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## Combustion behavior of polyethylene/modified montmorillonite clay nanocomposites prepared by ultrasonication

**Summary** — Composites of low density polyethylene with Cloisite 20A clay (OMC) were prepared using ultrasonication. Atomic force microscope (AFM) images showed that ultrasonication could mostly decrease particle size and distribution of clay particles in the polymer matrix. Due to better dispersion of clay and smaller particle size, the flammability properties of PE-LD composites were reduced. Thermogravimetric studies showed that incorporation of OMC to PE-LD matrix improved the thermal stability of samples and enlarge the char yield.

**Key words:** low density polyethylene, organically modified montmorillonite, ultrasonication, flammability properties, thermal stability.

BADANIE SPALANIA NANOKOMPOZYTÓW POLIETYLEN/MODYFIKOWANA GLINKA MONTMORYLONITOWA OTRZYMYWANYCH ZA POMOCĄ DZIAŁANIA ULTRADŹWIĘKAMI

**Streszczenie** — Nanokompozyty polietylenu małej gęstości (PE-LD) z gliną Cloisite 20A (OMC) w ilości 5 lub 10 % mas. przygotowywano działając ultradźwiękami o mocy 200 W/cm<sup>2</sup> w ciągu 5, 10, 15 lub 20 min (tabela 1). Otrzymane próbki badano za pomocą skaningowego mikroskopu elektronowego i stwierdzono, że fale ultradźwiękowe powodują zmniejszenie wymiarów cząstek gliny rozproszonych w matrycy polimerowej (rys. 1). Stosując kalorymetr stożkowy zbadano palność przygotowanych próbek (rys. 2 i 3, tabela 2). Zaobserwowano znaczną redukcję właściwości palnych próbek nanokompozytów (M2—M9) w porównaniu z kontrolną próbką czystego PE-LD (M1). Badania termogravimetryczne pokazały, że próbki zawierające OMC charakteryzują się lepszą stabilnością termiczną niż czysty PE-LD.

**Słowa kluczowe:** polietylen małej gęstości, organicznie modyfikowany montmorylonit, działanie ultradźwiękami, właściwości palne, stabilność termiczna.

Recently, the potential of using inorganic minerals as fillers in a polymeric composite has become appreciated in area of commercial and scientific applications [1–3]. Polymer nanocomposites with organophilic montmorillonite (MMT) or its organically modified silicate (OMC) has been studied extensively because they often exhibit the unusual combination of improved physical properties [4, 5] and reduced flammability [6–11], compared with neat polymers in layered conventional micro- and macrocomposites [12–14].

Intercalation of polymer in layered has been a successful approach to synthesis of polymer layered silicate nanocomposites (PLSN). There are three ways to prepare PLSN:

- intercalation of polymer from a solution,

- *in situ* intercalation polymerization,
- melt intercalation method.

Thus there is a great interest in finding new ways to prepare nanocomposites. Ultrasonic irradiation has been widely used in preparation of nanoparticles [15–18]. Here we report preparation of polyethylene (PE) based nanocomposites in two formulations with Cloisite 20A clay with ultrasonic irradiation technique and study flammability and thermal stability properties of prepared polyethylene composite.

### EXPERIMENTAL

#### Materials

The polymer used for preparation of PLSN was low density polyethylene MG20 (PE-LD), supplied by HMC polymer company (Thailand).

Montmorillonite modified with ditallowdimethylammonium (OMC) with trade name Cloisite 20A was provided by Southern Clay Products, Inc.

Toluene was supplied from EDWIC (Egypt).

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## Preparation of samples

PE-LD and OMC were mixed in toluene solution in composition 5 or 10 wt. % of OMC in PE-LD matrix. Preparation of the PE/OMC nanocomposite was carried out using ultrasonication (Branson Sonifier — 450 USA).

**Table 1. Compositions and preparative conditions of investigated samples**

Symbol of sample	Sample compositions	Time of ultrasonication, min
M1	PE-LD (control sample)	—
M2	PE-LD + 5 wt. % OMC	5
M3	PE-LD + 5 wt. % OMC	10
M4	PE-LD + 5 wt. % OMC	15
M5	PE-LD + 5 wt. % OMC	20
M6	PE-LD + 10 wt. % OMC	5
M7	PE-LD + 10 wt. % OMC	10
M8	PE-LD + 10 wt. % OMC	15
M9	PE-LD + 10 wt. % OMC	20

The samples processing were carried out in specially designed stainless cell. The cell was designed to allow the flow of conditioning water to keep the cell temperature at  $25 \pm 3$  °C. The samples were processed using Branson-Sonifier 450 attached to a solid titanium horn 0.5 inch in diameter; they were excited with constant irradiation power of about  $200 \text{ W/cm}^2$  at 20 KHz for 5, 10, 15 and 20 min. Prepared materials were then pressed at the temperature about 195 °C under pressure 10 bars to obtain disk samples 5 cm in diameter and 0.2 cm thick for cone calorimeter. Formulations of the prepared samples are shown in Table 1.

## Methods of sample characterization

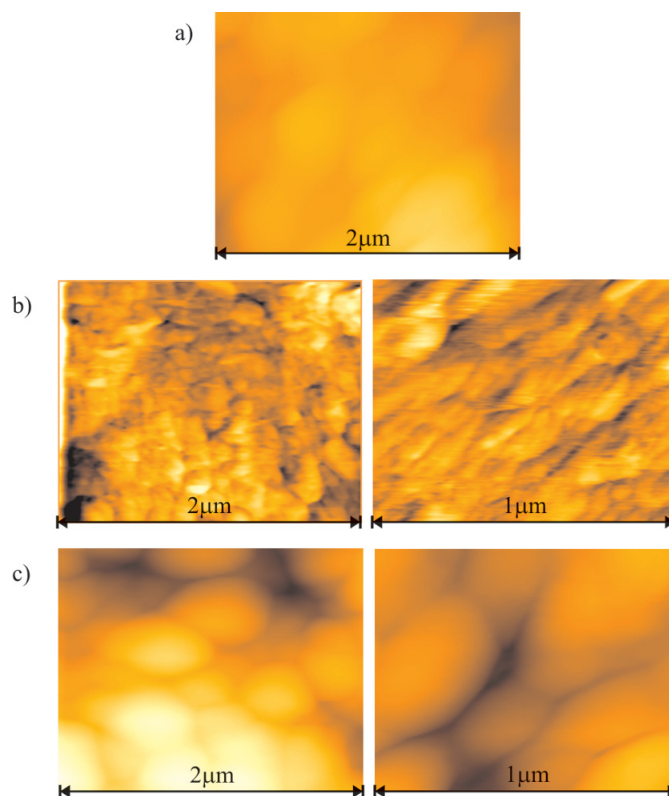
Atomic Force Microscope (AFM) CP-II (Veeco, USA) was used to investigate the morphology of dispersed phase in the polymer matrix.

Thermogravimetric analysis (TGA) of prepared compositions was performed using Shimadzu Analyzer TGA-50. All measurements were conducted under nitrogen flow, with a sample weight about  $10 \pm 0.5$  mg. All samples were investigated between the ambient temperature and 700 °C at heating rate of 10 deg/min.

Flammability characteristic was assessed using the cone calorimeter (Fire Testing Technology) according to ASTM 1354-95 standard.

## RESULTS AND DISCUSSION

AFM images shown in Figure 1 reveal the morphology of PE-LD based nanocomposite. The results of AFM



**Fig. 1. Exemplary AFM images of contact mode topography of sample: a) M1, b) M4, c) M9; symbols of samples as in Table 1**

investigations show that ultrasound can improve the dispersion of clay into the polymer matrix. The OMC aggregates are broken into small particles and dispersed homogeneously into the PE-LD matrix and the particles are about 300–700 nm in diameter. The decrease in size of OMC particles caused by ultrasonic treatment is clearly observed by comparison of the sample M9 (10 wt. % of OMC) and M5 (5 wt. % of OMC) with M1 (pure PE-LD). It can be noticed that M1 sample has greater particle size than M5 and M10. The decrease in particle size and improvement of homogeneity in the order  $M1 > M5 > M9$  was observed.

## Flammability

The potential fire hazard of any materials depends on many factors; including the ignitability, rate of surface flame spread, heat release rate (maximum, average and total), mass loss rate, smoke evolution and evaluation of toxic gases (e.g., CO). Cone calorimeter data address most of these factors. The following parameters were calculated and used as criteria to compare the influence of incorporation of OMC on the flammability of PE-LD; maximum of heat release rate ( $HRR_{max}$ ), ignition time, total heat release (THR), average effective heat of combustion (HC), average specific extinction area (SEA), average CO and CO<sub>2</sub> yield.

Cone calorimeter experiments were performed at incident heat flux of  $35 \text{ kW/m}^2$  using cone heater.  $HRR_{max}$

**Table 2.** Results of investigations of prepared samples obtained using cone calorimeter

Symbol of sample	$t_{ign}$ , s	$HRR_{max}$ , kW/m <sup>2</sup>	$HRR_{avg}$ , kW/m <sup>2</sup>	$THR$ , MJ/m <sup>2</sup>	$SEA$ , m <sup>2</sup> /kg	$HC$ , MJ/kg	Average CO, kg/kg	Average CO <sub>2</sub> , kg/kg
M1	16	1807	909	261	1955	35	0.016	1.518
M2	28	770	456	331	2398	32	0.009	0.999
M3	33	737	442	353	2425	31	0.010	0.991
M4	30	773	399	390	2433	32	0.010	0.990
M5	31	750	375	379	2652	32	0.009	0.996
M6	38	642	301	369	3468	28	0.007	0.685
M7	37	663	339	356	3476	32	0.008	0.770
M8	30	689	347	329	2687	30	0.006	0.946
M9	30	623	368	359	2466	31	0.007	0.846

$SEA$ , ignition time ( $t_{ign}$ ), CO yield, CO<sub>2</sub> yield and  $HC$  were reproducible to within  $\pm 10\%$ . The residue yield was reproducible to within  $\pm 0.5\%$ . The cone calorimeter data reported here are the averages of three repeated experiments. Cone calorimeter results for different samples of PE-LD composites are listed in Table 2.

### Ignitability

Ignition data are reported as time to sustained ignition ( $t_{ign}$ ), which is defined as ignition with the assistance of a spark igniter. M6 and M7 samples (10 wt. % of OMC) have the highest value of  $t_{ign}$  i.e., 38 and 37 s respectively, while M1 sample (pure PE-LD) has 16 s. Values of  $t_{ign}$  for other samples are also higher than that of M1 sample. M6 and M7 samples have also the longest total burning times ( $T_{tot}$ ) 525 and 455 s, respectively. Values of  $T_{tot}$  for other samples containing OMC are also higher than that of M1 sample.

### Heat release properties

Heat release properties are considered the most important variables in fire hazard. The heat release rates as a function of time for all prepared samples are shown in Figs. 2 and 3. The data in Table 2 indicates that pure PE-LD has the highest value of  $HRR_{max}$  of 1807 kW/m<sup>2</sup>. Addition of 5 wt. % of OMC has decreased the  $HRR_{max}$  by 57–59 % (samples M2–M5), while addition of 10 wt. % of OMC has decreased the  $HRR_{max}$  by 60–65 % (samples M6–M9). Some of the earlier works on nanocomposites showed that immiscible systems showed no reduction in  $HRR_{max}$ , while intercalated and exfoliated nanocomposites gave significant reduction [7, 19]. These observations have been confirmed by J. Zhang *et al.* [20] and shown that there seems to be a correlation between the extent of nano-dispersion and the reduction in  $HRR_{max}$ . In this study we stated high reductions in  $HRR_{max}$  values for all PE-LD/OMC composites by 57 to 65 %. This indicates the effect of ultrasonic irradiation to increased dispersion of clay particles in polymer matrix. Formation of

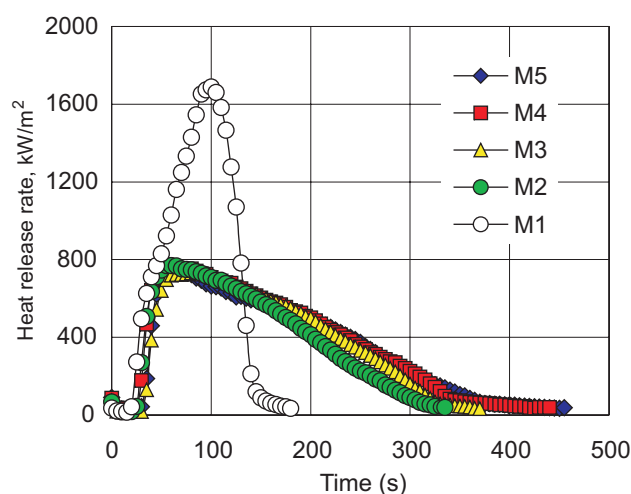


Fig. 2. Heat release rate (HRR) as a function of time for PE-LD composites with 5 wt. % of OMC compared with pure PE-LD; symbols of samples as in Table 1

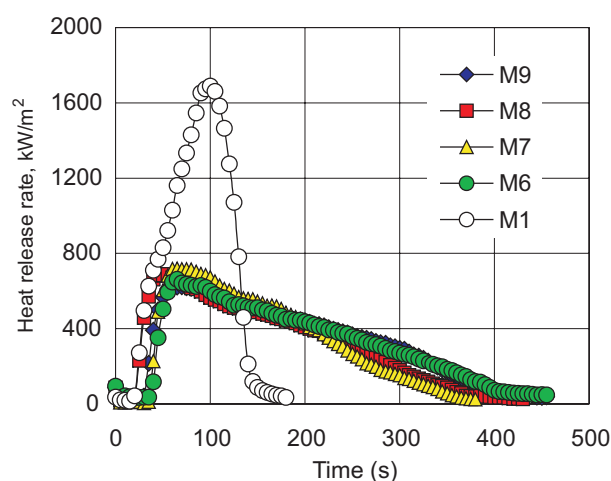


Fig. 3. Heat release rate (HRR) as a function of time for PE-LD composites with 10 wt. % of OMC compared with pure PE-LD; symbols of samples as in Table 1

intercalated polyethylene nanocomposites was confirmed by AFM.

In Table 2 data of average heat release ( $HRR_{avg}$ ) are also collected. The value of  $HRR_{max} = 909 \text{ kW/m}^2$  for pure PE-LD is much higher than for all prepared composites ( $301\text{--}456 \text{ kW/m}^2$ ). For samples containing 5 wt. % of OMC  $HRR_{avg}$  values decrease (in comparison to M1 sample) in the order of M2, M3, M4 and M5. In the case of samples containing 10 wt. % of OMC the decrease in the order of M9, M8, M7 and M6 was observed. The M6 sample has the lowest reduction in  $HRR_{avg}$  about 67 % ( $301 \text{ kW/m}^2$ ) in comparison to M1 sample ( $909 \text{ kW/m}^2$ ).

The  $THR$  values are listed in Table 2. It can be noticed that addition of OMC to PE-LD has increased  $THR$  from  $261 \text{ MJ/m}^2$  for M1 to  $329\text{--}390 \text{ MJ/m}^2$  for other samples.

$HC$  value of pure PE-LD is equal to  $35 \text{ MJ/kg}$  and is reduced by addition of OMC. For samples with 5 wt. % of OMC  $HC = 31\text{--}32 \text{ MJ/kg}$ , but for samples with 10 wt. % values are slightly lower  $HC = 28\text{--}32 \text{ MJ/kg}$ .

### Smoke release properties

$SEA$  data specified in Table 2 show that addition of OMC increases  $SEA$  values from  $1955 \text{ m}^2/\text{kg}$  for pure PE-LD to  $2398\text{--}2652 \text{ m}^2/\text{kg}$  for samples with 5 wt. % of OMC and  $2466\text{--}3476 \text{ m}^2/\text{kg}$  for samples with 10 wt. % of OMC.

### Gas analysis

Overall average values of CO and CO<sub>2</sub> released were also investigated. From results presented in Table 2 it can be seen that decrease in amounts of CO and CO<sub>2</sub> released during combustion clearly occurred after addition of OMC to PE-LD. Amounts of CO and CO<sub>2</sub> released for control sample M1 were 0.016 and 1.518 kg/kg, respectively, but for samples M2–M5 were 0.009–0.010 kg/kg and 0.990–0.999 kg/kg. This effect is still bigger for higher content of OMC in samples M6–M9 and observed amounts of CO and CO<sub>2</sub> released were 0.006–0.008 and 0.685–0.946 kg/kg, respectively.

**Table 3. Results of thermogravimetric analysis of prepared samples**

Symbol of sample	Onset temperature, °C	Peak temperature, °C	Char yield at 700 °C, %
M1	402	433	0.14
M2	408	446	5.29
M3	417	450	5.03
M4	404	443	3.80
M5	415	451	5.18
M6	408	446	6.28
M7	403	440	6.26
M8	400	441	6.52
M9	410	447	6.75

### Thermal stability

The results of thermogravimetric analysis have been collected in Table 3. It can be seen that both onset temperature of decomposition and peak temperature (the temperature at which maximum rate of weight loss occurs) of all samples of composites are higher than corresponding values for control sample 402 and 433 °C, respectively. Simultaneously with increase of onset and peak temperatures increase of char yield was observed from 0.15 % for M1 to 3.80–6.75 for composites.

### CONCLUSIONS

– Ultrasonication is useful in preparation of PE-LD composites due to the increase of clay dispersion into polymer matrix.

– Reduction in flammability properties of PE-LD composites with OMC prepared with ultrasonication in comparison to pure PE-LD was observed.

– Incorporation of OMC into PE-LD matrix improves slightly thermal stability of PE-LD composites and increases char yield.

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