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Effect of modified layered double hydroxide on the flammability and mechanical properties of polypropylene

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Abstract: Copper-aluminum layered double hydroxides (Cu-LDHs) and nickel-aluminum layered double hydroxides (Ni-LDHs) were synthesized using co-precipitation method. LDHs were organically modified by long chain sodium stearate. Polypropylene (PP)/layered double hydroxides (LDHs) and polypropylene (PP)/organically-modified layered double hydroxides (m.Cu-LDHs or m.Ni-LDHs) were prepared through the melt bending of the PP with either nanosized LDHs or m.LDHs without any other additives. The effect of stearate on the dispersibility of LDHs was investigated by X-ray diffraction (XRD). The surface morphology of LDHs was also studied using scanning electron microscope (SEM), and the thermal stability properties of PP/LDHs composites were studied by thermogravimetric analysis (TGA). The mechanical properties of the PP/LDH composites, tensile strength, and modulus of elasticity were investigated. The flammability properties were investigated using the cone calorimeter test. The intercalation of modified LDHs was determined by XRD in the presence of stearate. Results showed that modified LDHs presented good disperasbility in the PP matrix. The thermal stability of PP has been improved by up to 6% using m.Ni-LDHS. Unmodified and modified nanosized LDHs decreased the fire growth rate of PP from 10.8 kW/m².s to 4.1 kW/m².s and 4.5 kW/m².s, respectively.

Keywords: flame retardancy; modified layered double hydroxide; polypropylene composites.

1 Introduction

The incorporation of layered double hydroxide (LDH) into polymers to form polymer –LDH nanocomposites has gained increasing research interest, along with the improvement of their properties like thermal, mechanical, and fire retardant is increasing interest in the research of material chemistry. LDHs, also known as hydrotalcite-like materials, are anionic clays that are inexpensive and environment friendly [1–5]. The introduction of long-chain organic anions into LDH leads to the formation of alternating metal hydroxide layer-organic anion layer hybrids, in which the intercalation of many long-chain surfactant anions, including alkyl carboxylates, alkyl sulfate, and alkyl sulfonates, have been reported [6, 7].

The interlayer anions can be exchanged by other organic anions, a process that leads to the modification of their chemical and environmental properties. Furthermore, increasing the compatibility of LDH with the polymer is difficult, because the clay is polar, whereas the polymer is non-polar. Many nanocomposites were prepared using non-polar polymers with compatiblizers such as maleic anhydride were published [8, 9]. The compatibility of the polymer with inorganic filler is increased by the surface modification of inorganic fillers with small organic compounds, which have a polar group [10–13]. The harmonization of organically-modified Mg-Al-layered double hydroxides with polypropylene was carried out by melt blending the polymers with LDH [14, 15]. The creation of PP/LDH nanocomposites was carried out by melt intercalation using PP-g-MAH as a compatible agent. The interaction between the LDH and PP matrix was improved via organic modification, the mechanical properties of tensile strength and modulus increased as LDH content increased, and the thermal stability of the PP/LDH composites was improved [16, 17]. Different types of PP/LDH nanocomposites have been reported, including PP/Mg-Al-LDH [18, 19], and PP/Co-Al-LDH [20].

The effects of nanosized Ni-Al LDHs, Cu-Al LDHs, modified Ni-Al LD, and modified Cu-Al LDH by sodium

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stearate on the mechanical and flame retardancy of PP are reported in this study. The results of this study should stimulate future research on the further development of polymer/LDH composites for a wide range of practical applications.

2 Materials and methods

2.1 Materials

All materials were used as received without any further purification. Anhydrous aluminum chloride (AlCl_3), sodium chloride (NaCl), and methanol (CH_3OH) were purchased from Alfa Aesar Co. Sodium stearate ($\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}$) and sodium hydroxide (NaOH) were received from Merck Aldrich (Germany), whereas nickel chloride ($\text{Co. NiCl}_2 \cdot 6\text{H}_2\text{O}$) and copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were supplied by Sdfine. Chem Limited, Co (UK).

2.2 Preparation of nanosized copper aluminum LDH and nickel-aluminum LDH

Nanosized LDHs were synthesized by using the co-precipitation method [21]. Anhydrous aluminum chloride (13.33 g) was dissolved in 200 ml distilled water in the presence of 19.99 g (0.342 M) of NaCl in a three-neck round-bottom flask under magnetic stirrer (800 rpm). Copper chloride dehydrate (34.52 g) was separately dissolved in 200 ml distilled water. Copper solution was mixed with aluminum solution for 30 min at 800 rpm and at room temperature. The pH of the resulting copper and aluminum salt mixture solution was around 3.95. Sodium hydroxide (50 wt%) solution was added drop-wise to the salt mixture solution with vigorous stirring to reach pH of 10.28. The resulting slurry was aged in the mother liquid for 24 h at 70°C . LDH precipitate was collected by filtration using a Buchner funnel. The collected LDH precipitate was washed several times by using distilled water and dried at 70°C in an oven for 24 h. Ni-Al LDH was typically synthesized and processed as Cu-Al LDH. The resulting LDHs were marked as Cu-LDH and Ni-LDH for Cu and Ni ion, respectively.

2.3 Preparation of nanosized modified copper-aluminum LDH and nickel- aluminum LDH by sodium stearate

Cu-LDH (15 g) or Ni-LDH (15 g) was dispersed in 400 ml of sodium stearate solution (0.008 M) and then vigorously

stirred for 48 h at 100°C . The resulting organic modified LDHs were collected by filtration, washed several times using distilled water, and then dried at 70°C in an oven for 24 h. The resulting modified LDHs were labeled as m.Cu-LDH and m.Ni-LDH.

2.4 Processing of PP/LDH nanocomposites

Different percentages (0.5, 1, 1.5 and 2 wt%) of LDHs without further additives were mixed with polypropylene powder. The PP/LDHs mixture was fed into an extruder (at 220°C and 36 rpm). The PP/LDH composites were shredded using a crusher and injected using injection molding. The composition of the PP/LDH composites is listed in Table 1. Organic m.Ni-LDH with three different loadings (0.5, 1, and 1.5 wt%) are illustrated in Figure 1. The critical limit of Ni-LDHs and Cu-LDHs in the PP

Table 1: Compositions of the PP/LDH nanocomposites.

Sample code	PP (wt%)	Ni-LDH (wt%)	m.Ni-LDH (wt%)	Cu-LDH (wt%)	m.Cu-LDH (wt%)
H0	100	–	–	–	–
H1	99.5	0.5	–	–	–
H2	99	1	–	–	–
H3	98.5	1.5	–	–	–
H4	99.5	–	0.5	–	–
H5	99	–	1	–	–
H6	98.5	–	1.5	–	–
H7	99.5	–	–	0.5	–
H8	99	–	–	1	–
H9	98.5	–	–	1.5	–
H11	99.5	–	–	–	0.5
H12	99	–	–	–	1
H13	98.5	–	–	–	1.5

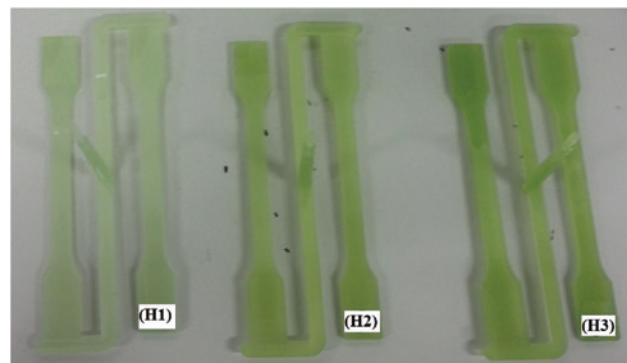


Figure 1: PP/m.Ni-LDHs (H1:0.5 wt%, H2:1 wt%, and H3:1.5 wt%).

matrix was found to be 1.5%, at which LDHs aggregated at 2% and were no longer completely spattered by the PP matrix loading. Therefore, in this study, different percentages of LDHs were dispersed and processed in neat PP, namely, 0, 0.5, 1.0 and 1.5 (wt./wt)%.

2.5 Characterization

2.5.1 X-ray diffraction (XRD)

XRD patterns were recorded using Philips XPERT-PRO (USA) with nickel-filtered CuK α ($k=1.5405$) radiation.

2.5.2 Thermogravimetric analysis (TGA)

Thermal stability was studied by TGA (TA Instruments-Q50, USA). The thermal degradation process was carried out under N₂ atmosphere from 30°C to 500°C at a heating rate of 20°C/min.

2.5.3 Mechanical test

The tensile strength of the PP/LDH composites was measured using universal mechanical testing machine (ZWIC B066550) at 25°C. Specimens were manufactured according to ISO 37. Tensile speed for the tests was 2 mm/min. Each datum of the tensile test was the average of the three values.

2.5.4 Scanning electron microscopy (SEM)

The morphological studies for Ni-LDH and Cu-LDH powder were carried out using scanning electron microscope (SEM), FE-SEM Zeiss Leo Supra 55 (American University in Cairo unit). Samples were sputtered by thin film made of gold to improve conductivity.

2.5.5 Flammability testing

Cone calorimeter represents a small-scale testing configuration, which provides important correlating parameters

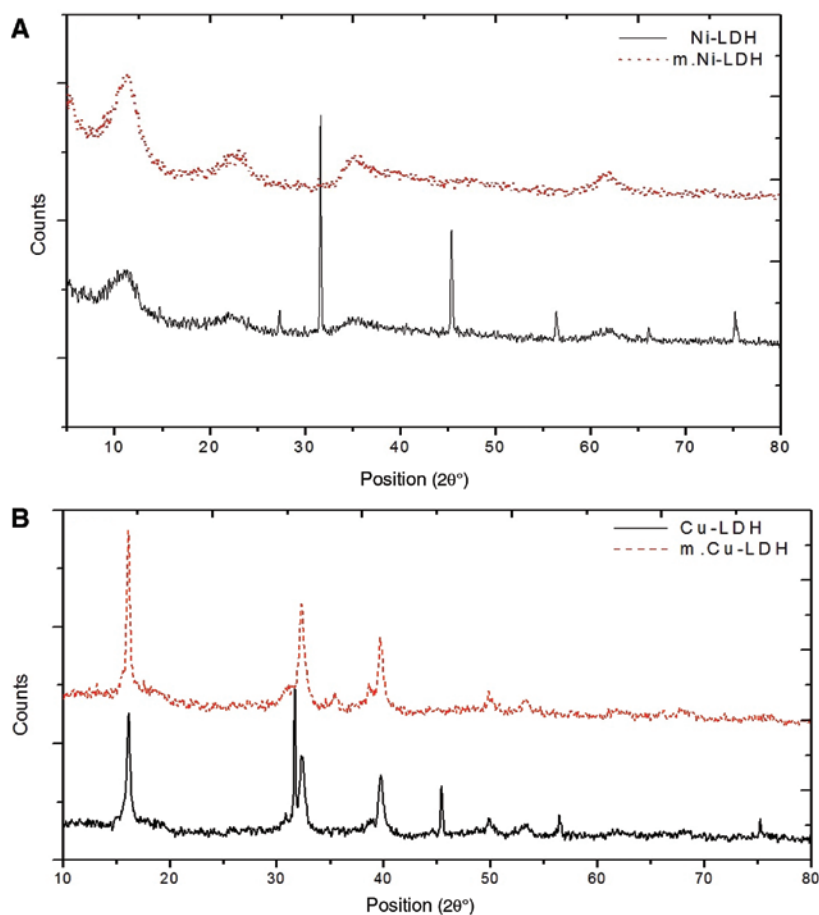


Figure 2: XRD patterns of (A) nanosized Ni-LDH and m.Ni-LDH and (B) Cu-LDH and m.Cu-LDH.

with real fire scenarios. The values provided by a cone calorimeter mainly consist of time to ignition (TTI), which corresponds to the period at which combustible materials can withstand the heat when exposed to a constant radiant heat flux before igniting and undergoing sustained flaming combustion. Peak of heat release rate (PHRR) and heat release rate average (HRR average) are quantitative measures of thermal energy released by a material per unit area when exposed to a fire radiating at constant heat flux (or temperature).

Flammability cone calorimeter testing was conducted based on ISO 5660-I standard using a cone calorimeter (Fire Testing Technology, Ltd., UK). Square samples with a dimension of 100×100 (mm) were placed in a horizontal direction. Samples were irradiated with the heat flux of 50 kW/m^2 . Measurable parameters were detected as follows: (i) TTI, (ii) HRR and PHRR, (iii) mass loss rate (MLR), (iv) specific extension area (SEA), (v) effective heat of combustion (EHC), (vi) total heat release (THR), and (vii) carbon monoxide and carbon dioxide yield. Measurements were conducted before and after the addition of the flame retardants.

3 Results and discussion

3.1 X-ray diffraction (XRD)

The XRD patterns of nanosized Ni-LDH, m.Ni-LDH, Cu-LDH, and m.Cu-LDH, are shown in Figure 2(A) and (B). The peaks of Ni-LDH are recorded at $2\theta = 32^\circ$, 46° , and 56° . The sharp peaks of Cu-LDH are recorded at $2\theta = 15^\circ$, 32° , 40° , and 46° . The peaks of m.Ni-LDH and m.Cu-LDH are broad, and the peaks at 46° and 56° could not be detected for the m.Ni-LDH sample. Meanwhile, the peak at $2\theta = 46^\circ$ is not found in m.Cu-LDH. These broad and non-detectable peaks in the m-LDH sample can be attributed to the intercalation of modified hydroxide layers in the presence of stearate. The extension between the layers of double hydroxide was achieved as a result of the intercalation of stearate chains onto the layered double hydroxide [22]. The shifting and broadening of peaks due to an increase of basal spacing) and the increase of inter layer space depended on the intercalation nature of the functional group, the size of the surfactant, and the alkyl chain length of sodium stearate [23].

3.2 Thermogravimetric analysis (TGA)

Figure 3(A) shows that the thermal stability of PP can be significantly improved in the presence of m.Ni-LDH

compared with PP, PP/Ni-LDH, and PP/Cu-LDH. This can be ascribed to the enhanced interfacial force between PP and Ni-LDH in the presence of stearate. PP and PP/LDH composites exhibit a one-step degradation process. The thermal degradation of neat PP starts dramatically at 425°C . The degradation stage of neat polypropylene shifts from 421.85°C to 426.6°C , 450°C and 421.85°C for H3, H9, and H6, respectively. The highest thermal stability of the PP/m.Ni-LDH composite is observed when the weight decreased significantly at 437.9°C . The values of onset decomposition temperature values are presented in Table 2. The temperature values at weight loss (10%) and (50%) are presented as (T_{10}) and (T_{50}), respectively.

3.3 Scanning electron microscopy (SEM)

Figure 4(A) shows the SEM images of Ni-LDH. As can be seen, the unit cell of the LDH is in the nanoscale range of $<50 \text{ nm}$. Figure 4(B) shows that the LDH size is $<100 \text{ nm}$ in the Cu-LDH. These results are similar with those reported by Choi et al. [24].

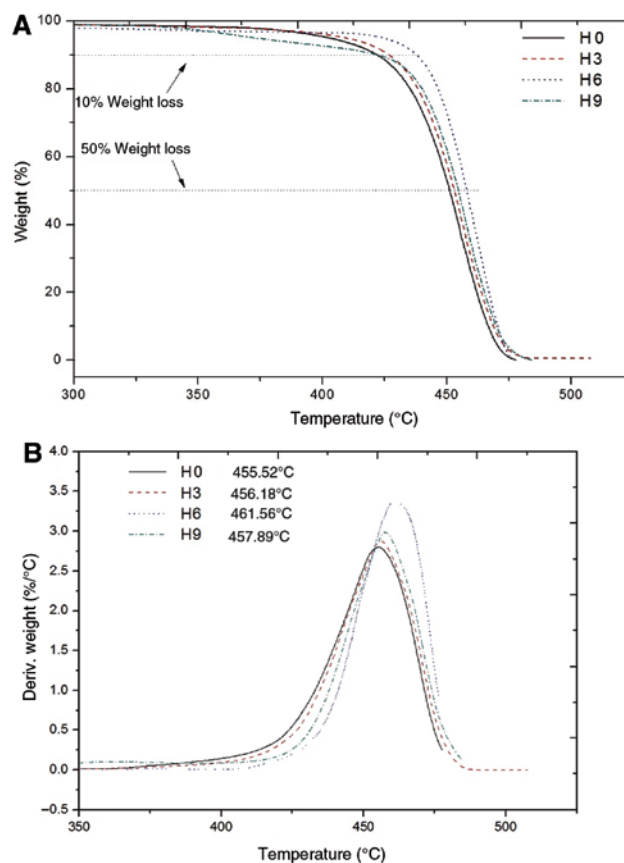
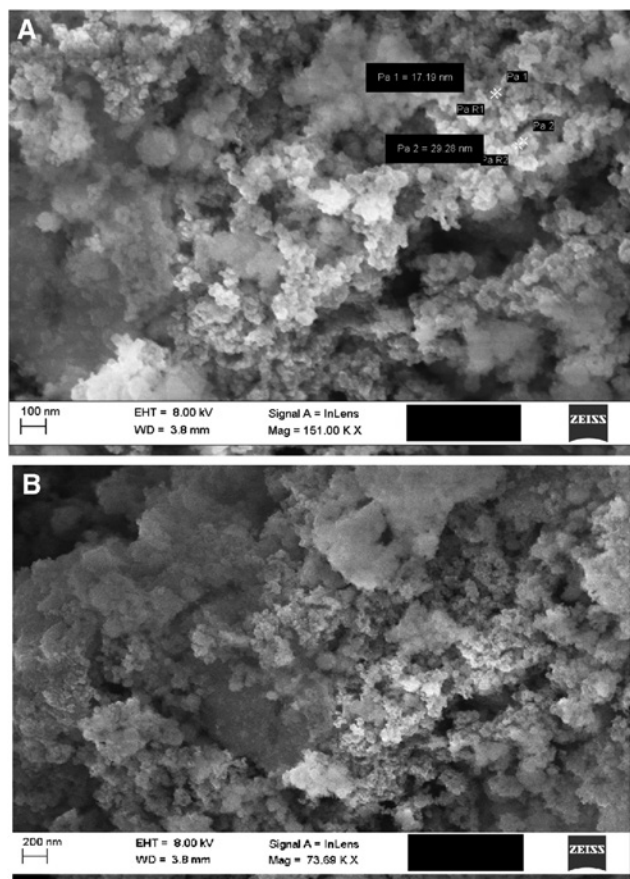


Figure 3: (A) Thermogravimetric analysis (TGA) and (B) derivative TGA of the PP/LDH composites containing different LDH contents.

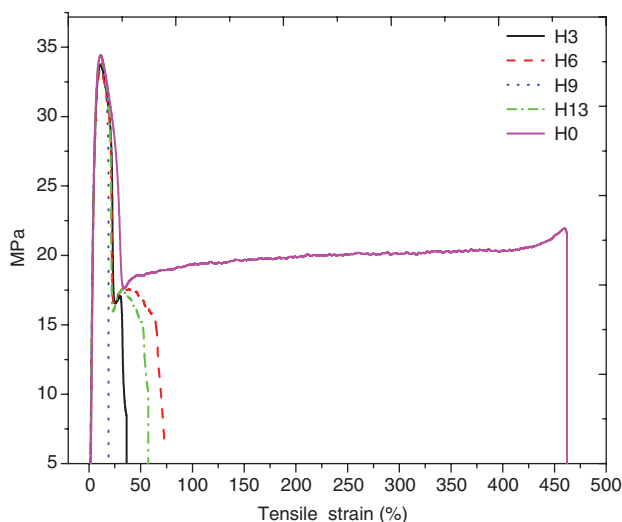
Table 2: TGA data of neat PP and the PP/Ni-LDH, PP/m.Ni-LDH, and PP/Cu-LDH composites.

Sample	T_{10} (°C)	T_{50} (°C)
H0	421.85	451.18
H3	426.68	452.99
H6	450.17	458.18
H9	421.85	454.68

**Figure 4:** (A) SEM of nanosized Ni-LDH, (B) SEM of nanosized Cu-LDH.

3.4 Mechanical properties

The results of tensile modulus, as presented in Figure 5, suggest that LDHs are able to impart stiffness to the composites. The addition of stearate to PP does not seem to contribute to the significant improvement of the tensile strength of the composites. The mechanical properties of PP and the PP/LDH nanocomposites were tabulated in Table 3. Bassyouni [23] suggests that stiffness does not primarily depend on the particle-matrix interface, but more likely on the entire particle's contents in the tensile loading direction, because the modulus of elasticity is defined as a tangent modulus at low strain values (off set

**Figure 5:** Stress-strain curve for the PP and PP/LDH nanocomposites.

0.05%–0.25%). According to Abalov et al. and Zoromba et al. [25–27], the incorporation of inorganic fillers into a thermoplastic matrix can increase or decrease the tensile strength of the resulting nanocomposites. A slight improvement in tensile strength has been detected in presence of stearate (PP/m.Cu-LDH and PP/m.Ni-LDH). For the H3 composite, the tensile strength improved to 33.7 [N/mm²] and elongation at break decreased to 31%. For the H6 composite, the elongation at break was enhanced to 62%; its modulus of elasticity also improved by 18% with 489 [N/mm²] compared with neat PP.

3.5 Flammability properties of PP/Ni-LDH and PP/m.Ni-LDH nanocomposites

The flammability properties of the PP/Ni-LDH and PP/m.Ni-LDH nanocomposites were evaluated using a cone

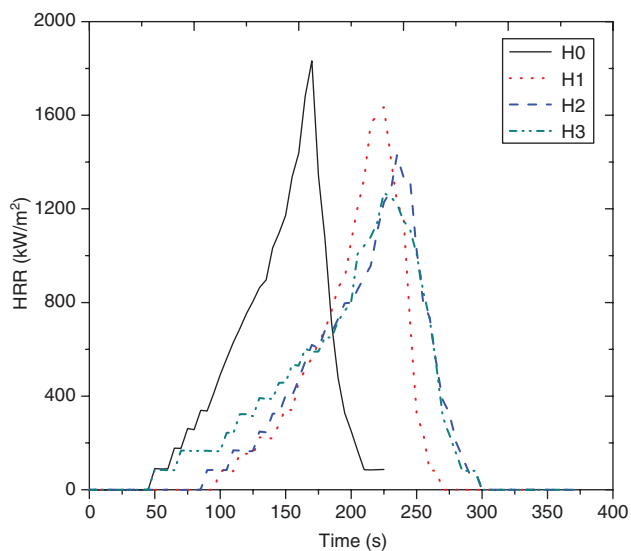
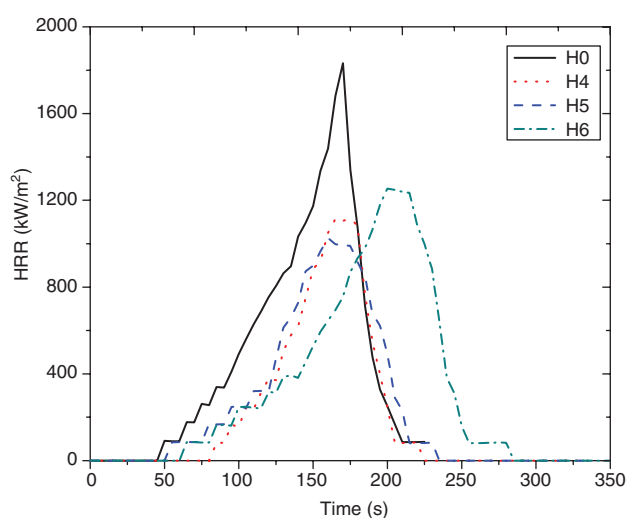
Table 3: Mechanical properties of PP and the PP/LDH nanocomposites.

	Modulus of elasticity	Tensile strength	Elongation at break
	E	σ_m	ϵ_B
	[N/mm ²]	[N/mm ²]	[%]
H0	410	33.3	419
H3	484	33.7	31
H6	489	34.0	62
H9	488	33.4	16
H13	488	34.3	49

Table 4: Cone calorimetric data for the PP/Ni-LDH and PP/m.NiLDH nanocomposites.

Parameter	H0	H1	H2	H3	H4	H5	H6
T_{ign} (s)	45	53	92	41	59	45	49
PHHR (kW/m^2)	1831.96	1635.53	1430.59	1266.66	1116.37	1026.86	1254.95
AHRR (kW/m^2)	615.47	368.37	361.16	368.78	255.25	358.45	358.45
THR (MJ/m^2)	110.8	106.8	117.8	129.1	70.2	81.24	111.1
EHC (MJ/kg)	62.13	69.02	76.89	68.48	61.21	60.9	74.12
SEA (m^2/kg)	2308.50	1464.23	3507.77	2845.69	1114.55	1124.55	3857.66
Time to PHHR (s)	170	225	235	225	175	160	200
Time to end (s)	225	228	304	273	192	335	242
FIGRA ($\text{kW/m}^2\text{s}$)	10.776	7.269	6.087	5.629	6.379	6.417	6.274
FPI (s)	0.02456	0.06430	0.03236	0.05244	0.5284	0.04382	0.03904
Residue yield (%)	0.05	0.25	0.21	0.27	0.27	0.26	0.21

calorimeter. The cone calorimeter data are listed in Table 4. The neat PP (H0) burns very fast after ignition, and a sharp PHHR appears at 1831.96 kW/m^2 . For the PP/Ni-LDH samples (H1, H2, and H3 for 0.5%, 1.0%, and 1.5% Ni, respectively), all composites showed a reduction in PHHR compared with neat PP. The reduction rates are 10.72%, 21.90%, and 30.80% for H1, H2, and H3, respectively, indicating that, with the increase in Ni-LDH loading to PP, the PHHR decreases, as shown in Figure 6. The same behavior reduction of PHHR is detected (39.06%, 43.95%, and 31.59%) for the modified composites PP/m.Ni-LDH (H4, H5, and H6, respectively, as shown in Figure 7. The PHHR values increase in relation to PP/Ni-LDH and PP/m/Ni-LDH nanocomposites by increasing the percentage of Ni-LDH or m.Ni-LDH. The increasing PHHR values in case of PP/m/Ni-LDH is lower than in the case of PP/Ni-LDH. This can be attributed to the existence of stearate in the

**Figure 6:** Heat release rate curves of neat PP (H0) and the PP/Ni-LDH nanocomposites.**Figure 7:** Heat release rate curves of neat PP (H0) and the PP/m.Ni-LDH nanocomposites.

modified LDH. The H4 and H5 composites show THR of 70.2 MJ/m^2 (36.64% reduction) and 81.24 MJ/m^2 (26.67% reduction), respectively, in comparison to neat PP, which has a THR of 110.8 MJ/m^2 . Meanwhile, the H4 and H5 composites showed reduced EHC and SEA values compared with H0, as shown in Table 4.

The fire growth rate (FIGRA) was calculated as PHRR/time to PHRR. This can serve as the basis of predicting fire spread rate and the size of a fire [28]. The FIGRA values for the PP/Ni-LDH and PP/m.Ni-LDH composites show a positive sign in terms of the contribution to the fire growth of materials, as listed in Table 4. The decrease in FIGRA value presents better cone calorimeter performance. Table 4 shows that all PP/Ni-LDH and PP/m.Ni-LDH composites have decreased FIGRA values when the content of Ni-LDH loading increased in the following order $H1 > H2 > H3$ for PP/Ni-LDH and $H4 > H6 > H7$ for PP/m.Ni-LDH compared with neat PP (H0). Furthermore, the fire performance

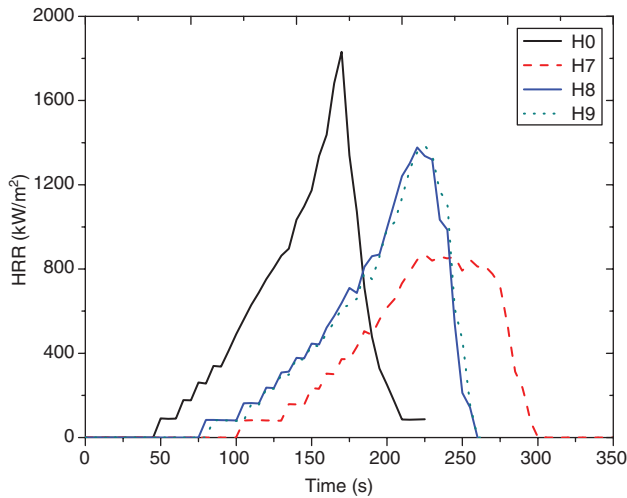


Figure 8: Heat release rate curves of neat PP and the PP/Cu-LDH nanocomposites.

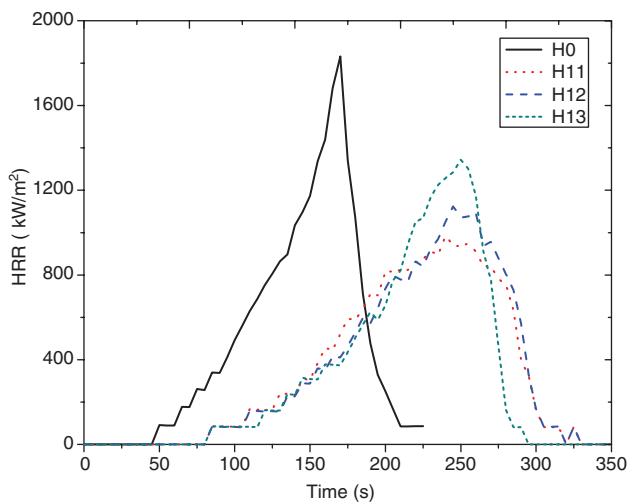


Figure 9: Heat release rate curves of neat PP and the PP/m.Cu-LDH nanocomposites.

index (FPI) was calculated as the ratio between TTI to PHRR, as given in Equation (1) below.

$$\text{FPI} = \text{TTI} / \text{PHRR} \quad (1)$$

This FPI value gives interesting information about all PP/Ni-LDH and PP/m.Ni-LDH compositions. These results are used in this study as a reference for the degree of fire hazard involved [29–31]. The properties of the final masses of the samples are presented in Table 4. The highest final masses corresponding to the PP show the highest FPI values. Hence, all PP/Ni-LDH and PP/m.Ni-LDH composites (H1, H3, H4, and H5) are completely effective.

3.6 Flammability properties of PP/Cu-LDH and PP/m.Cu-LDH nanocomposites

PP/Cu-LDH composites (H7, H8, and H9), show a reduction in PHRR compared with neat PP (H0). The reductions are detected by 43.94% for H7, 30.32% for H8, and 20.85% for H9, as shown in Figure 8. These values refer to the increase in PHRR with increasing Cu-LDH % loadings, as shown in Figure 9. The modified composites (H11, H12, and H13) show a reduction in PHRR values by 46.18%, 35.81%, and 26.57%, respectively, as shown in Figure 9. With increasing percentage of m.Cu-LDH, the PHRR also increases with respect to PP/Cu-LDHs. The H7 sample shows THR of 81.2 MJ/m² (36.64% reduction), whereas all samples have a THR value greater than that of neat PP. All PP/Cu-LDH and PP/m.Cu-LDH composites showed slightly changed EHC and SEA values compared with neat PP.

The fire growth rates (FIGRA) of all PP/Cu-LDH and PP/m.Cu-LDH composites are shown in Table 5. As can be seen, FIGRA decreases with the increase in the unmodified Cu-LDH loadings in the following order: H7 > H9 > H8

Table 5: Cone calorimetric data for the PP/Cu-LDH and PP/m.Cu-LDH nanocomposites.

Parameter	H0	H7	H8	H9	H11	H12	H13
T_{ign} (s)	45	45	57	50	69	54	54
PHRR (kW/m ²)	1831.96	1026.86	1276.46	1449.98	985.91	1175.99	1345.14
AHRR (kW/m ²)	615.47	280.15	487.59	487.03	358.72	328.55	289.29
THR (MJ/m ²)	110.8	81.2	123.0	121.8	120	121.6	114.3
EHC (MJ/kg)	62.13	74.47	67.86	66.80	68.17	76.36	67.70
SEA (m ² /kg)	2308.50	4514.18	3401.63	2209.30	3524.45	2742.48	2742.48
Time to PHRR (s)	170	160	230	225	240	260	250
Time to end (s)	225	215	243	240	405	305	305
FIGRA (kW/m ² s)	10.776	6.417	5.549	6.444	4.107	4.523	5.380
FPI (s)	0.02456	0.04382	0.02663	0.03448	0.06998	0.04591	0.04014
Residue yield (%)	0.05	0.29	0.21	0.23	0.25	0.24	0.21

for PP/Cu-LDH. The FPI values of all PP/Cu-LDH and PP/m. Cu-LDH are presented in Table 5.

4 Conclusions

Nanosized copper-aluminum layered double hydroxides (Cu-LDH) and nickel-aluminum layered double hydroxides (Ni-LDH) were synthesized by using the co-precipitation method. LDHs were organically modified by chain sodium stearate. The intercalation of the stearate was carried out into the layered double hydroxides (LDHs). Polypropylene nanocomposites were prepared with 0.5%, 1%, and 1.5% of unmodified LDHs and stearate-modified LDHs. Thermal stability can be significantly improved using modified LDHs by up to 6% in the presence of m.Ni-LDH. Modulus of elasticity is improved as LDH particle loadings increased. Modified and un-modified LDHs have no effect on the tensile strength of PP. The intercalation of sodium stearate among LDHs is successfully demonstrated and proven by XRD analysis. The flame retardancy of PP can be improved significantly in the presence of nanosized Cu-LDHs and Ni-LDHs. However, modified LDHs have less effect on flame retardancy because of the presence stearate chains.

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