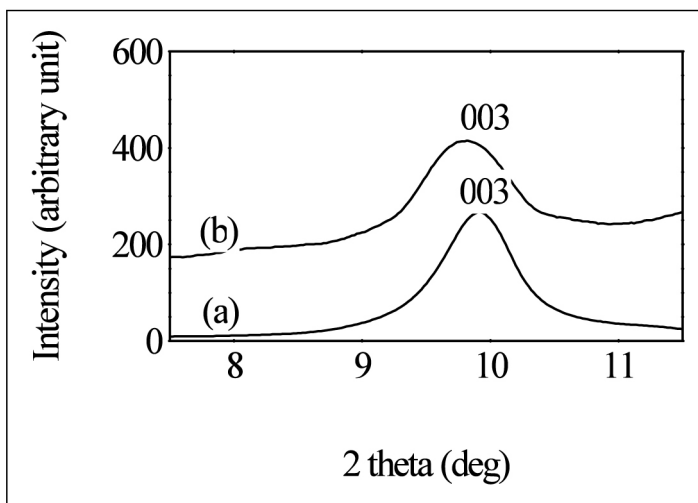


Figure 5: XRD diffractograms of ZnAl LDH-NO₃⁻ (a) and hybrid NR / ZnAl LDH-NO₃⁻ 7phr (b)

Table 3: Interlayer spacing for composites NR/ Zn-Al LDH

LDH Content (phr)	Interlayer spacing (nm)	
	Zn-Al LDH- NO ₃ ⁻	Zn-Al LDH- DS
1	0.89	3.90
3	0.89	3.72
5	0.88	3.50
7	0.89	3.35
10	0.89	3.34
18	0.89	3.27

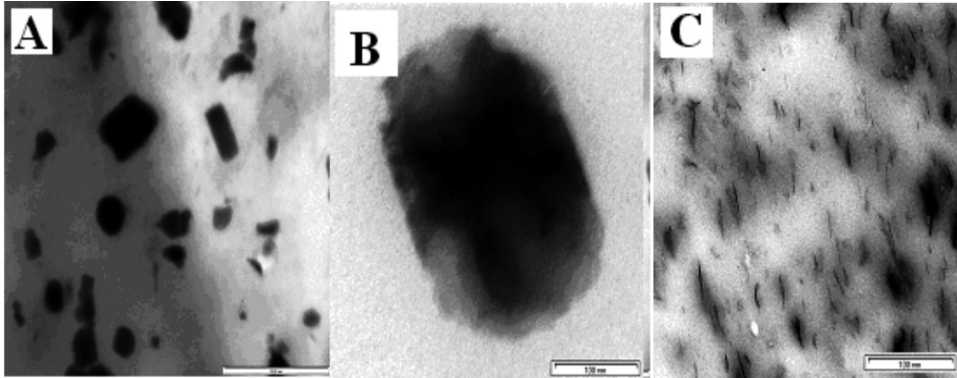


Figure 6: TEM micrographs for hybrid NR/ ZnAl LDH-NO₃- 7 phr at low magnification (A); high magnification (B) and NR/ ZnAl LDH-DS high magnification (C)

In the case of NR/ZnAl-LDH-DS composites (Figure 7), the diffraction of d_{003} plane was shifted to the lower angle with the higher d -spacing value in comparison to ZnAl-LDH-DS. This indicates that the expansion of interlayer spacing is due to the intercalation of NR leading to the formation of intercalated structure of nanocomposites. The second and the third peaks (d_{006} and d_{009} diffraction plane) represent the collapse (reduction in d -spacing) of the LDH layers. From the interlayer spacing results (Table 3), the interlayer distance of the LDH is inverse proportionate to the LDH content. This means when the number of LDH increases at the same content of NR matrix, the distance between the layers becomes closer. However, the TEM image of NR filled with 7 phr of ZnAl LDH-DS loading (Figure 6(c)) shows the exfoliation in addition to the intercalation of the nanolayers formed in this composite.

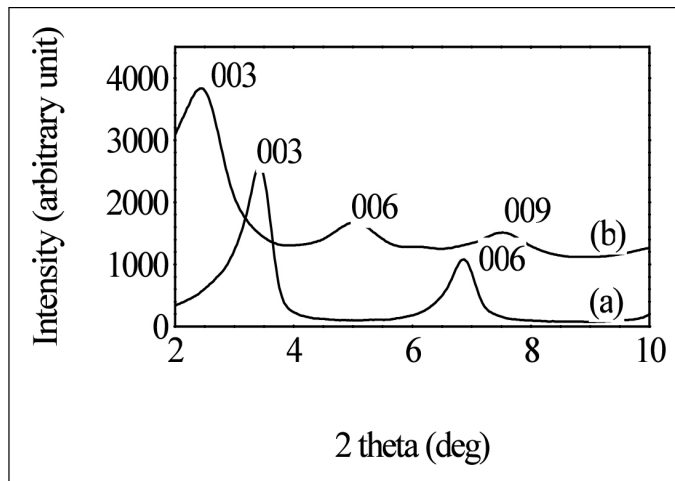


Figure 7: XRD diffractograms of ZnAl LDH-DS (a) and hybrid NR /ZnAl LDH-DS 7phr (b)

Tensile Properties

In this study, the DS anion was used with the objective of trying to increase the compatibility between organic polymer, NR and hydrophilic Zn/Al LDH in the blends. Data of tensile strength versus the LDH loading are shown in the Table 4. It is well known that the mechanical properties of nanocomposites are enhanced relatively to those of the conventional macrocomposites.

Table 4: Tensile strength and percentage increment for composites

LDH content (Phr)	Tensile Strength (MPa)		% Increment
	NR/Zn-Al-LDH-NO ₃ ⁻	NR/ Zn-Al LDH -DS	
1	17.98	20.88	16.13
3	17.61	21.41	21.58
5	17.55	21.88	24.67
7	17.60	22.45	27.57
10	16.64	18.84	13.22
15	15.49	17.14	10.65

For the conventional macrocomposites, tensile strength decreased with the content of ZnAl LDH-NO₃⁻ and maximum strength was achieved at 1 phr with the tensile strength of 17.98 MPa. The addition of DS into the ZnAl LDH promoted the dispersion of LDH layers resulting in the significant increase of tensile strength. At a loading 1, 3, 5, 7, 10 and 15 phr ZnAl LDH-DS, tensile strength is increased by 16.13, 21.58, 24.67, 27.57, 13.22 and 10.65 %, respectively. The optimum tensile strength was at 7 phr, with the tensile strength of 22.45 MPa. This observation is due to the intercalation of NR into the interlayer galleries of ZnAl LDH-DS. The increase of the interlayer spacing helps the NR molecules to intercalate into the clay layers (Alexandre and Dubois, 2002). However, the ultimate tensile strength decreases for 10 and 15 phr LDH loading, probably due to the poor dispersion or agglomeration of clay in the NR matrix or collapsed structure of the composite due to the thermodegradation.

Conclusions

Nanocomposites of NR/ZnAl LDH-DS were successfully prepared through melt intercalation method. XRD data indicates that the LDH was dispersed in the NR matrix at a nanometer scale and an intercalated structure was obtained. However, TEM images showed the formation of exfoliate together with the different grade of intercalated nanolayers are formed in this composite structure. Their tensile strength is better in comparison to macrocomposite of NR/ZnAl LDH-NO₃⁻.

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