

Synthesis and Characterization of Nanocomposites Based on Polyethylene and Mg-Al Layered Double Hydroxide with Intercalated Compounds

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Abstract-Anionic layered Mg-Al Layered Double Hydroxides (LDHs) have the potential to develop a broad range of new polymer nanocomposites with improved properties viz flame-retardancy (FR), retention or stabilization of dyes, additives, etc. New Low density polyethylene (LLDPE) based nanocomposite materials containing Mg-Al LDH and biocides (BIT) have been designed, synthesized and characterized. MAH-g-PE is used as a compatibilizer. Modification of LDH changes interlayer spacings (distance). Thermogravimetry analysis (TGA) depicted that the loss of biocides due to diffusion/ evaporation is clearly reduced by LDH. Scanning transmission electron microscopy (STEM) images of diluted samples show that most LDH still consist of several layers indicating incomplete or little exfoliation.

Keywords- Low Density Polyethylene; Nanocomposite; Biocides; Compatibilizer; Scanning Transmission Electron Microscopy

I. INTRODUCTION

Preparation of novel polymer nanocomposites based on exfoliated inorganic layered materials is rapidly expanding. Layered Double Hydroxides (LDHS) through the incorporation or exchange of anions into layered host, exhibit an interesting combination of chemical, physical and mechanical properties when compared to those of two separate components [1-11]. Layered Double Hydroxides (LDHs), based on Al/Mg (or other metals) have flexible chemistry options, good anion exchange capacity in the interlayer and good thermal stability. These properties of Layered Double Hydroxides (LDHs) make it a material that has the potential to develop a broad range of new polymer nanocomposites with improved functionality such as flame-retardancy (FR), retention or stabilization of dyes, anti-microbial additives and other additives.

Layered Double Hydroxides (LDHs) have a layered structure similar to clays such as Montmorillonite (MMT), and it is possible to separate these layers [3-4], thus forming large sheets of thickness in the nanoscale. This makes the material suitable for the production of nanocomposites. It is also known as “mixed metal double hydroxides” or “anionic clays”.

Layered Double Hydroxides (LDHs) possess anion exchange property and incorporate a wide variety of inorganic or organic functional anions into the interlayer [12-14]. Such anions are more abundantly available than the cations required modifying MMT. This helps for development of novel products containing polymers and Layered Double Hydroxides (LDHs).

The use of Layered Double Hydroxides (LDHs), for flame retardancy (FR) enhancement, as a carrier for dyes and antimicrobial additives, in which are widely known to people. Layered Double Hydroxides (LDHs) improve the FR performance compared to virgin material [15]. However, due to limitations on the maximum loading of Layered Double Hydroxides (LDHs), in a polymer matrix, it will be extremely difficult to claim any novel IPR on the concept of combining metal(OH)_x with nano-Layered Double Hydroxides (LDHs), for flame retardancy (FR). The focus was shifted to polymeric compounds containing Layered Double Hydroxides (LDHs) for their use as carriers for antimicrobial compounds. Layered Double Hydroxides (LDHs), are known to host/intercalate various anionic molecules including biomolecules and to show controlled release properties (in absence of polymers) [16-17]. The combination of Layered Double Hydroxides (LDHs), with antimicrobial molecules could lead to novel and more durable anti-microbial plastics.

Plastic materials can easily host pathogens, helping them grow both in mass and number by providing them support in the form of surface. Besides, the pathogen (bacteria, algae and fungi) can derive their nutrition from the material used to constitute plastic. This corrosion of plastic by pathogens is represented as staining and pitting of plastic. Several materials from different classes of biocides are used to counteract with the pathogens/microorganisms e.g. arsenic based or Ag-based compounds [18]. Despite this, these materials do produce some serious problems regarding the properties of plastic like color i.e. these materials cause discoloration of plastic. Although, organic biocides are available and can be used, they prove inefficient many times considering their thermal sensitivity and so their leaching out of the plastics renders them inactive. This could be overcome if these organic

biocides are stabilized, but unfortunately still there is not any protocol developed for the same. Reports on polymer nanocomposites in the combination of Polymer + Layered Double Hydroxides (LDHs) +Antimicrobial compounds are still very rare. The aim of present exploratory work is to develop a novel polymer composite that consists of LDH, organic biocides along with plastics, producing a material that would possess impressive thermal stability and consistent antimicrobial activity. LLDPE based nanocomposites have been formulated and synthesized using organically modified Mg-Al-Layered Double Hydroxides (LDHs).

The efforts have been concentrated on synthesizing potential biocides which would fulfill the criteria like their availability in the active form, i.e. anionic form, besides they must sustain and remain active at a temperature of 200 °C or more, they should be active to target micro-organisms and these compounds must show neutral nature towards human beings and other living organisms. For all these reasons, 1,2-benzisothiazolin-3-one, *o*-phenylphenol and 1,2-thiazol-3-one were selected as potential biocides (Fig. 1).

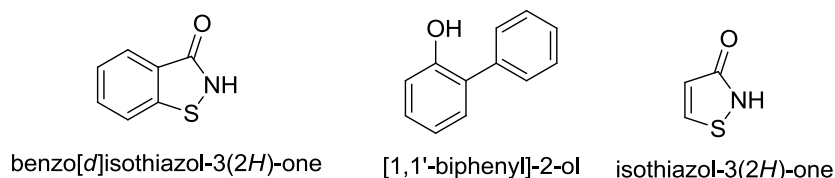


Fig. 1 Structure of biocides

II. EXPERIMENTAL

A. Preparation of PE Nanocomposites Containing LDH and Biocides

PE nanocomposites were prepared by compounding the ingredients using the melt blending technique and then by molding the samples into required shape and size using a compression press. The preparation is limited to a moderate temperature range (160-200 °C) for both processing and molding, as organically modified LDH as well as biocides have poor thermal stability. This temperature range is also suitable for the processing of LDPE and MAH-g-polyolefins.

B. Compounding of Materials Using Melt Blending

Materials were compounded in a Haake PolyLab 6 compounder with the sigma mixer assembly for duration of 5 minutes. The processing temperature used was 160 °C and the compounder speed was set at 60 rpm. Compounding was carried out in two steps. The initial step included preparation of master batch wherein amount of biocide and LDH were much more than the one required in the final composition but the ratio of LDH: Biocide was maintained (Table 1).

TABLE 1 MASTERBATCH COMPOSITIONS

Ingredients	Weight , %				
LLDPE	85	55	97.5	90	90
Perkalite FR100	0	30	0	7.5	20
0 phenyl phenol	15	15	0	0	0
Canguard BIT 20AS E (contains 20% BIT)	0	0	2.5	2.5	0

The second step involved dilution of the master batches in polymer along with addition of compatibilizer to get the desired composition (Table 2). Compounding the material in two steps not only helps in better dispersion of LDH and compatibilizer but also makes it easy to handle the biocide. The possibility of variation in composition from batch to batch is also minimized as below.

TABLE 2 DILUTED COMPOSITIONS

Batch Name	03B	04LB	07B	08L	05L
Ingredients	Weight , %				
LLDPE	97.5	91.5	99.95	98.8	94
Perkalite FR100	0	5	0	0.15	5
0 phenyl phenol	2.5	2.5	0	0	0
Canguard BIT 20AS E (contains 20% BIT)	0	0	0.05	0.05	0
Amplify GR 216	0	1	0	1	1

C. Compression Molding

The compounded samples were molded into sheets using a compression molding press for further testing. The molding temperature was maintained to 170 °C and the compressive pressure applied was 6 Kg/cm². The total molding duration was 20 minutes which included 5 minutes heating and cooling cycle of 15 minutes. The samples were molded between two PET sheets to avoid any contamination by the mold surface.

III. RESULTS AND DISCUSSIONS

A. X-ray Diffraction Analysis

The pristine LDH materials are not suitable for intercalation by large species like polymer chains because the intergallery space is too short to (Fig. 2 and Table 3) allow polymer chains to penetrate in and the charged nature of the metal hydroxide layers makes them incompatible with non-polar species. In order to make such layered materials suitable for intercalation and ultimately exfoliation by polymer molecules, it is necessary to make interlayer regions compatible and large enough so that the polymer molecule could penetrate either as a whole or in its segment form. Therefore pristine LDH materials were treated with anionic surfactant stearic acid which replaced carbonate ion and water molecules in the interlayer regions. This modified LDH is Perkalite FR100.

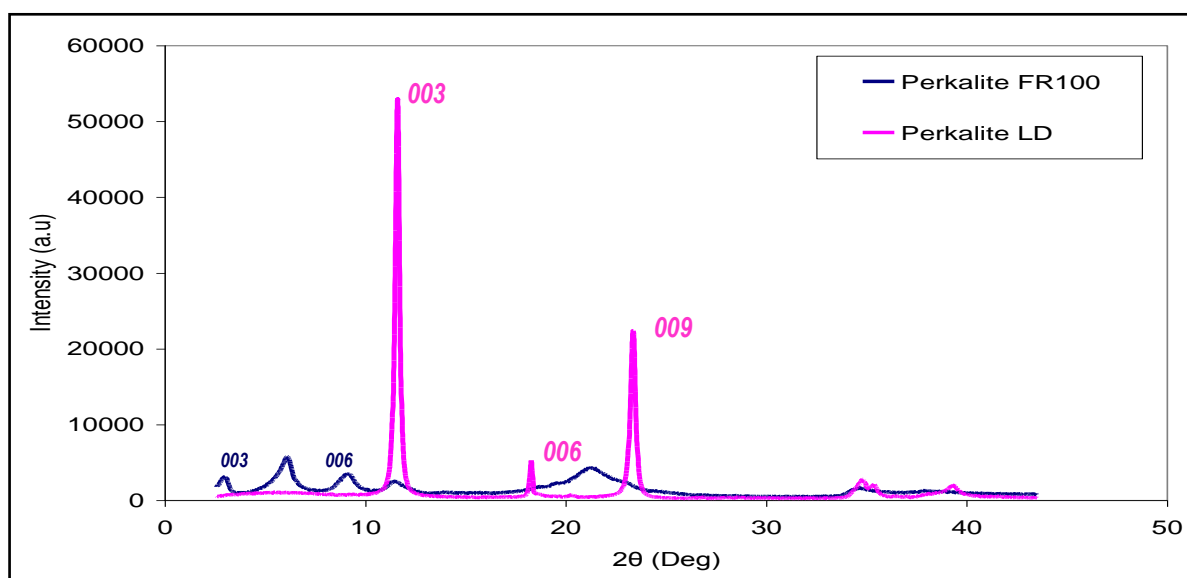


Fig. 2 XRD spectra of Perkalite LD (pristine LDH) and Perkalite FR100 (modified LDH)

TABLE 3 ASSIGNMENT OF XRD REFLECTIONS OBTAINED FOR LDH, ITS MODIFIED FORM AND PE COMPOSITES

Materials	Peak position of (003) reflection 2θd (Å)		Remarks
Pristine LDH(Pural MG 63 HT)	13.49	7.62	Highly crystalline, layered
Mod.LDH(Perkalite FR100)	3.47	29.58 ↑	Enlargement of inter layer distance
01L05L(PE+PerkaliteFR100)	3.25	30.08 ↑	Much broader peaks, smaller crystal size
02L(PE+Pural MG 63HT)	Same as Pristine LDH		No change in interlayer spacing d
03B(PE+0 phenyl phenol)	No peaks		-
04LB (PE+PerkaliteFR100+0 phenyl phenol)	Presence of LDH structure		Much broader peaks, no change in d
07B (PE+BIT)	No peaks		-
08LB(PE+PerkaliteFR100+BIT)	Presence of LDH structure, No change in d-spacing similar to Perkalite FR100.		Final does not show much PerkaliteFR100, could be due to too low concentration

The XRD spectrum of synthesized Mg–Al LDH (Perkalite LD) illustrated here, it shows that the synthesized material has highly crystalline nature and layered geometry. The position of the basal peak (003) indicates that the distance between two adjacent metal hydroxide sheets (d_{003} in Fig. 2 and Table 3) is about 7.6 Å. With such small interlayer distance, it becomes necessary to modify the basic LDH materials so that the crystal layers are moved apart and penetration of polymeric chains becomes less difficult. As a result, the position of the basal peak in the XRD spectrum shifts to lower value of 2θ (Fig. 2). This results in an enlargement of interlayer distance from 7.6 to 29.58 Å.

The assignment of XRD reflections obtained for LDH, its modified form and PE composites are given in Table 3. Upon compounding with LLDPE, there is a slight increase (or no increase) of interlayer distance by $\sim 0.05 - 1 \text{ \AA}$. Here a clear shift of the basal 003 peak is observed with broadening and lowering of peak intensity or disappearance of the higher order reflection peaks indicating the preservation of the short range ordering of the stacked metal hydroxide layers due to high degree of exfoliation of the LDH crystallites (Fig. 3).

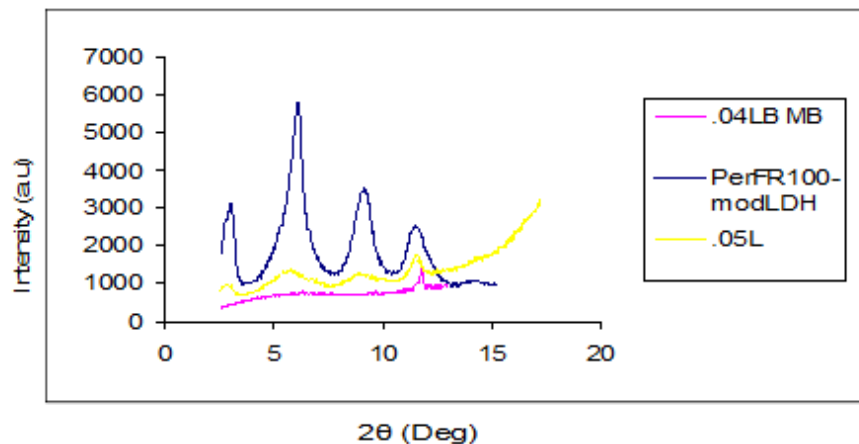


Fig. 3 XRD spectra of Perkalite FR100 (modified LDH), PE/LDH and PE/LDH/Biocide composites

B. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectrum (Fig. 4) of Mg-Al LDH revealed that the presence of interlayer carbonate ions (1356 cm^{-1}) and water molecules (the broad band in the range $3150\text{--}3600 \text{ cm}^{-1}$). The hydrogen bonding in the interlayer region between water molecules and the hydroxide sheet is evident for the shoulder at $3050\text{--}3100 \text{ cm}^{-1}$ in Mg-Al LDH spectrum. In Perkalite FR100, the loss of interlayer, carbonate anions and water molecules results in disappearance or weakening of the corresponding peaks in FTIR spectrum. The weak and broad peak around 3400 cm^{-1} in Perkalite FR100 spectrum might be due to some adsorbed water molecules on the surface of it. In nanocomposites, the IR spectrum is similar to PE.

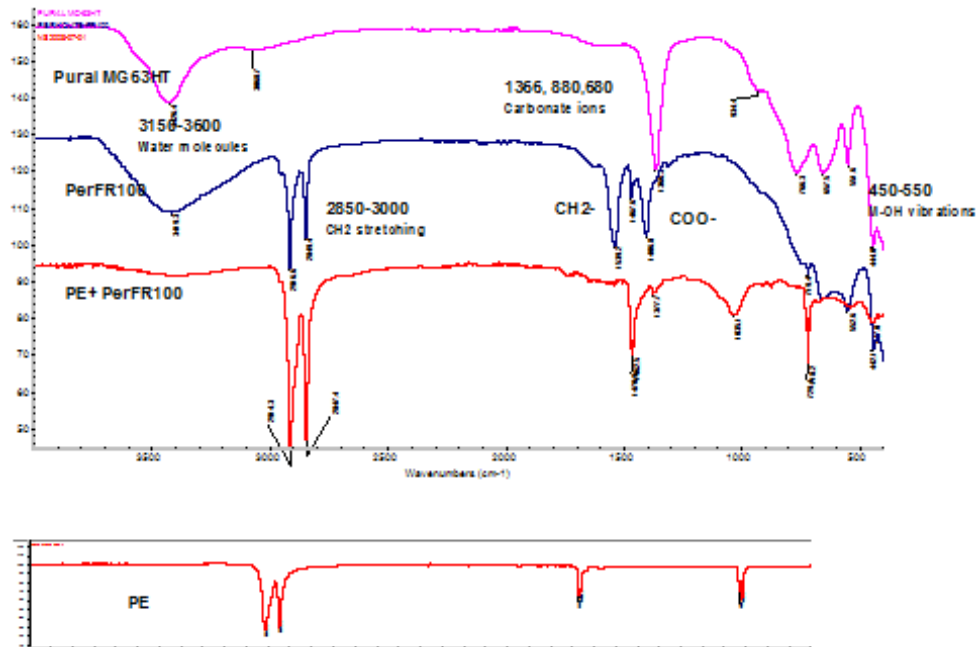


Fig. 4 FTIR spectra of Perkalite LD, Perkalite FR100 and PE/Perkalite FR100

C. Scanning Transmission Electron Microscopy (STEM)

Electron microscopy analysis of the composites revealed a very complex nature of the morphology of the dispersed LDH particles, which varied widely in sizes and shapes. The distribution of the particles in the LLDPE matrix appeared as homogeneous as shown in Fig. 5. However higher magnification STEM images showed diffused nature of these particles. The detection of single LDH layers was not possible in these STEM images this might be due to the resolution limit of the instrument, as the thickness of single metal hydroxide layers of LDH ranges from 4.8-4.9 Å or may be the absence of the high degree of the exfoliation or incomplete exfoliation.

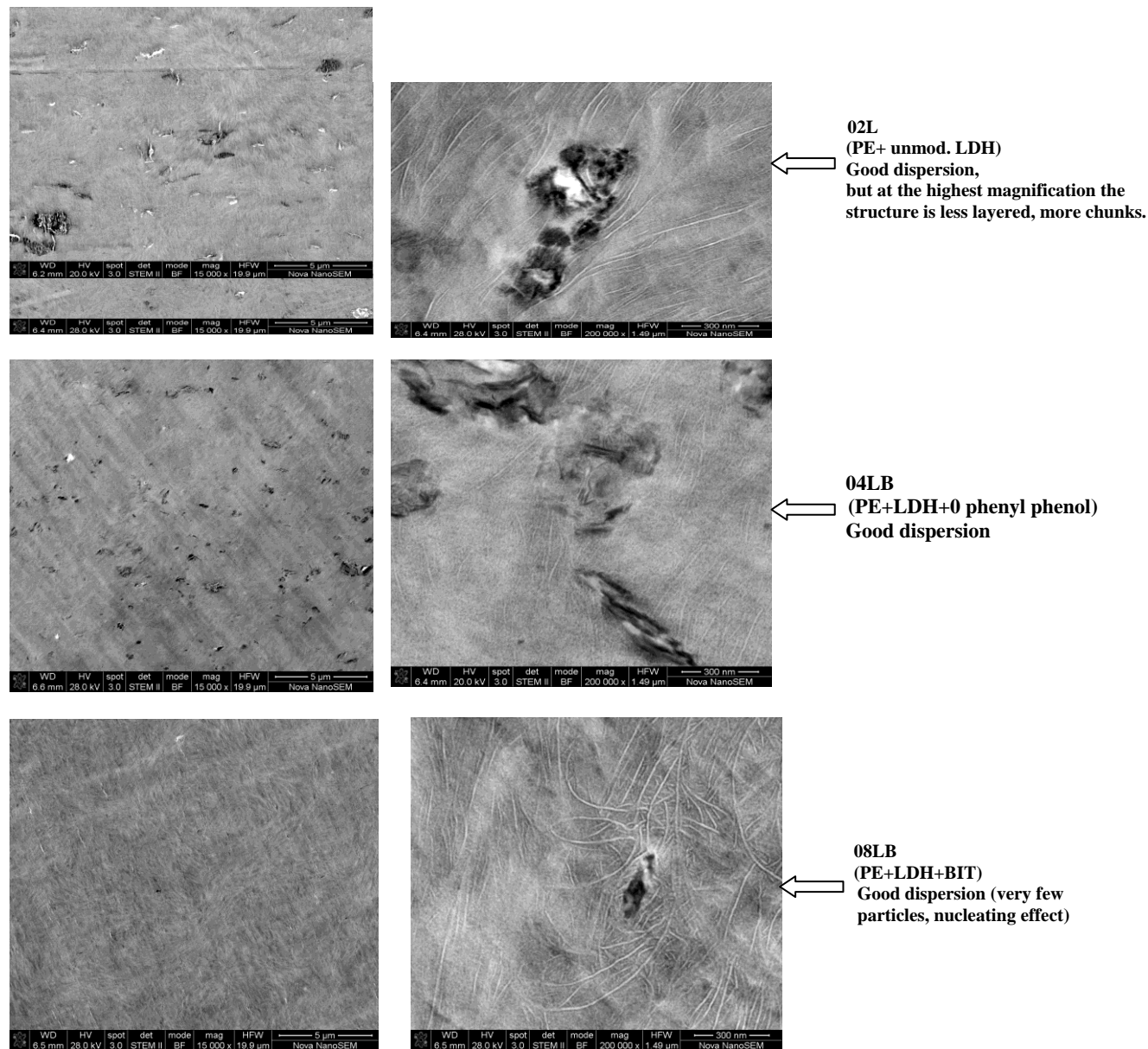


Fig. 5 STEM images of PE + LDH (Modified and Unmodified) along with BIT

1) Thermogravimetric Analysis (TGA)

The thermal behavior of LDH is a two-stage decomposition process: at low temperature up to about 225 °C the interlayer water is desorbed however at higher temperatures ranging from 225 to 500 °C (Fig. 6) decomposition occurs due to the loss of interlayer carbonate and dehydroxylation of the metal hydroxide layer. Often the high temperature decomposition proceeds in two distinct steps depending upon the Mg+2/Al+3 ratio. This tendency becomes more prominent as the Mg+2/Al+3 ratio increases. However, it has also been observed that the release of interlayer carbonate started as early as 250 °C and continued till 500 °C.

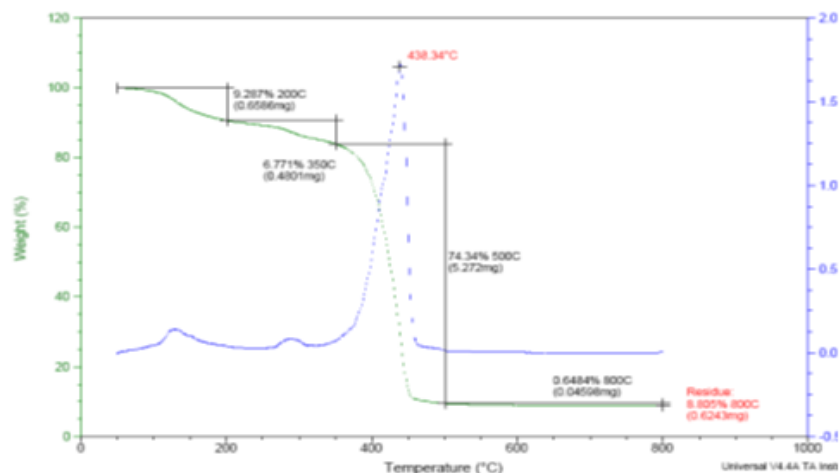


Fig. 6 TGA curves for PE nanocomposite (PE+LDH +Biocide1) 04LB

In the present study, the LDH showed thermal decompositions in three stages (Fig. 6) the first curve is weight versus temperature while the second one is first derivative curve of weight versus temperature. The weight loss is up to 430 °C. It was essential to estimate the amount of each additive after compounding with polymer PE. For this purpose calculation of the residue weight of pure Perkalite FR100 (modified LDH) and Perkalite FR100 in composites by TGA analysis was done. The results are enlisted in Table 4. It can be said that the residue weight of Perkalite FR100 in composites was comparable to that of calculated for Perkalite FR100.

TABLE 4 THE RESIDUE WEIGHT BY TGA

Master batch sample	03B	04LB	07B	08LB	05L
Ingredients	Weight, %				
LLDPE	85	55	97.5	90	80
Perkalite FR100	0	30	0	7.5	20
Pural MG 63HT					
o- phenyl phenol	15	15	0	0	0
CANGUARD BIT 20AS E (contains 20% BIT)	0	0	2.5	2.5	0
Residue TGA	0.20	8.80	0.24	2.74	6.53
Calculated LDH	0.66	29.14	0.79	9.07	21.62

2) Isothermal TGA: Sample Heated at Constant Temperature

Preliminary of Isothermal TGA results indicated that the loss of o-phenyl phenol due to diffusion/ evaporation was clearly reduced by LDH. LDH did slow down the loss of o-phenyl phenol but for BIT it was not much measurable. In the sample containing o-phenyl phenol and LDH, the weight loss seemed mainly due to loss of water from the LDH. The Isothermal TGA of pure material - the rapid loss of o-phenyl phenol - suggested that 150 °C may be too high. Isothermal TGA was repeated at 130 °C (Table 5).

TABLE 5 ISOTHERMAL TGA AT 150 °C AND 130 °C

Master Batch sample	03B	04LB	05L
Ingredients	Weight, %		
LLDPE	85	55	80
Perkalite FR100	0	30	20
o-phenyl phenol	15	15	0
Isothermal TGA (Wt loss in 60min)	0.86	0.47	0.52
Weight at 150C	98.81	96.1	98.28
Weight at 150C + 60min Isothermal	97.95	95.63	97.76
Isothermal TGA (Wt loss in 60min)	0.90	0.94	0.91
Weight at 130 °C	99.31	96.89	98.66
Weight at 130 °C + 60min Isothermal	98.41	95.95	97.75

IV. CONCLUSION

LLDPE/LDH-Biocides nanocomposites have been synthesized using MAH-g-PE as the compatibilizer. The interlayer spacings in particular and clay structure in overall are changed dramatically and good intercalation is achieved for LDH. The loss of interlayer, carbonate anions and water molecules have been confirmed using FTIR. The crystal structure of LDH in composites remained intact up to 450 °C. The TGA analysis revealed that the residue weight of LDH in composites is comparable to that of calculated for pure LDH.

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