Polyethylene composites flame retarded with aluminum hydroxide as coatings for electrical cables

(*Rapid Communication*)

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DOI: dx.doi.org/10.14314/polimery.2018.6.7

Abstract: The investigations on linear low density polyethylene (PE-LLD) based composites flame retarded with packaged aluminum hydroxide (AH) coated with calcium stearate (AH40CD) and uncoated (AH40D) have been carried out. Loading of AH in composites was 60 wt %. It was found that for composites with coated AH (K2, K3 samples), fire resistance and mechanical properties were improved.

Keywords: polyethylene, aluminum hydroxide, flame resistance, mechanical properties.

Kompozyty polietylenowe uniepalnione wodorotlenkiem glinu stosowane na powłoki kabli elektrycznych

Streszczenie: Zbadano kompozyty na osnowie liniowego małocząsteczkowego polietylenu (PE-LLD) uniepalnione wodorotlenkiem glinu (AH) o budowie pakietowej, niepowlekanym (AH40D) i powlekanym powierzchniowo stearynianem wapnia (AH40CD). Udział AH w kompozytach wynosił 60 % mas. Kompozyty PE-LLD zawierające powlekany AH (próbki K2, K3) wykazywały lepszą odporność ogniową oraz korzystniejsze właściwości mechaniczne niż kompozyty PE-LLD z udziałem niepowlekanego AH (próbka K1).

Słowa kluczowe: polietylen, wodorotlenek glinu, odporność na płomień, właściwości mechaniczne.

The increase in interest and demand for composites with inorganic flame retardants results from introduced changes regarding environmental protection and safety of polymeric products [1, 2].

Metal hydroxides with a particle diameter from 100 to 300 nm or from 1.3 up to 10 μm and specific surface area from 3 to 50 m^2/g [3] are the most effective in the process of flame retardation. Composites with the addition of aluminum hydroxide (AH) are characterized by low smoke emission, low toxicity and negligible corrosiveness. The low price of this flame retardant makes composites a desirable solution in the plastics industry. As a result of temperature increase in the range of 190–230 °C AH, start to decompose, with emission of water vapor at a temperature of 350 °C, resulting in a weight loss 35 % of the initial mass [4]. Emitted vapor results in cooling of the burned polymer which reduces the speed of pyrolysis. Diluting volatile pyrolysis products of the polymer reduce the concentration of combustible gases below the lower combustion limit [5].

As a result of AH dehydration, crystalline alumina oxide (Al_2O_3) is formed. AH undergoes endothermic decomposition after the following reaction:

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O,\ \Delta H = 298\ kJ/mol$$

Along with the charred products formed on the surface of Al_2O_3, it acts as an insulating protective layer [6, 7]. However, AH flame retardant properties are noticeable only at high filling levels [8–12]. Due to its relatively low decomposition temperature, AH is used for polymers with low processing temperatures, such as ethylene-vinyl acetate copolymer (EVA) and low density polyethylene (PE-LD). Depending on the structure of the polymer, the type of application and the required degree of flame retardation, $Al(OH)_3$ is added in quantities of 5–200 wt % and even higher [13].

The experience gained in the work on flame-resistant nanocomposites [5] prompted us to work on the development of new polyethylene compositions with the addition of AH coated and uncoated, which are resistant to fire.

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EXPERIMENTAL PART

Materials

The following raw materials were used for preparation of tested composites:

– Linear low density polyethylene 1001 (PE-LLD), manufactured by ExxonMobile;

– Aluminum hydroxide $Al(OH)_3$, APYRAL 40D (AH40D), manufactured by NABALTEC;

– Aluminum hydroxide $Al(OH)_3$, coated with calcium stearate, APYRAL 40CD (AH40CD), manufactured by NABALTEC;

– Antioxidant, pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], IRGANOX 1010 (AI), manufactured by BASF;

– Grafted maleic anhydride (*g*-MAH), used as a compatibilizer, manufactured by BYK;

– Ethylene-vinyl acetate copolymer (EVA), used to improve the flexibility of the composition under the name EVATANE 2803, manufactured by Arkema.

Preparation of polymer compositions based on the PE-LLD matrix

The composites (summarized in Table 1) in the form of granules were obtained by a mixing extrusion process on a co-rotating twin screw extruder, L/D = 40. AH was added in 1/3 of the length through the side feeder and all other components directly into the main hopper. The temperature profile of the composite extrusion was: first zone 60 °C, zones from two to five 145 °C, zones from six to seven 155 °C, and the melt temperature was 165 °C.

Preparation of specimens for mechanical tests

From the produced granulate, a cable coating was extruded. The temperature range of the extruder barrel was 145–170 °C, a cross head was used with a temperature of 175 °C and a puller at a speed of 1.5 m/min. The specimens were cut from the extruded cable coatings obtained in accordance with PN-EN 60811-501:2012 E.

Preparation of specimens for glow wire test and flammability according to UL-94

Specimens for glow wire test and flammability according to UL-94 were obtained in the injection molding process using the BATTENFELD PLUS 350/75 injection molding machine. The process parameters were: mold temperature 90 °C, nozzle temperature 165 °C, I and II cylinder zone 180 °C, injection pressure 16 MPa, hold pressure 7 MPa, plasticizing pressure 2 MPa, hold pressure time 30 s, cooling time 40 s, injection speed 50 cm^2/s, rotation of the screw 230 rpm.

Conditioning and aging of specimens tested composites

The specimens of the tested composites were exposed to the aging process in air, water and oil in accordance with the guidelines of standards for cable: DIN VDE 0276-604:2008-02, DIN VDE 0250-214:2002-04, BS 7655-0:2006, PN-EN 50363-4-1:2010, IEC 60092-360:2014. Table 2 presents conditions for conditioning and aging of composites specimens (K1, K2, K3).

Methods of testing

Determination of flame resistance of tested composites

Specimens were exposed to conditioning and aging, in the above conditions, degree of flame retardation has been determined by:

– glowing wire (*GWFI*) in accordance with PN-EN 60695-2-11:2005;

Table 1. Composition of obtained composites

Composite symbol	Content of composite component, wt %					
	AH40D	AH40CD	PE-LLD	AI	*g*-MAH	EVA
K1	60	–	34.8	0.2	2	3
K2	–	60	34.8	0.2	2	3
K3	–	60	33.8	0.2	3	3

Table 2. Conditions of conditioning and aging of specimens

Conditions of conditioning/aging of specimens	Medium	Temperature, °C	Time, h
I	Air, humidity 55 %	23	24
II	Air	110	168
III	Water	70	168
IV	Water	20	168
V	Industrial oil IRM 902	70	4

– vertical combustion test according to UL-94 and oxygen index test (*LOI*) according to PN-EN ISO 4589-2:2006.

Determination of tensile strength at the yield

Tensile strength at the yield was determined in accordance with PN-EN ISO 527-2:2012 on Instron 5967 testing machine, at travel speed of 250 mm/min. The measurement and conditioning temperatures of the samples were the same (23 °C).

Morphology evaluation

Samples of tested composites were placed into a container with liquid nitrogen using tweezers, and then crushed with a hammer to receive brittle fracture surface. Then, to receive pictures using JEOL JSM-5500LV SEM brittle fracture surface of composites were sputter-coated with gold to get information on their morphology.

RESULTS AND DISCUSSION

The results of tests of the flame retardation efficiency and mechanical properties of K1–K3 composites after their conditioning and aging are collected in Table 3. In order to assess the degree of dispersion of the flame retardant in the polymer matrix, SEM analysis was performed. Specimens of composites conditioned under conditions I (Table 2) were tested. It was observed that increasing dosage of grafted maleic anhydride (*g*-MAH, compatibilizer) had a positive effect on the homogenization of K3 composite (Fig. 1c) with respect to K1 (Fig. 1a) and K2 (Fig. 1b) composites.

For K2 and K3 composites that were flame retardant with AH coated, higher flame retardation parameters were achieved (Table 3). This is probably due to a better flame retardant dispersion and a significant reduction in

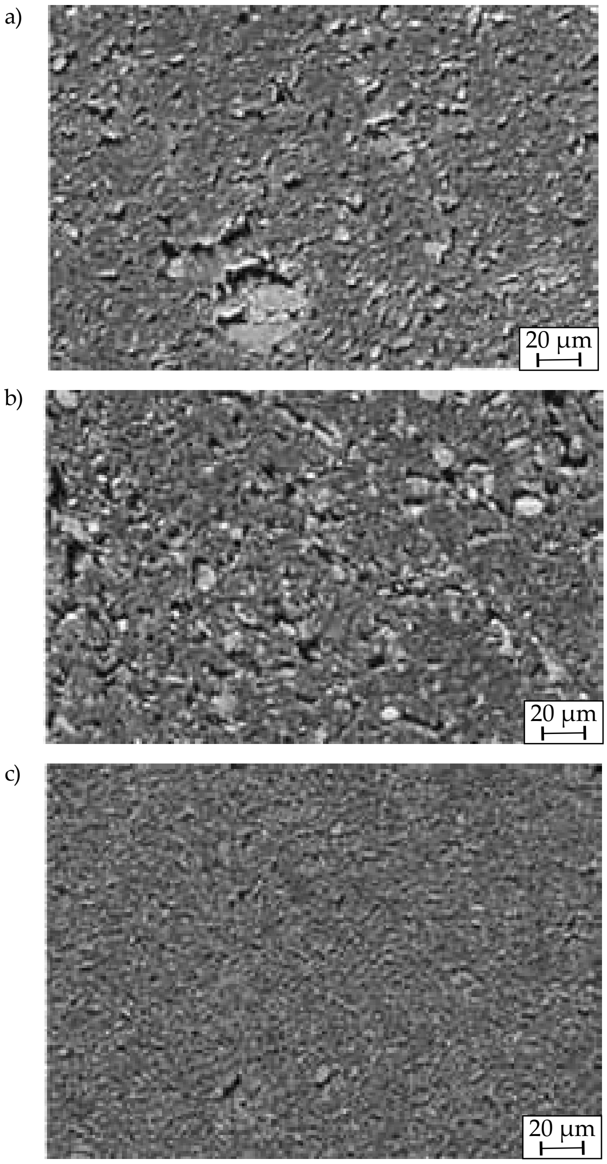

Fig. 1. SEM micrographs of brittle fracture surfaces of composites: a) K1, b) K2, c) K3

Table 3. Results of flame resistance tests and mechanical properties of the tested composites after conditioning and aging

Composite symbol	Aging condition	*GWFI*, °C	UL-94	*LOI*, %	Tensile strength, MPa	Elongation at break, %
K1	I	960	V0/1.6 mm	36	11.2	147
	II	960	V0/1.6 mm	36	12.1	125
	III	850	V1/1.6 mm	29	8.0	95
	IV	960	V0/1.6 mm	34	9.1	107
	V	850	V1/1.6 mm	30	8.2	164
K2	I	960	V0/1.6 mm	38	11.5	156
	II	960	V0/1.6 mm	39	12.8	134
	III	960	V0/1.6 mm	36	9.6	121
	IV	960	V0/1.6 mm	35	9.8	134
	V	960	V0/1.6 mm	34	9.2	178
K3	I	960	V0/1.6 mm	42	11.4	160
	II	960	V0/1.6 mm	41	12.9	139
	III	960	V0/1.6 mm	38	9.9	125
	IV	960	V0/1.6 mm	39	10.3	134
	V	960	V0/1.6 mm	39	9.5	181

Fig. 2. ***GWFI*** **test for K3**

the amount of AH agglomerates in the polymer matrix (Fig. 1). This has a positive effect on the results of testing specimens after aging, because it limits the ability to absorb water and oil by the tested composites. Irrespective of the aging conditions for the composites K2 and K3, the flammability class V0 and high *LOI* values were in the range of 34 to 39 % for K2 and 38 to 42 % for K3. In the case of composite K1, a slight deterioration of the flame resistance for specimens subjected to aging in water at 70 °C and oil (Table 2) was observed. For samples aged in water and oil flame class was reduced to V1 and *LOI* decreased up to 29 % and 30 % (Table 3). The same unfavorable effect was observed in case of testing with glowing wire, the *GWFI* parameter was reached at 850 °C. In all other cases (Table 3), the *GWFI* parameter reached 960 °C. Figure 2 shows realization of *GWFI* test for K3.

As expected results of strength at the break were significantly better for composites K2 and K3 (Table 3). There is a clear influence of the aging process on the results of measurements.

Tensile strength results at the yield and elongation at break for the specimens aged under conditions II to IV were decreased for all tested composites. For specimens aged under conditions V tensile strength results at the yield were also decreased but results of elongation at break were increased and were higher than for conditions I. Significantly better aging resistance of K2 and K3 composites that contain coated AH was also observed (Table 3).

CONCLUSIONS

It was confirmed that modification with aluminium hydroxide coated with calcium stearate AH40CD significantly improves the fire resistance of the composites. Addition of compatibilizer improves its dispersion in the polymer matrix, as observed in SEM photomicrographs. Composites containing $Al(OH)_3$ coated with calcium stearate AH40CD are characterized with better strength properties, both before and after aging.

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Received 23 I 2018.