Flammability Properties of HDPE Nanocomposites Based on Modification of Na-MMT with Organo Silane and Ammonium Phosphate Mono and Di basic

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ABSTRACT

Sodium montmorillonite clay was successfully modified by double modification one organic modification and the other inorganic phosphate. The nanodispersion was proven by transmission electron microscope which showed mixed morphology (intercalated, exfoliated and immiscible structures) in polymer matrix. In general, the thermal stability and flammability properties were improved by loading high density polyethylene by double modified clay.

Introduction

Polymer-clay nanocomposites still attract researcher's attention and efforts all over the world because of the enhancement of thermal, mechanical, and flame retardancy properties. In the field of fire retardancy, a low concentration of organo modified clay could reduce the peak of heat release rate, mass loss rate, and improve the char formation (Lei et al, 2011; Kiliaris and Papaspyrides, 2010; Camino et al, 2006; Morgan, 2006; Zhang and Wilkie, 2006; Harris et al, 2005; Wang et al, 2005; Zhu et al, 2002; Zanetti et al 2002; Alexandre and Dubois, 2000; Gilman et al, 2000). To obtain polymer nanocomposites, the clay undergo modification with organic surfactants to increase the compatibility between clay layers and polymer matrix. The interaction between organically modified clay and polymer may result in an immiscible nanocomposite where the clay acting as filler and not dispersed in the nanoscale, or intercalated structure where polymer chains could increase the distance between clay layer and the registry between clay layers maintained, or exfoliated structure where the registry between clay layers disappeared. In some cases, two of these structures or the three structures can co-exist. The exfoliated samples usually have the greatest improvement in different properties except fire retardancy where both intercalated and exfoliated structures have the same behaviour (Chigwada et al, 2005; Morgan and Gilman , 2002; wang and wilkie, 2003). This means that the improvement in properties of polymer-nanocomposites arises from the uniformly distribution of modified clay in polymer matrix. This can be contrasted to an additive, which typically not well-dispersed. So, if we could introduce a fire retardant material with the clay in the polymer matrix, nanodispersion of these material may be achieved, which may enhance the fire retardancy of the polymer. (Zheng and Wilkie, 2003) modified the clay with ammonium salt containing oligomers of styrene , vinybenzyl chloride and diphenylvinyl phosphate or diphenylvinylbenzylphosphate. The new modified clay succeeded in improving the flame retardancy of polystyrene.

The aim of this work is to melt blend newly modified clay with HDPE. The nanocomposite structures will evaluated by TEM and XRD. Also, the flammability properties will evaluated by cone calorimeter.

Experimental

Materials

Sodium montmorillonite clay was acquired from fluka chemika company. High-density Polyethylene with melt flow index 27 was obtained from Polymeri Europa, Eraclene ® , Italy. Ammonium phosphate monobasic was obtained from Viba laborchemie, APOLDA, Germany. 1,1,1,4,4,4-hexamethyl2,2,3,3-tetraphenyl tetra-silane was prepared according to the procedure in reference [5].

Modification of sodium montmorillonite

Preparation of A4

50g Na-MMT was dispersed in 300ml chloroform by stirring using magnetic stirrer for 2h at room temperature. On the other hand, 20g of 1,1,1,4,4,4-hexamethyl-2,2,3,3-tetraphenylsilane was dissolved in 100ml chloroform. Then the dissolved silane compound and the dispersed montmorillonite were added in round flask with condenser and were refluxed with continuous stirring for 96hour at 80°C. The product was filtrated, washed by 400ml chloroform, dried at 70°C for 1hour, and coded with A4.

Preparation of A5

50g of A4 was dispersed in 400ml de ionized water for 3hours at room temperature using magnetic stirrer. 50g of ammonium phosphate mono basic was dissolved in 150ml of de ionized water. Then the aqueous solution of ammonium phosphate mono basic was added to A4dispersion and the stirring continued for 72hour at room temperature. The product was filtrated, washed by 500ml de ionized water, dried at 70°C for 5hours, and coded with A5.

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Preparation of A6

50g of A4 was dispersed in 400ml de ionized water for 3hours at room temperature using magnetic stirrer. 50g of ammonium phosphate di basic was dissolved in 150ml of de ionized water. Then the aqueous solution of ammonium phosphate di basic was added to A4dispersion and the stirring continued for 72hour. The product was filtrated, washed by 500ml de ionized water, dried at $70^{o}C$ for 5hours, and coded with A6.

Preparation of polymer nanocomposites

All polymer nanocomposites were prepared by melt blending method using Newplast twin screw extruder at zones temperature $163^{o}C$, $167^{o}C$, $167^{o}C$ for zone 1, zone 2, and zone 3. The twin screw speed was 30 rpm. The samples obtained from extruder were preheated using Morgan press injection unit at $160^{\square\square}C$ for nozzle zone and barrel zone and were injected to produce 7.5 x7.5 x $\square$0.4 cm and 10 x 0.9 x 0.4 cm molds. The composites formulations are tabulated in table (1).

Characterization

Wide-angle X-ray diffraction (WAXRD) was used to examine the dispersion of clay in HDPE nanocomposites. WAXRD analysis was carried out by using panalytical-empyrean X-ray. Diffractometer system empyrean. Cu K$\square$ radiation (radiation wave length =0.154 nm). The diffraction were obtained at room temperature, the scattering angles starts at ^{o} 2Th = 4.025 and finished at ^{o} 2Th = 60, scan step size ^{o}2Th: 0.0260, scan step time (s): 48.195 and scan Axis: Gonio.

Transmission electron micrographs were obtained with JEM-1230 electron microscope which having maximum magnification power 600KX, maximum resolving 0.2 nm/line, CCD-camera and maximum energy 120 kVolt on steps starting from 40kVolt. The samples for TEM were ultramicrotomed using LEICA EM UC6 ultra microtome with glass knife to produce 60 nm thick sections at room temperature.

Thermogravimetric analysis (TGA) experiments were done in a shimadzu TA-50 thermal analyzer using scanning rate of 10 $^{\square}$C /min under N_2 atmosphere with flow rate 20ml / minute, from room temperature to 750 ^{o}C.

Flammability properties of the nanocomposites were characterized using cone calorimeter. The test performed in duplicate with an FTT, UK device according to ISO 5660 at an incident flux of 35 kW/m^2 using a cone shaped heater. The cone data reported here are the averages of replicated experiments.

Limiting Oxygen Index (LOI) values were determined by Rheometric scientific device according to ISO 4589.

UL-94 test was done by staton redcroft UL94 flame chamber according to ISO 1210. Mechanical properties were measured according to ASTM638, using Zwick tensile testing machine model Z010, Germany.

Results and discussion

X-Ray Diffraction analysis (XRD)

The XRD curves in figure (1a) showed that clay has diffraction peak at ^{o}2 theta =5.84 with d-spacing 15.11^{o}A. This diffraction peak was disappeared for A4, and it was shifted to higher ^{o}2 theta values for A5 and A6. In case of A5 the characteristic peak of clay appeared at ^{o}2 theta = 6.90 with d-spacing 12.79 ^{o}A and for A6 it was appeared at ^{o}2 theta = 6.83 with d-spacing 12.93 ^{o}A.

On the other hand the XRD graphs in figure (1b) showed that the diffraction peak of the clay at ^{o}2 theta = 5.84 was disappeared for HDPE / 5% A4 and HDPE/10%A4 which indicates that A4 have good dispersion in polyethylene matrix.

The XRD pattern for HDPE containing 5%A5 and 10% A5 in figure (1c) showed that the characteristic peak at ^{o}2 theta = 6.90 was also disappeared for 5%A5 and 10%A5 samples. This means that A5 have good dispersion in polymer matrix too. The XRD pattern in figure (1d) showed that the diffraction peak at ^{o}2 theta =6.83 characteristic to A6 was disappeared at HDPE/5%A6 and HDPE/10%A6 formulations. This means that A6 have good dispersion in polymer matrix at 5%A6 and 10%A6 loading levels.
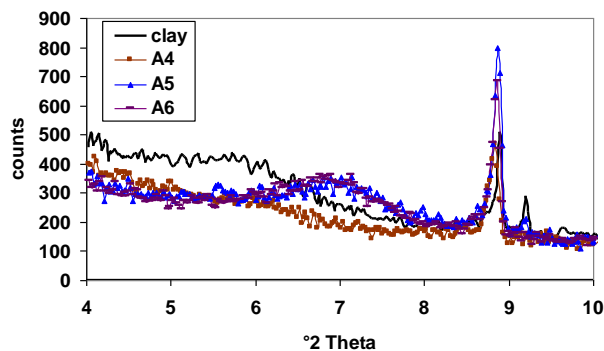
XRD analysis figures

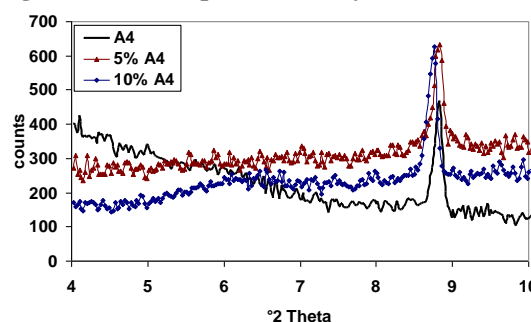**Figure (1a). XRD pattern of clay, A4, A5, and A6**

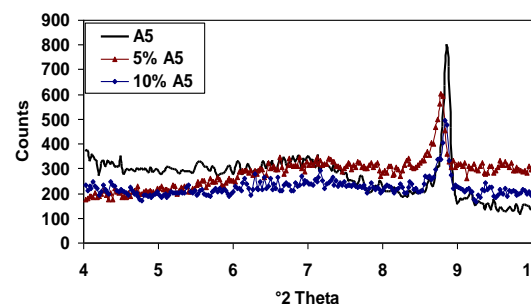**Figure (1b). XRD pattern for A4, HDPE/ 5% A4, and HDPE/10% A4.**

Figure (1c). XRD pattern for A5, HDPE/ 5% A5, and HDPE/10% A5.
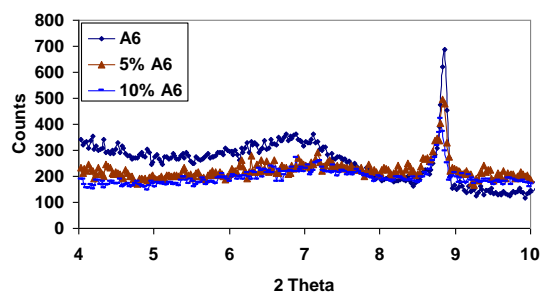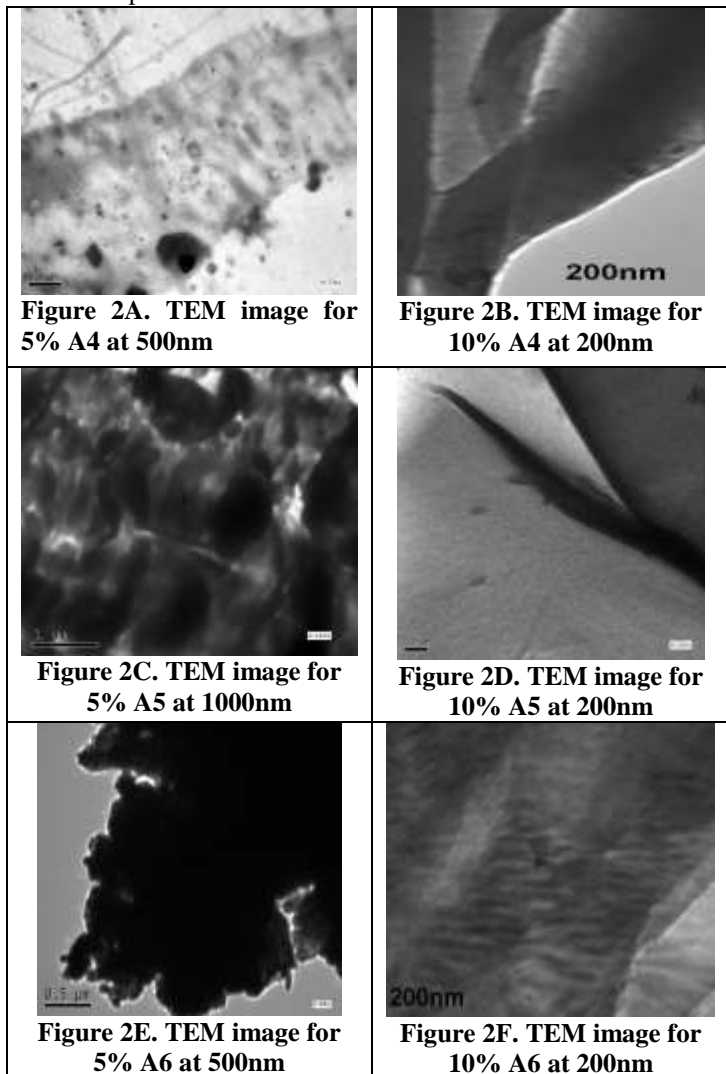

Figure (1d). XRD pattern for A6, HDPE/ 5% A6, and HDPE/10% A6.

Transmission Electron Microscopy

TEM images shown in Figures (2A,2B) indicated that 5%A4 formulation have good dispersion in polymer matrix although there are very little aggregates. We can say that microcomposite and exfoliated structures are coexisting. On the other hand, on loading HDPE with 10%A4 there is little distribution of A4 and large aggregate in the sea of polymer matrix which indicates the formation of microcomposite structure.

TEM images in figures (2C,2D) showed that A5 has good dispersion in the polymer matrix at 5%A5 and exfoliated dispersion was obtained but with certain aggregates. While at 10% A5 loading level aggregates are formed and microcomposite was obtained.

Figure 2A. TEM image for 5% A4 at 500nm

Figure 2B. TEM image for 10% A4 at 200nm

Figure 2C. TEM image for 5% A5 at 1000nm

Figure 2D. TEM image for 10% A5 at 200nm

Figure 2E. TEM image for 5% A6 at 500nm

Figure 2F. TEM image for 10% A6 at 200nm

TEM images shown in figures (2E,2F) illustrate that A6 at 5% loading level formed aggregates and microcomposite structure was obtained while at 10% loading level the high registry between clay layers and polymer chains was found which indicated formation of intercalated nanocomposite structure.

Thermal analysis

The thermal stability of HDPE nanocomposites was studied by Thermogravimetric analysis (TGA). The data available from TGA include $T_{10\%}$ (onset temperature) the temperature at which 10% degradation take place,$T_{50\%}$, the temperature at which 50% degradation occurs, T_{max}, the temperature at which maximum degradation take place, and char at750^{o}C.

The TGA data in table 2 and figures 3a, 3b showed that, in general the newly modified clay has improved the thermal stability of HDPE. The temperature of 10% weight loss for most samples are shifted to higher temperature except samples loaded with 5%A5 (410°C) and 10%A5 (404°C). The highest improvement in $T_{10\%}$ was noticed for HDPE samples loaded with 10%A6 (419°C).

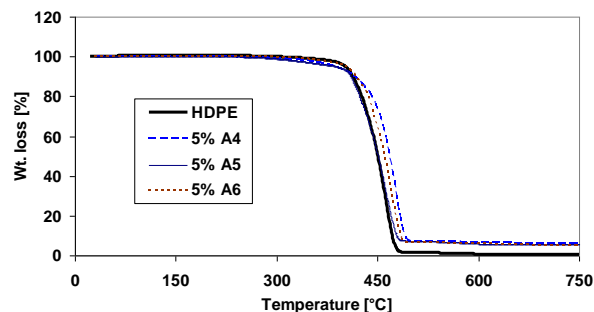### 3- Thermogravimetric analysis figures

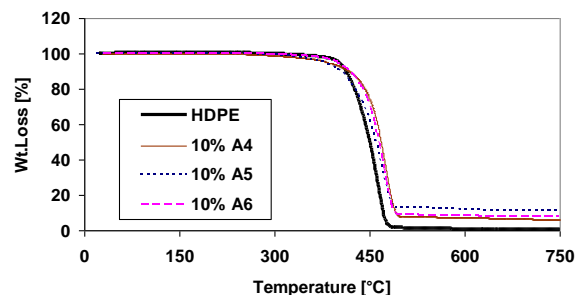**Figure 3a. TGA curves for HDPE containing 5%A4, 5%A5, and 5%A6.**

Figure 3b. TGA curves for HDPE containing 10%A4, 10%A5, and 10%A6.

On the other hand the temperature of 50% weight loss for all samples was shifted to higher values in comparison with that for pure HDPE. The temperature shift is ranged between (9-18°C). The improvement in T50% was 9°C for HDPE/5%A6 and 18°C for HDPE/10%A4. The temperatures at maximum decomposition also were increased for all HDPE nanocomposites relative to pure polymer. It was found the addition of 5%A4 and 10%A4 shifted Tmax by 15°C and 14°C respectively. The char residue data at 750°C indicated that a good char maintained at all 5% loading levels while the best char residue results at 10% loading levels was (10.3%) and obtained at 10%A5.

Flammability properties
Cone calorimeter results

Cone calorimeter is widely used to evaluate fire performance of materials. Various parameters can be obtained from cone calorimeter including mean of heat release rate(mHRR), peak of heat release rate (pHRR), total heat release (THR), time to ignition (Ti), time to flame out (Tf), mass loss rate (MLR), specific extinction area (SEA), and other parameters (Schartel and Hull, 2007). Fire performance index (FPI) defined as a ratio of Ti/ pHRR can be calculated from cone calorimeter results. The peak of HRR of material is one of the important factors to determine the potential behaviour during fire. It can be used to express the intensity of a fire and so effective flame retardant systems normally show lower values for pHRR (Huang et al., 2010). The pHRR of HDPE and HDPE

composites are shown in figures (4A,4B) and all of the cone calorimeter data is present in table 3 .

The data in table 3 showed that pure HDPE burns very fast after ignition and a sharp pHRR appears at 1744Kw/m^2 was obtained. The addition of 5%A4 reduce the pHRR by 29.5% while addition of 5%A5 and 5% A6 reduce the pHRR by 22.4% and 15.8% respectively in comparison with HDPE.

Flammability properties
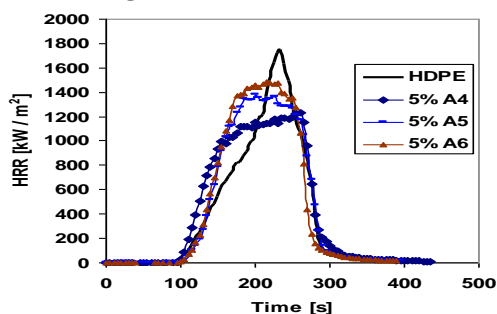**Cone calorimeter figures**

Figure 4A. HRR curves for HDPE and it's 5%A4,5%A5,5%A6 composites at heat flux 35 kW/m^2
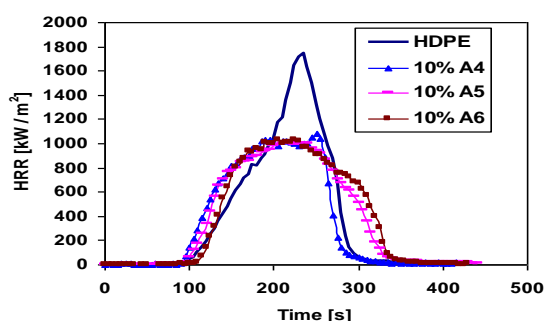

Figure 4B. HRR curves for HDPE and it's 10%A4,10%A5,10%A6 composites at heat flux 35 kW/m^2

On the other hand, the addition of 10% A4 reduce the pHRR by 37.7% while addition of 10% A5 and 10% A6 reduce pHRR by 42.4% and 40.8% relative to pure polymer. The time to reach pHRR was decreased for all loading levels relative to HDPE except for 5%A4 which showed very little increase in TpHRR. The mean of HRR was increased for all 5% loading levels, especially at 5% A6 where mHRR was increased to 681kW/m^2 in comparison with 502 kW/m^2 for pure polymer. But at 10%loading level, all modifiers (A4, A5, A6) reduced the mHRR and the best reduction in mHRR was obtained at 10%A5 (463 kW/m^2). The THR values were very close to HDPE value 174 MJ /m^2 at 5%A4,5%A5 and 5%A6 loadings while the addition of 10%A4 loading level has achieved the THR 147MJ/m^2 (15.5% reduction). The addition of 10%A5 and 10%A6 caused small reduction in THR (164MJ/m2). The results of Mass loss Rate (MLR) showed that MLR were decreased for all loading levels relative to pure polymer except 5%A6 which have mass loss rate value with very slight increase in comparison with HDPE. All HDPE composites contain A4, A5,A6 starts ignition earlier than pure polymer but there are certain nanocomposites have Ti values very close to pure polymer such as 5%A5(87s) and 5%A6(88s). The amount of smoke produced by adding A4, A5, A6 to HDPE at different loading levels showed variable values. Although it was maintained very close to pure polymer at 5%A4 and decreased by adding 5% A5, 5% A6, it was increased by addition of 10% from A4, A5, A6. The highest increase in smoke production at

10% loading levels was at 10%A4 (604 m^2/Kg) and the lowest increase was at 10% A6 (536 m^2/ Kg).

The results of time to flame out (Tf) showed that addition of 5% loading level from A4, A5, A6 lead to decrease time to flame out values while the addition of 10% loading level lead to increasing Tf values relative to pure polymer. It is obvious in table 3 that 10% A5 loading level lead to the highest Tf (302s). The Addition of A4, A5, A6 to HDPE improved FPI values. It is notable that FPI was increased by increasing loading levels for the same modifier. The best FPI at 5% loading level was obtained at 5%A5 with 23% amount of improvement relative to HDPE While the best FPI for at 10% loading level was obtained for 10%A6 loading level with 36.5% improvement relative to HDPE.

LOI and flame spread

All data for LOI and UL94 of HDPE composites are shown in table (3). From the results shown in table 4, pure HDPE is easily flammable material with LOI value   19.6 %, and it can not give FH$_1$ class through UL-94 test according to ISO 1210 standard test method (ISO 1210, 1992). The LOI values for HDPE nanocomposites were increased relative to pure polymer except 10%A4 formulation which has LOI 19.1%. Generally, an LOI value of at least 28 is necessary for realistic degree of flame retardancy (Cullis and Hirshler, 1984). This means that neither addition of A4 nor addition of A5 and A6 to HDPE has effective effect in LOI test as shown in table 3.

Flame spread data (UL-94 test) in table 4, also indicated that addition of A4, A5, A6 to HDPE not have significant effect in decreasing the rate of burning of HDPE.

Mechanical properties

The mechanical test results in table 5 showed that addition of A4, A5, A6 to HDPE improved the young's modulus values at all 5% and 10% loading levels. The results for tensile strength indicated that addition of A4,A5, A6 at 5% and 10% loading levels reduce the tensile strength. The amount of reduction is variable where it reaches 9% at 10%A6 and increased to 18.1% (18MPa) at 10%A5 and 5%A4. The maximum reduction in tensile strength values was obtained at5%A5 (27.2%).

The third parameter measured in mechanical properties was elongation at maximum force. The data showed that except at 5% A5 loading, elongation at maximum force was improved by addition of A4, A5, A6 to HDPE at both 5% and 10% loading levels and the best improvement was obtained at 10%A4 and 10%A6 loading levels.

Conclusion

1- The modification of Sodium montmorillonite clay undergo double modification was firstly approached.

2- The structures of polymer-nanocomposites formed were proved by X-ray diffraction and transmission electron microscopy.

3- The double modification of the clay by 1,1,1,4,4,4-hexamethyl-2,2,3,3-tetraphenyltetrasilane and ammonium phosphate mono basic or ammonium phosphate di basic has better effect in reduction the flammability of HDPE.

4- Another advantage of using double modification is the reduction of smoke production relative the organosilane modification for the clay.

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Table (1) codes of the melt blended HDPE with modified clay

Modifier of sodium montmorillonite (clay)	Code	HDPE (%)	Modified clay (%)
1,1,1,4,4,4-heaxmethyl-2,2,3,3-tatraphenyl tetrasilane	5% A4	95	5
	10% A4	90	10
(A4) and ammonium phosphate mono basic	5% A5	95	5
	10% A5	90	10
(A4) and ammonium phosphate di basic	5% A6	95	5
	10% A6	90	10

Table 2. TGA results for HDPE, HDPE/A4, HDPE/A5, andHDPE/A6 nanocomposites

Sample	$T_{10\%}$ [°C]	$T_{50\%}$ [°C]	T_{max} [°C]	Char at 750 °C [wt %]
HDPE	412	450	462	0.31
5% A4	415	468	477	5.9
5%A5	410	450	463	5.5
5% A6	418	459	470	5
10% A4	417	468	476	7
10% A5	404	460	468	10.3
10% A6	419	465	474	7.9

Table 3.cone calorimeter data for HDPE, HDPE/A4, HDPE/A5, HDPE/A6 nanocomposites at heat flux 35kW/m^2

Sample	HRR [kW/m^2]			THR [MJ/m^2]	MLR [g/s]	Ti [s]	SEA [m^2/Kg]	Tf [s]	FPI [s.m^2/kW]
	mHRR [kW/m^2]	pHRR [kW/m^2]	T$_{pHRR}$ [s]						
HDPE	502	1744	258	174	0.072	91	453	287	0.052
5% A4	526	1229	260	173	0.065	78	457	270	0.063
5% A5	573	1352	202	171	0.069	87	390	275	0.064
5% A6	681	1467	215	175	0.073	88	327	263	0.059
10% A4	499	1085	250	147	0.059	72	604	293	0.066
10% A5	463	1003	210	164	0.062	71	557	302	0.070
10% A6	483	1032	220	163	0.066	74	536	300	0.071

Table 4. LOI and flame spread results for HDPE, HDPE/A4, HDPE/A5, HDPE/A6 nanocomposites.

Sample	LOI (%)	UL94 (mm/s)
HDPE	19.6	0.30
5% A4	19.7	0.30
5% A5	19.7	0.29
5% A6	19.8	0.29
10% A4	19.1	0.29
10% A5	19.9	0.28
10% A6	20.1	0.28

Table 5. Mechanical properties of HDPE, HDPE/A4, HDPE/A5, HDPE/A6 nanocomposites

Sample	Young's modulus [MPa]	Tensile strength [MPa]	Reduction in Tensile strength (%)	ε F max [%]
HDPE	358	22	-	8
5% A4	565	18	18.1	9
5% A5	479	16	27.2	7
5% A6	499	17	22.7	10
10% A4	493	17	22.7	12
10% A5	554	18	18.1	10
10% A6	564	20	9	12