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Preparation and characterization of low density polyethylene nanocomposites with modified montmorillonite clay

Summary — Organically modified montmorillonite clay (OMC) and its iron complex (OMC-Fe) were prepared using 1-acetylpyridinium chloride salicylhydrazone. Low density polyethylene (PE-LD) was compounded with either OMC or OMC-Fe (in amount of 3 or 7 wt. %) using ultrasonic radiation. The morphology of polyethylene composites was characterized by atomic force microscopy (AFM). The thermal stability and flammability properties of polyethylene composites were evaluated using thermogravimetric analysis and cone calorimetry, respectively. The resultant composites exhibited improved flammability relative to the pure polyethylene.

Key words: low density polyethylene, modified montmorillonite clay, ultrasonication, atomic force microscopy, cone calorimeter.

OTRZYMYWANIE I CHARAKTERYSTYKA NANOKOMPOZYTÓW POLIETYLENU MAŁEJ GĘSTOŚCI Z MODYFIKOWANĄ GLINKĄ MONTMORYLONITOWĄ

Streszczenie — Montmorylonit (MMT) modyfikowano za pomocą surfaktantu (H_2ACSH). Z części uzyskanej organicznie modyfikowanej glinki montmorylonitowej (OMC) otrzymano jej kompleks z kationami żelaza (III) (OMC-Fe). Następnie używając fal ultradźwiękowych przygotowano nanokompozyty polietylenu małej gęstości (PE-LD) z OMC lub OMC-Fe w ilości 3 lub 7 % mas. Metodą mikroskopii sił atomowych (AEM) wykonano charakterystykę morfologiczną próbek nanokompozytów. Stabilność termiczną tych próbek zbadano metodą analizy termogravimetrycznej, a palność za pomocą kalorymetru stożkowego. Stwierdzono, że dodatek OMC lub OMC-Fe do PE-LD praktycznie nie wpływa na stabilność termiczną nanokompozytów w porównaniu z czystym PE-LD, ale zmniejsza ich palność.

Słowa kluczowe: polietylen małej gęstości, modyfikowana glinka montmorylonitowa, działanie ultradźwiękami, mikroskopia sił atomowych, kalorymetr stożkowy.

In spite of intense efforts undertaken by numerous research groups worldwide during past years, nanocomposite of polymers with layered silicates are still challenging materials [1] and have attracted attention due to the anticipated improvement in properties, such as mechanical and flammability properties. Polyethylene (PE) is one of the most widely used polyolefin polymer. Syntheses of PE composites appear to be difficult because polyolefins are so hydrophobic that suitable interactions with the polar aluminosilicate surface of the clay are missing. In most cases, maleic anhydride grafted PE is used as a compatibilizer [2, 3] allowing to form the composites. Small addition of maleic anhydride during melt blending can assist in the formation of PE composites [4, 5]. Solution blending using energy mixing technique

such as ultrasonic has been used to prepare polymer/clay composites [6—9].

The aim of the present work is to develop a new flame retardant nanocomposite material by modification of montmorillonite clay. Modification was done using 1-acetylpyridinium chloride salicylhydrazone. The prepared flame retardant system was used in low density polyethylene blends with organically modified montmorillonite clay (OMC) or its iron complex (OMC-Fe). The effects of OMC and OMC-Fe on the thermal and flammability properties of polyethylene composites were evaluated using thermogravimetric analysis and cone calorimetry.

EXPERIMENTAL

Materials

The polymer used for the preparation of composites was low density polyethylene (PE-LD type MG20), supplied by HMC Polymers Company (Thailand). The sodium montmorillonite (MMT) was provided by Southern Clay Products, Inc. 1-(Carboxymethyl) pyridinium chloride hydrazide (Girard-P), salicylaldehyde, ferric

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chloride, and anhydrous calcium chloride were delivered by Aldrich, while ethanol and toluene by EDWIC (Egypt).

Synthesis of 1-acetylpyridinium chloride salicylhydrazone (H₂ACSH)

5 g of Girard-P with 4 ml of salicylaldehyde in 50 ml of absolute ethanol were refluxed over water bath for 4 hours. The reaction mixture was left to cool till white crystals were separated. These were filtered off, recrystallized from ethanol and finally dried in vacuum desiccator over anhydrous calcium chloride. The yield of synthesis was 74 % (6.50 g of H₂ACSH). From elemental analysis it was found: C, 51.10; H, 4.25; N, 15.85. Calculated for C₁₂H₁₁ClN₄O₂ (278.58) values are equal: C, 51.35; H, 4.31; N, 15.97 %.

Synthesis of organically modified montmorillonite (OMC)

10 g of montmorillonite was added to 200 ml of ethanolic solution (95 %) containing 2 g of (H₂ACSH) and refluxed with vigorous stirring for 24 hours. The yellowish montmorillonite was filtered off and washed with ethanol followed by water. Modified montmorillonite clay was dried in vacuum at 80 °C for 6 hours. Elemental analysis indicated that montmorillonite was loaded with 8 % of H₂ACSH.

Synthesis of iron complex of modified montmorillonite (OMC-Fe)

Modified montmorillonite (OMC) and ferric chloride (1.0 mol) in 30 ml of ethanol were refluxed for 2—3 h to form the corresponding iron complex of modified montmorillonite. The formed complex was filtered while hot, washed with ethanol followed by water and dried in vacuum over CaCl₂.

Preparation of the polymer-clay composites

PE-LD was mixed with 3 or 7 wt. % of OMC or OMC-Fe in toluene as a solvent. The samples were processed using Branson-Sonifier 450 attached to solid tita-

nium horn of 0.5 inch diameter; it was excited at 20 KHz and constant irradiation power of about 100 Watt/cm² for 10 min was used. The samples' processing was carried out in specially designed stainless cell. The cell was designed to allow conditioning of water to flow maintaining the cell temperature at 25 ± 3 °C. The prepared materials were dried in oven at 80 °C overnight. Samples for testing were prepared by compression molding at temp. 195 °C under pressure 10 bars. The samples codes and preparation conditions are listed in Table 1.

Methods of testing

Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 2400 Series II Analyzer.

Infrared spectra were recorded by Perkin-Elmer FT-IR Spectrometer 2000, using KBr pellets and Nujol mulls in the 4000—370 cm⁻¹ wave number range.

Thermogravimetric measurements were performed using TGA-50 Shimadzu instrument.

The surface morphology was studied using atomic force microscope (AFM) type CP – II (Veeco – USA). Flammability properties were evaluated according to ASTM 1354-95 standard using cone calorimeter produced by Fire Testing Technology.

RESULTS AND DISCUSSION

Characterization of organically modified clay

FT-IR spectra

Infrared spectra of OMC and OMC-Fe are shown in Figure 1. The characteristic bands of montmorillonite appear at 3630, 1043 and 523 cm⁻¹. The bands at 3236, 3123 and 3078 cm⁻¹ are assigned to NH (4), NH (1) and NH (2) modes, respectively. The two strong bands at 1710 and 1640 cm⁻¹ are attributed to CO and C=N moieties, respectively. Also, two bands at 1595 and 1620 cm⁻¹ are assigned to pyridine and phenyl rings, respectively. The medium intensity band at 970 cm⁻¹ is attributed to the N-N vibration. The bands at 3500 cm⁻¹ and 2550 cm⁻¹ are assigned to OH vibrations group. Comparison of MMT and OMC-Fe spectra (see Figure 1) indicates that no change occurs in NH band, the bands of C=O and OH are shifted to lower values (10 cm⁻¹) and the band of C=O disappeared. These results indicate that the sorption mechanism is mainly through the chelating of metal ions *via* phenolic OH and keto/enol groups.

TGA analysis

TGA curves of original MMT and two organically modified clays, OMC and OMC-Fe are shown in Figure 2. The decomposition of montmorillonite at 95 and 650 °C are attributed to the loss of water molecules. The first peak corresponds to the loss of adsorbed water, whereas the second peak is due to dehydroxylation of MMT. TGA curve of OMC in Figure 2 shows three degradation

Table 1. Compositions and denotations of the polymer-clay composites prepared

Symbol of sample	Composition, wt. %		
	PE-LD	OMC	OMC-Fe
R1	97	3	—
R2	93	7	—
R3	97	—	3
R4	93	—	7
R5	100	—	—

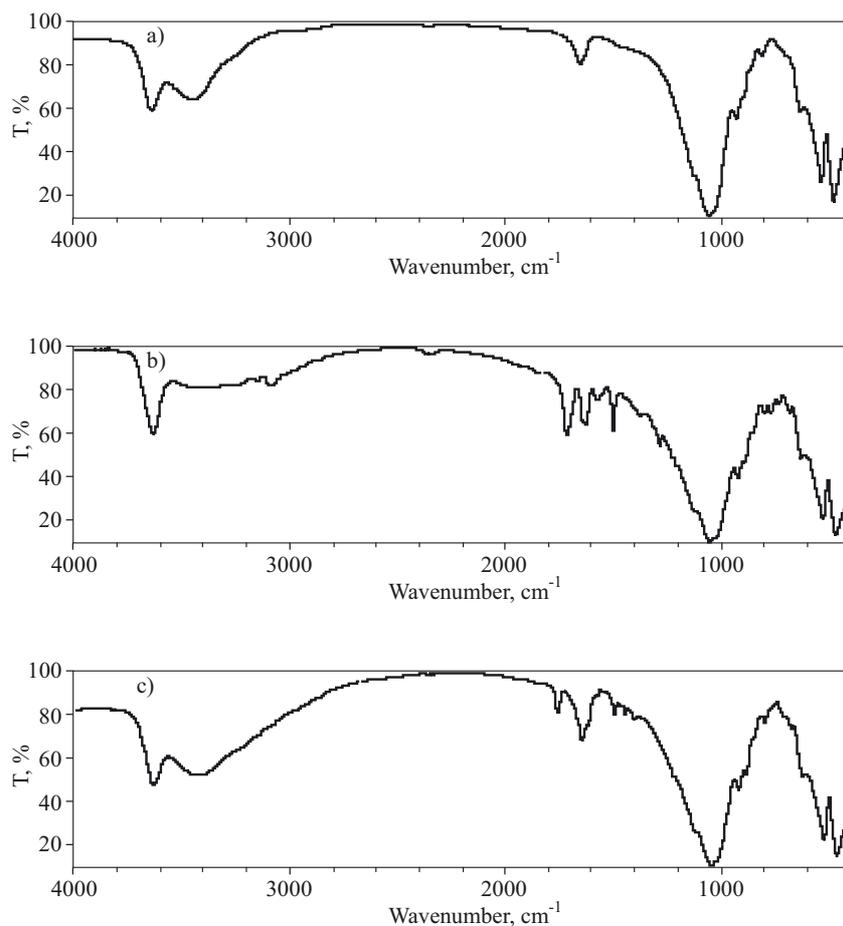


Fig. 1. FT-IR spectra of virgin MMT (a), OMC (b) and OMC-Fe (c)

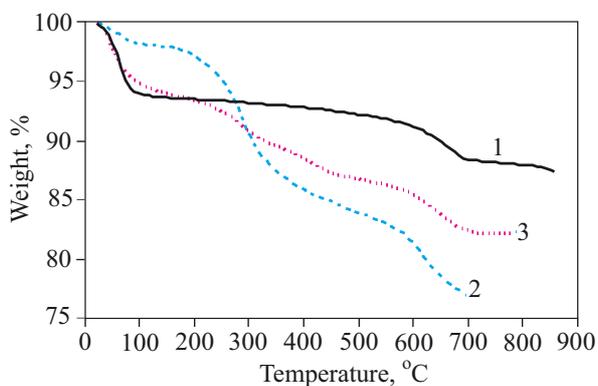


Fig. 2. TGA curves of: 1 — virgin MMT, 2 — OMC, 3 — OMC-Fe

stages. The weight loss (8 %) attributed to the organic part in the temperature range 200—500 °C is in good agreement with the results obtained by elemental analyses which predicted a weight loss of 7.05 % giving rise to a grafting capacity. TGA curve shows that OMC is thermally stable up to 200 °C. The TGA curve of OMC-Fe complex has three main stages. The water loss occurs at 100 °C (4.0 %), whereas the second and third peaks correspond to the organic degradation which ends up at 750 °C (10.14 %).

Polyethylene composites

Morphology by AFM

AFM can be performed in two modes, tapping or contact mode. In the contact mode, a cantilever is forced to drag on the surface of the specimen. The force between the tip of the cantilever, which is a pure silicon single crystal, and the sample is measured at each point on the surface and a feedback loop keeps the force at a constant value by translating the sample vertically with the piezoelectric scanner reflecting the topography of the surface. In the tapping mode, the cantilever is forced to oscillate at a frequency close to its resonance frequency with adjustable amplitude. Unlike in contact mode, the tip contacts briefly the film surface at the bottom of each travel of the cantilever and the amplitude of the oscillation varies. Tapping mode was developed particularly for soft materials such as polymers in order to prevent any possible damage of the sample surface during continuous contact. In this mode, the height image, which is the topography of the surface, is obtained by using the feedback loop, which keeps the amplitude of the oscillation at a constant value. Besides the variation of the amplitude, the dephasing of the cantilever oscillation relative to the signal exciting the piezoelectric driver can be measured and this is called phase detection imaging

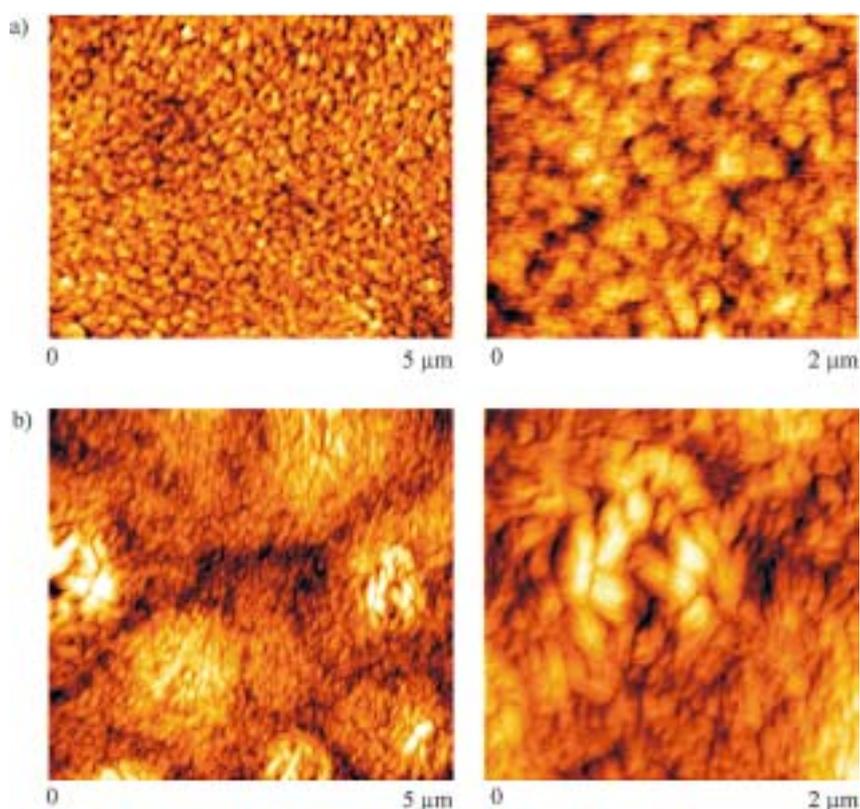


Fig. 3. Exemplary AFM images of contact mode topography of: a) pure PE-LD, b) PE-LD/OMC-Fe nanocomposite; left images correspond to 5 μm size and right images to 2 μm of sample size

(PDI). Phase imaging is usually used to probe the local elastic or adhesive properties at the surface. The images have high contrast especially if the surface of the sample varies in stiffness (or elasticity). A polymer layered silicate composite system containing stiff inorganic filler and soft polymer is ideal for AFM imaging.

Figure 3 includes two pairs of contact mode topography images. The upper pair is for pure PE-LD and the lower is for PE-LD/clay composite. The left images in both pairs correspond to 5 μm size and the right ones to 2 μm size. In the upper pairs of images, a homogeneous surface topography structure of pure PE-LD is evident. Meanwhile, in the left image of lower pair, it can be clearly seen that aggregates of modified clay are dispersed in PE-LD matrix as white areas. Magnification of these aggregates as it can be noticed in the right image (2 μm) reveals that they in the form of platelets. This confirms the formation of nanostructures by intercalation of modified montmorillonite clay in PE-LD. The particle size of the obtained nanostructure is in the range 150–250 nm. The distance between neighboring aggregates was also measured in order to know their dispersion in PE-LD matrix. These distances were found to be about 1.5–2 μm . This means that a homogeneous nanocomposite structure has been obtained.

Thermal properties

TGA data of PE composites have been collected in Table 2. The results indicated that OMC and OMC-Fe have no effects on the thermal stability of polyethylene composites. It can be seen that the peak decomposition

temperatures of PE-LD composites are lower than that of pure PE-LD (R5). It was noticed that the incorporation of OMC or OMC-Fe into PE-LD samples showed a good effect on enhancement of char formation.

Table 2. TGA data of PE-LD/clay composites

Symbol of sample	Onset decomposition temperature, $^{\circ}\text{C}$	Peak decomposition temperature, $^{\circ}\text{C}$	Weight loss at 700 $^{\circ}\text{C}$, % (Char Yield)
R1	396.99	429.57	2.213 (- 97.787)
R2	391.93	428.33	5.798 (- 94.202)
R3	404.80	434.61	3.142 (- 96.858)
R4	398.89	431.17	8.249 (- 91.751)
R5	401.54	433.33	0.137 (- 99.863)

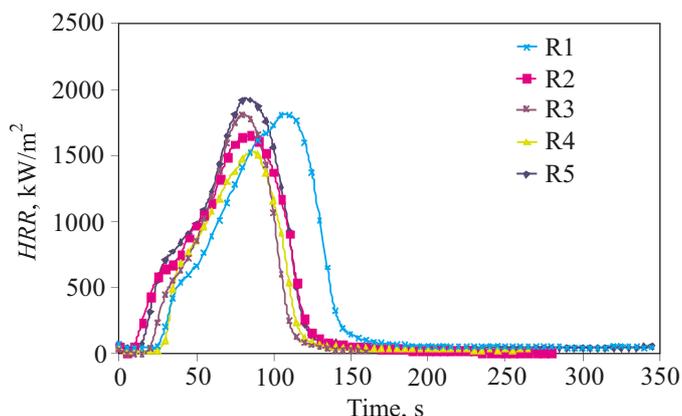


Fig. 4. Cone calorimetry data for samples prepared

Table 3. Cone calorimetry data of PE-LD/clay composites

Symbol of sample	Time to ignition, s	Maximum HRR kW/m ²	Average HRR kW/m ²	Total HRR MJ/m ²	Time to end, s	Average SEA m ² /kg	Average heat of combustion MJ/kg	Average CO amount kg/kg	Average CO ₂ amount kg/kg	Residue yield, %
R1	26	1806.685	463.156	353.16	330	785.731	10.810	0.005	0.438	3.06
R2	11	1652.034	471.601	294.75	260	514.088	8.288	0.004	0.420	5.54
R3	20	1810.442	806.147	241.84	140	3047.304	35.815	0.017	1.572	2.677
R4	30	1527.246	432.406	323.42	245	699.194	7.127	0.004	0.333	5.739
R5	19	1922.468	424.567	329.04	325	2776.582	36.757	0.017	1.685	0.331

Flammability properties

The flame retardant properties of PE-LD composites have been determined using cone calorimetry under a heat flux of 35 kW/m². Under such conditions, simulating a small fire scenario, the effect of organically modified clay can be observed. The parameters that may be obtained from cone calorimeter include the time to ignition, the peak heat release rate (*HRR*), the total heat release rate and the smoke extinction area (*SEA*). The cone calorimetry data for PE-LD/clay composites samples are summarized in Table 3. The results indicate that all PE-LD/clay composites samples show lower peak *HRR* relative to the pure PE-LD, being indicative of good fire performance. The *HRR* data shown in Figure 4 reveal that the best result was obtained for sample R4 (containing 7 wt. % of OMC-Fe) where a decrease by about 20 % in the peak of *HRR* as well as a shift to longer ignition time were observed when compared to virgin PE-LD. As a decrease in the peak of *HRR* indicates a reduction of the volatile degradation products generated by the degradation of the polymer matrix, such a drop clearly indicates that the flame retardant effect is due to the presence of organically modified clay.

CONCLUSIONS

PE-LD/OMC and PE-LD/OMC-Fe composites were prepared using solvent blending with sonication. Com-

pounding of PE-LD with OMC leads to small reduction in peak heat release rate. PE-LD composite based on OMC-Fe shows a significant reduction in flammability properties compared to pure PE-LD. The incorporation of OMC or OMC-Fe into PE-LD has a good effect on char enhancement.

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