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Effect of iron(III) acetylacetonate additive on selected properties of composites of low density polyethylene with magnesium hydroxide

RAPID COMMUNICATION

Summary — The preliminary investigation of the effects of using iron(III) acetylacetonate (acacFe) in low density polyethylene (PE-LD) composites with magnesium hydroxide (MH) after different modifications on flammability was conducted. The results showed that employment of a small amount of acacFe in composites with MH, modified with a silane compound (Magnifin H10A) may reduce the total burning times for a whole series of samples in the vertical position and it may increase tensile strain at break (ε_B) of samples.

Keywords: iron(III) acetylacetonate, low density polyethylene, magnesium hydroxide, fire retardation.

WPŁYW ACETYLOACETONIANU ŻELAZA(III) NA WYBRANE WŁAŚCIWOŚCI KOMPOZYTÓW POLIETYLENU MAŁEJ GĘSTOŚCI Z WODOROTLENKIEM MAGNEZU

Streszczenie — Artykuł przedstawia wyniki wstępnych badań wpływu dodatku acetyloacetonianu żelaza(III) (acacFe) na palność kompozytów polietylenu małej gęstości (PE-LD) z wodorotlenkiem magnezu (MH) poddanym różnym modyfikacjom (tabela 1). Nie obserwowano zadowalająco korzystnych zmian palności, gdy acacFe stosowano razem z niemodyfikowanym MH (Hydrofy 1.5), MH modyfikowanym stearynianem wapnia (Duhor C09), czy MH w postaci brucytu (Securoc B9) (tabela 2, rys. 1 i 2). Stwierdzono natomiast, że palność kompozytu zawierającego obok 45 % mas. MH modyfikowanego związkiem silanowym (Magnifin H10A), także 0,1 % mas. acacFe (próbka B1), była mniejsza niż przed wprowadzeniem acacFe (próbka A1) (tabela 2, rys. 1). Palność próbki B1 była również mniejsza, niż kompozytu ze zwiększonym do 50 % mas. udziałem tego samego wodorotlenku (tabela 2, próbka C1). Obecność związku żelaza miała ponadto korzystny wpływ na wartości wydłużenia materiału przy zerwaniu (ε_B) (rys. 2).

Słowa kluczowe: acetyloacetonian żelaza(III), polietylen małej gęstości, wodorotlenek magnezu, zmniejszanie palności.

Applications of plastics in different branches of the industry involve the need to assure safe use of those materials. Polyolefins, including polyethylene, which find numerous usages, are able to burn even in the atmosphere which contains less oxygen than earth atmosphere. The oxygen index (*OI*) for polyethylene is about 17 vol. % of O_2, while the index value for the materials classified as "slow-burning" is at least 28 vol. % of O_2. Hence, when fire safety is the issue, polyolefins have to be modified to reduce their flammability. It is possible to reach that goal by introducing fire retardants to the polymer matrix. Aluminium hydroxide (ATH) and magnesium hydroxide (MH) are the most popular additives with that performance. They have one more advantage — they alone and products of their thermal degradation have relatively low toxicity. Unfortunately, the content of hydroxides in the material must be very high to ensure its satisfactory reduction of flammability. The admixture of ATH is about 35—70 wt. %, and that of MH is about 50—70 wt. %, in the composites which do not contain halogenated compounds. The amount of the additive is dependent *inter alia* on the required fire retardation level and on the type of the polymer matrix to be modified. Such a high contents of inorganic additives will strongly and adversely affect the processability and functional properties of the product materials [1, 2].

That problem can be overcome by incorporation of additional compound(s) to facilitate processing of composites, or by modification of the hydroxide itself. Another method is based on employing of one more substance which interacts with the basic fire retardant to further reduce combustibility of the composite, hence to reduce the total content of modifiers in the polymer matrix. The use of synergism is the most favourable then — the total effect exceeds the sum of individual effects offered by the agents employed in the formulation. Zinc borate [3, 4], red phosphorus, polyacrylonitrile [1], nickel and cobalt oxide [4], calcium carbonate [6] or silicon compounds [5, 6] may be used together with ATH/MH in polymer composites to decrease the total content of hydroxide in the polymer matrix by a few wt. %. Despite the positive effects of such additional components, the amount of additives in the polymer remains still rather high. Moreover, the use of at least some of those booster compounds may be limited since they could change the color of the final product. Flammability of polyolefins makes the point of concern in many cases and the volume of fire retardant additives consumed in that case is considerable. The market demand in that field justifies further research and drives it to improve efficiency of the fire retardant agents.

The goal of this research on polyethylene composites with metal hydroxides is to identify the additives which can efficiently interact with the basic fire retardant to considerably reduce composite combustibility, and thus to reduce the total amount of modifiers added to the polyethylene composites. Simultaneously, the impacts of additives on processability and on performance properties of plastic composites are important criteria when evaluating those additives. This paper presents the preliminary results of our research on iron(III) acetylacetonate, introduced into a low density polyethylene composite with magnesium hydroxide.

EXPERIMENTAL

Materials

The following materials were used in this work:

— low density polyethylene (PE-LD) type FGNX 23D022, characterized by melt flow rate *MFR* = 2.0 g/10 min (Basell Orlen);

— magnesium hydroxide modified with a silane compound with trade name Magnifin H10A (Abemarle Corporation);

— magnesium hydroxide named Hydrofy 1.5 (Nuova Sima Srl);

— magnesium hydroxide modified with a calcium stearate with trade name Duhor C09 (Duslo);

— brucite which is mineral form of magnesium hydroxide named by producer as Securoc B9 (Ankerport NV);

— iron(III) acetylacetonate (acacFe, Sigma-Aldrich Chemical Company).

Composites preparation

Three series of PE-LD composites with different amount and type of fillers, specified in Table 1, were prepared. Selected additives were introduced into the polymer, and the composite material was then homogenized with a laboratory two-roll mill for 10 min at the temperature of 150—160 °C.

Table 1. Composition of low density polyethylene (PE-LD) composites with different types of magnesium hydroxide (MH) and iron(III) acetylacetonate (acacFe)

Type of MH	A Series			B Series				C Series		
	Symbol of sample	Content, wt. %		Symbol of sample	Content, wt. %			Symbol of sample	Content, wt. %	
		MH	PE-LD		MH	PE-LD	acacFe		MH	PE-LD
Magnifin H10A	A1	45	55	B1	45	54.9	0.1	C1	50	50
Hydrofy 1.5	A2	45	55	B2	45	54.9	0.1	—	—	—
Securoc B9	A3	45	55	B3	45	54.9	0.1	—	—	—
Duhor C09	A4	45	55	B4	45	54.9	0.1	—	—	—

In order to obtain test samples with expected thickness and shape, the composite material samples were placed in a metal frame between two metal plates, and that set was placed in a laboratory press which had been heated up to 180 °C. The time of preheating was 4 min, and the pressing action took 2 min. Hot specimens were cooled down in a cold laboratory press.

Methods of testing

The oxygen index (*OI*) was determined in a flammability test apparatus (FTA), for type I specimens, with type A ignition method according to the Polish Standard PN-ISO 4589-2:1999. The reported test results are average values of three test findings according to own lab procedures.

Combustibility of the materials in the horizontal and vertical flame test methods was determined in accordance with the standard PN-EN 60695-11-1:2002.

Tensile properties — tensile stress at break (σ_B) and tensile strain at break (ε_B) of specimens — were measured using the Instron 4466 machine, in accordance with the standard PN-EN ISO 527-1:1998. The adopted strain rate was 100 mm/min.

The melt flow rate (*MFR*) measurements were made at 190 °C, under the load of 2.16 kg, using the Zwick plastometer, in accordance with the standard PN-EN ISO 1133:2006.

Density of composites (*d*) was established by the gravimetric analysis, using the analytical balance AG 204 (Mettler Toledo) equipped with an accessory set for examination of density of solids.

RESULTS AND DISCUSSION

Taking into account the assumptions adopted for our research as mentioned above, the combustibility tests for all samples were supplemented by determination of the following parameters: *MFR* (to evaluate the possibility of material processing), *d* and σ_B. Combustibility of the composites was evaluated on the grounds of their *OI* values, and of the results of horizontal and vertical flame tests. Resulting from those tests, the combustibility category is obtained for the composite materials, which is the resultant of parameters established during the tests. Those parameters are not important for the processor, but they could be valuable indicators in the research process. Hence, adding to the final classification, *i.e.* combustibility category, some partial findings were also specified in this report for comparison, *i.e.* total burning times for the whole series of samples in the vertical position (t_f), and rates of burning in the horizontal position (υ) (PN-EN 6095-11-1:2002). It should be explained here that the materials classified as one of V category will not burn at all in the horizontal position, and their combustion time in the vertical position is very short as compared to the materials in the lower HB categories.

Composites with MH (A series)

Preliminary investigation of the effects of acacFe was conducted for PE-LD composites with 45 wt. % of MH which was obtained from different sources. MH without any modification (Hydrofy 1.5) was applied, and then fire retardant after modification with silane compound (Magnifin H10A) or with calcium stearate (Duhor C09) was used as well as its version in the form of brucite (Securoc B9). The findings for reference composites, which contained the mentioned modifiers only, showed that the characteristics of a fire retardant is very important to the properties of blends. The values of some parameters, like σ_B and *MFR*, were different for various types of hydroxides (Table 2). Other parameters — *d* (Table 2), *OI* (Figure 1) or ε_B (Figure 2) — were less dependent on the type of the modifier employed. All reference composites were classified as HB-40, and their total burning times in the vertical position (t_f) were similar to each other. The composite with Magnifin H10A (sample A1) was the only material which did not burn in the horizontal position (Table 2).

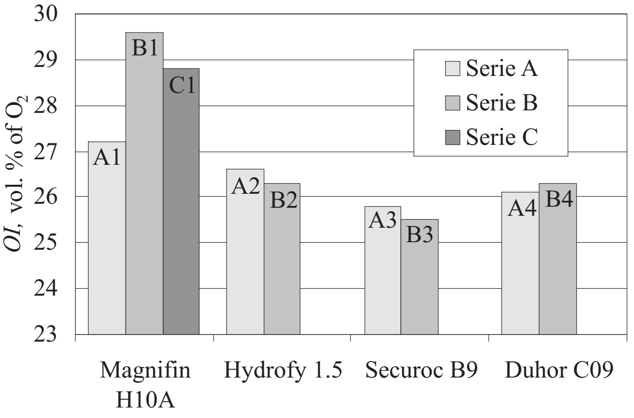

Fig. 1. Oxygen index (OI) values for investigated polyethylene composites without and with 0.1 wt. % of acacFe; meaning of samples symbols as in Table 1

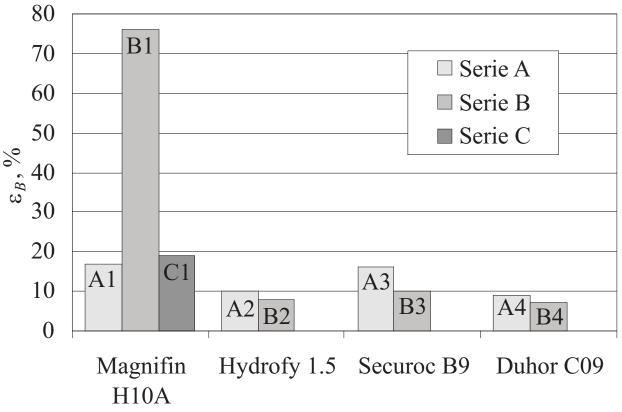

Fig. 2. Tensile strain at break (ε_B) *values for investigated polyethylene composites without and with 0.1 wt. % of acacFe; meaning of samples symbols as in Table 1*

T a b l e 2. Selected properties of PE-LD composites with different type and amounts of fillers

Symbol of sample	*d* g/cm³	*MFR* g/10 min	σ_B MPa	Flammability	
				$t_f^{a)}$, s	υ $^{b)}$, mm/min
A1	1.268	0.61	15.8	925	—
A2	1.262	1.02	14.1	850	9.8
A3	1.273	0.88	17.1	842	16.4
A4	1.257	1.01	11.9	922	19.9
B1	1.270	0.38	13.5	854	—
B2	1.267	0.73	14.0	1065	—
B3	1.272	0.91	17.0	1115	—
B4	1.258	0.78	13.5	1132	—
C1	1.322	0.49	16.4	1050	—

a) t_f — total burning times for the whole series of samples in the vertical position.

b) υ — average rate of burning for samples in the horizontal position.

Composites with MH and acacFe (B series)

No density changes were observed after addition of 0.1 wt. % of acacFe into polyethylene composites, in relation to *d* values for corresponding materials from A series (Table 2). *MFR* values dropped for three composites, but that change did not disqualify the possibility of processing those materials. *MFR* did not change for the polymer with Securoc B9 after the iron compound was added to that material (compare A3 and B3 samples in Table 2).

The nature of changes in σ_B was dependent on the type of MH used. A slight decline was observed for the specimens with Magnifin H10A (A1 and B1 samples), while some increase was observed for the material with Duhor C09 (A4 and B4 samples). No changes were noted for the last two composites (samples A2, A3, B2 and B3).

A strongly advantageous effect took place when acacFe was added to the composite with Magnifin H10A — its ε_B value increased more that three times (Figure 2). In addition, the *OI* value for that material increased in relation to the material without any iron compound (Figure 1). The obtained value justifies classification of that composite into the group of slow burning materials.

In the second test, the total burning time (t_f) for the composite with Magnifin H10A (B1 sample, in the vertical position) was also considerably shorter than for the composite samples of B series with other types of MH (Table 2). However, the findings were not sufficient to change the classification for any better than HB-40. As regards other samples covered by the test, their burning times increased somewhat after incorporation of acacFe, and their burning retardation in horizontal position was superior considerably as compared to composites with no addition of acacFe.

It was found finally that flammability of the described polyethylene composite, with 45 wt. % of Magnifin H10A and with 0.1 wt. % of acacFe (B1 sample), was lower in relation to that of the material containing 50 wt. % of Magnifin H10A only (C1 sample, Table 2). Moreover, the material with the iron compound had lower *d* and advantageously higher ε_B value.

Summary

The results of our preliminary research show that a small amount of acacFe, employed in PE-LD composites with MH (especially hydroxide modified with a silane compound), may reduce the amount of the mentioned fire retardant in the polymer matrix, and in addition it may increase the tensile strain at break of that material. It is reasonable to carry out further research on the use of acacFe in order to evaluate the most advantageous composition of the blend from the viewpoint of the best performance properties of that material.

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Rapid Communications

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