Fly ash used as a reinforcing and flame-retardant filler in low-density polyethylene

Anna Porąbka[1), *)], **Kamil Jurkowski**[1)], **Jadwiga Laska**[1)]

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Abstract: In this study, the possibility to modify low density polyethylene (PE-LD) with fly ash (FA) was tested. Four series of PE-LD composites filled with 1, 5, 20 or 50 wt % of FA were prepared by injection molding. The samples in each of the series differed in particle size of the filler used (0—15 μm, 15—30 μm, 30—60 μm). The influence of amount and the particles size of filler on morphology, mechanical properties, thermal stability and flammability of the composites were investigated. The results show that composites with the addition of FA in the amount up to 20 wt % are characterized by good mechanical properties and processability, and also smaller than the pure PE-LD, flammability.

Keywords: low-density polyethylene, fly ash, composites, mechanical properties, thermal properties, flammability.

Popioły lotne jako napełniacze i środki zmniejszające palność polietylenu małej gęstości

Streszczenie: W ramach pracy zbadano możliwości modyfikacji polietylenu małej gęstości (PE-LD) za pomocą popiołów lotnych (FA). Metodą formowania wtryskowego przygotowano cztery serie próbek kompozytów PE-LD zawierających 1, 5, 20 lub 50 % mas. FA. Próbki w każdej z serii różniły się wielkością cząstek użytego napełniacza (0—15 μm, 15—30 μm, 30—60 μm). Oceniono wpływ ilości oraz wielkości cząstek napełniacza na morfologię, właściwości mechaniczne, stabilność termiczną oraz palność otrzymanych kompozytów. Wyniki badań wskazują, że kompozyty z dodatkiem FA w ilości do 20 % mas. charakteryzują się dobrymi właściwościami mechanicznymi i przetwórczymi, a także mniejszą palnością, niż czysty PE-LD.

Słowa kluczowe: polietylen małej gęstości, popioły lotne, kompozyty, właściwości mechaniczne, właściwości termiczne, palność.

Polymers are the materials whose structure can be very easily influenced by physical modification, which determines at the same time the manner of their use. One way of the mentioned modification is the introduction of various kinds of fillers: organic, inorganic, and others, including waste. In the 80s, a disposal of waste products resulting from combustion of brown and hard coal in the furnaces of power plants became a very important issue. Fly ash (FA) has become particularly bothersome causing air and water pollution with dust [1]. In the high-temperature reactions the solid component is nowadays captured from the gas and dust mixture and used on a large scale in the industry of construction materials (concrete), road- and plastics industry [2—4]. FA as an additive to other materials can act as a filler and reinforcing phase. Table 1 presents a few types of the obtained FA due to their chemical composition [4—6]. Out of hard coal one can obtain FA, which in its structure contains large amounts of SiO_2 and Al_2O_3 [5]. FA from less popular brown coal is the source of CaO. The main component of FA is glass whose amount exceeds even 80 % [4]. Grain size is another feature which divides FA into three types. The first one is characterized by small grains and content of the particles with diameter $d \geq 60$ μm below 30 %. The next in the classification is medium FA, whose particles meeting the above requirement comprise 30—50 % of all grains, and coarse FA with the share of grains of $d \geq 63$ above 50 %.

Physical parameters determine the way in which FA can be used. Summarizing, a good quality of FA is assured by: high content of glassy phase, low alkali content

Table 1. Chemical composition of fly ashes (FA) obtained from combustion of coal

Type of FA	Symbol	SiO_2, %	Al_2O_3, %	CaO, %	SO_3, %
Siliceous	K	>40	<30	<10	<4
Aluminous	G	>40	>30	<10	<3
Calcic	W	>30	<30	>10	>3

[1)] AGH University of Science and Technology, Faculty of Materials Sciences and Ceramics, al. Mickiewicza 30, 30-059 Kraków, Poland.

[*)] Author for correspondence; e-mail: poranna@agh.edu.pl

and high surface development (2000—6000 m^2/kg) [3, 6]. It appears to be well suited to modify the properties of plastics, which by their nature rarely meet the requirements for construction materials [2, 4].

Polyethylene (PE), in turn, is one of the most widely used polymers in the world. The world annual production capacity of linear low density polyethylene in 2012 totaled above 34.5 million tons [7]. As the technology of production and processing of PE is not expensive, researchers look for some methods to improve its mechanical strength, so that it could be successfully used in the construction industry. The benefits that characterize thermoplastics in general include: easy forming of various objects with complex shapes, favorable strength-to-weight ratio, good mechanical properties and excellent electrical insulating properties, relatively good chemical resistance, possibility of long-term use without the need of additional maintenance and possibility of multiple processing (recycling) [8, 9]. An indisputable fact is that in a large group of plastics, one of the most popular is PE available in the types like: PE-HD, PE-MD, PE-LD and PE-LLD (high-, medium-, low- and linear low-density polyethylene, respectively) [8]. Key features of the PE-LD are: easy processability [8], low melting point (about 100 °C) facilitating processing, and high impact strength. It is worth to mention the reported optical properties, *e.g.* high transparency. Operators of injection molding machines and extruders acknowledge its excellent processing performance — the best of all types of PE. On the other hand, the disadvantage, exhibited by films and plates made of PE-LD, is primarily unsatisfactory tensile strength (Rm), which results in difficulties in obtaining a range of materials resistant to all kinds of mechanical loads [10]. Some kind of prevention against these drawbacks can be modifying PE-LD with other PE plastics or reinforcing filler. For example, composites of PE-HD with fly ash have been investigated [11, 12]. A wide range of PE-LD users recognizes it mainly under commercial names Malen E and Lupolen.

In this work, Malen E was modified with particular amounts of FA, and the mechanical tests as well as flammability tests were carried out to answer the questions about the effectiveness of such modification.

EXPERIMENTAL PART

Materials

Low-density polyethylene (PE-LD), with trade name Malen E, in the form of granulate was purchased from Basell Orlen. This PE-LD intended for the use in films is characterized by the density of 0.919—0.923 g/cm^3 and melt flow rate MFR = 1.6—2.5 g/10 min.

Fly ash (FA) of type „S" was purchased from Połaniec power plant (Poland). It was separated on ALPINE fine classifier into three fractions: 0—15 μm, 15—30 μm and 30—60 μm (P-001/F1, P-001/F2, P-001/F3, respectively).

Sample preparation

Samples of the composites of PE-LD + FA were produced by injection molding in the form of paddles 2 × 5 × 75 mm with a single screw injection molding machine Multiplas V4-S-15 N. The samples had dimensions compatible with the PN-81/C-89034 standard and were selected in the final part of injection because of their required composition. Before molding both materials, *i.e.* PE-LD granulate and FA particles, were mixed manually using the FA in amount of 1, 5, 20 or 50 wt %.

Samples, with the same contents of FA, were prepared for the static compression test. They were obtained by hot pressing of the PE-LD + FA films in the temperature of 100—105 °C in the form of straight cylinders according to PN-83/C-89031 standard using manual press PROMA LIS AP-3 and a temperature controller INTECH type RC-10A. The height of the samples was calculated according to the equation:

$$h = i \cdot \lambda = \frac{\lambda}{4} \cdot d \qquad (1)$$

where: h — sample's height, i — the smallest radius of gyration, λ — fineness ratio, d — diameter of the straight cylinder.

The specified standard gives a value of fineness at the level of 10. In exceptional circumstances, *e.g.* when the samples undergo buckling during strength testing, this parameter may be reduced to 6. The diameter of the straight cylindrical samples was equal to the diameter of the hole in the matrix and in this case $\lambda = d = 6$ mm. The height of the tested samples calculated according to eq. (1) is 9 mm.

Methods of testing

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses were carried out on SEM/EDS FEI NOVA NanoSEM 2000 (USA).

Studies of mechanical properties of the obtained samples, depending on the content and granulation of FA, were performed with the use of a universal strength testing machine Zwick 1435. Measurements of tensile strength, resistance to break and compressive strength were performed. Brinell hardness tests were made with the use of durometer Universal-Hardness Testing Machine KB Prüftechnik.

Differential scanning calorimetry (DSC) was made on a differential scanning calorimeter, Netzsch STA 449 F3 Jupiter (Germany).

Flammability tests were performed using a furnace and thermal imager NEC Thermo Gear G100 NEC Avio Infrared Technologies Co. Ltd. with measuring temperature range up to 500 °C.

The applied testing methods provide valuable information including thermal properties, and also enable an assessment the topography and elemental composition of the tested material.

RESULTS AND DISCUSSION

SEM/EDS analysis

Surface morphology of the obtained samples as well as the shape and size of the grains of the fly ash were observed using SEM method. Fig. 1 shows a SEM image of the FA particles from the fraction 0—15 μm and of the composite containing the 30—60 μm fraction of FA. The image in Fig. 1a clearly shows the spherical shape of FA particles and their dimensions. In the SEM image of PE-LD + 5 % of FA composite (Fig. 1b) the smooth surface with microdefects resulting from injection molding can be seen, this SEM image confirms good dispersion of FA in the matrix and that only very few FA grains remained on the surface. Data of elemental analysis collected for the surface of a grain show the presence of carbon indicating PE-LD film. The elemental analysis of FA performed using EDS is shown also in Fig. 1. These analyzes show that the FA contains mainly elements like C, Si, Al and O. Regardless of the point at which the analysis was made, Si and Al contents are similar, what indicates the „G" (aluminous) type of FA (see Table 1). Therefore, analyses performed on the surface of the composite present the composition characteristic of the pure FA, and the presence of carbon indicating the smooth layer of the polymer on the FA.

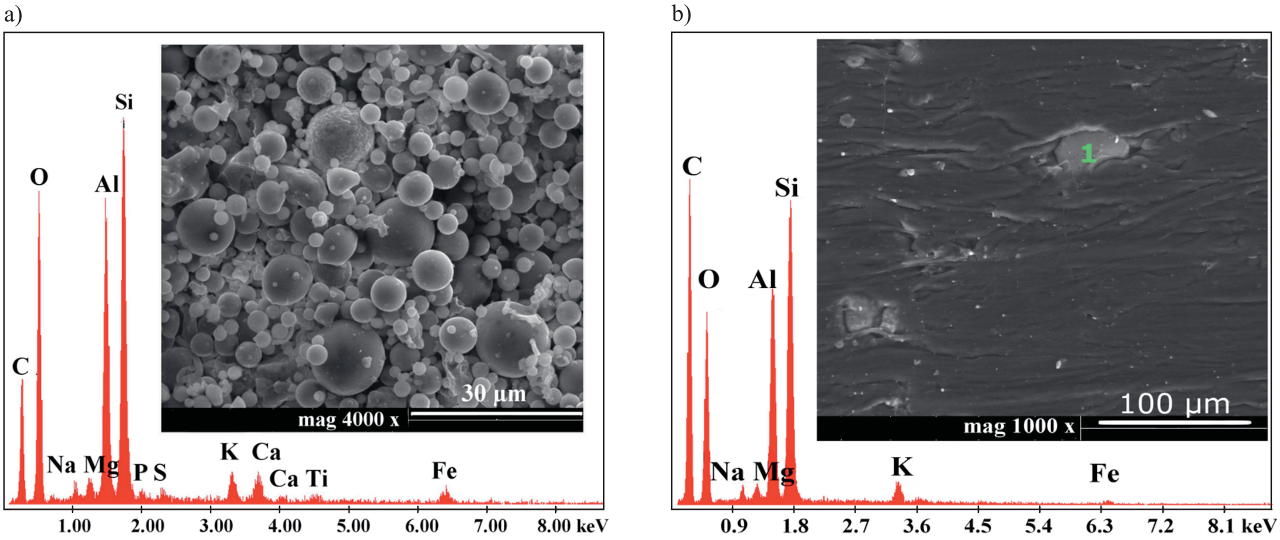

Fig. 1. a) SEM image and average elemental analysis (EDS) for: a) 0—15 μm fraction of FA particles, b) the surface of PE-LD composite with 5 wt % of 30—60 μm fraction of FA particles (EDS analysis in the point labeled 1)

Static tensile strength

All samples were tested depending on the content of FA in the composites and grain size of this filler. The number of samples was always in the range of $n = 20—28$. In the case of the samples containing 50 wt % of FA technological difficulties occurred during injection, especially for the larger particle size. Samples containing the 30—60 μm FA fraction in the amount of 50 wt % resulted in blocking the machine, while the samples containing the 15—30 μm FA fraction were obtained in a smaller number. Results of mechanical properties investigation are presented in Fig. 2. On the basis of the obtained graphs it can be concluded that an increase of FA filler content in the composite leads to a significant increase of the average Young's modulus (E) in comparison with pure PE-LD (Fig. 2a). One example may be the composite containing 50 wt % of 0—15 μm FA fraction, whose E modulus of 425 MPa is more than three times larger than E of neat PE-LD (127 MPa). No significant differences between mean values of Rm were observed for the composites and pure PE-LD when the content of FA did not exceed 20 wt % (Fig. 2b). However, for the higher loads, especially 50 wt %, the decrease in the value of this parameter compared to unfilled material can be noticed. For example, for the samples with 20 wt % of 30—60 μm FA fraction and 50 wt % of 15—30 μm FA fraction the decrease of Rm compared to pure PE-LD was about 15 %. In all samples Rm was reduced along with the increase of FA content as shown in Fig. 2b. It was observed, that the best effects were obtained after adding the FA of medium grain size (15—30 μm). In the case of other fractions, preferred is the low content of the FA in the composites. An increase in the E modulus, suggests that the average elongation (ε) also changes. The average ε of the unfilled PE-LD is higher than for the composites. It was noticed that ε decreased with increasing FA content regardless of the particles size. The lowest value of this parameter was recorded for PE-LD with 50 wt % of 0—15 μm FA fraction and was more than 70 % lower compared to that obtained

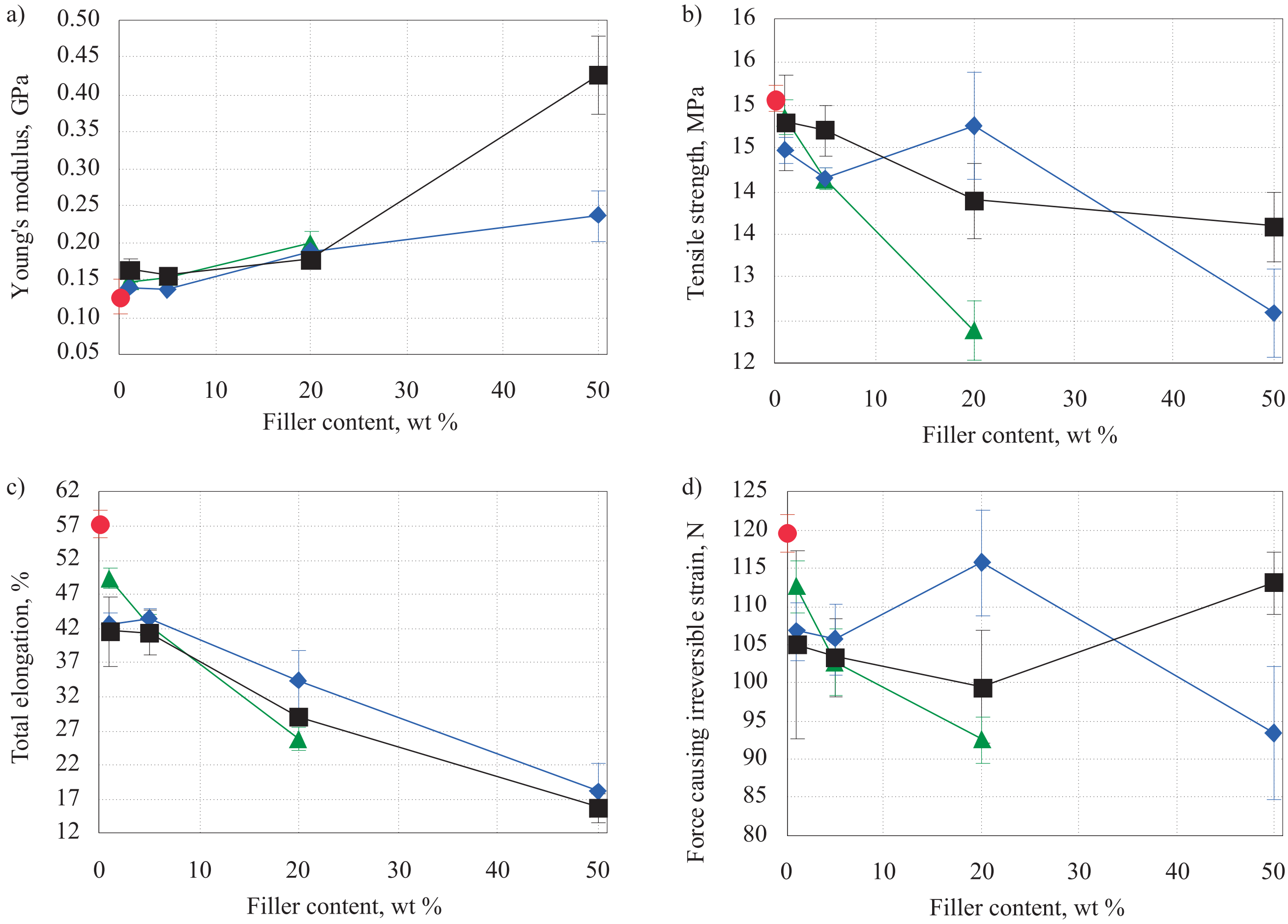

Fig. 2. The influence of the FA content and FA grain size (black — 0—15 μm, blue — 15—30 μm, and green — 30—60 μm, red — pure PE-LD) on: a) average Young's modulus (*E*), b) average tensile strength, c) average total elongation, d) average force causing irreversible strain

for the pure PE-LD (Fig. 2c). Also the force needed for irreversible strain is lower in the case of the composites compared to pure PE-LD (Fig. 2d).

Static compression test

The research concerning compressive strength also showed that the increase of the filler content in the composite leads to an increase in the average compressive modulus in all cases under consideration (Fig. 3) compared to the unfilled PE-LD. The maximum value (nearly twice higher than that of the pure polymer) was achieved in the composite containing 1 wt % of the 15—30 μm FA fraction. It seems that obtaining high compressive modulus apparently is not a result of gradual increase in the percentage of the filler in the composite or the size of its grains, but it may result from an interaction between the polymer matrix and filler. With the applied compressive force between 0 and 1000 N the samples exhibited relatively easy plastic deformation, while after compressing 9 mm thick sample to the thickness of 3 mm, this sample exhibited the properties of an elastic material. Further increasing the pressing force failed to cause significant deformations until the end of the measurement range.

Brinell hardness test

The results of examining Brinell hardness (*HB*) are shown in Fig. 4. The increase in the filler content generally leads to an increase of *HB* in comparison with unfilled PE-LD paddle-shaped sample. The maximum *HB* was

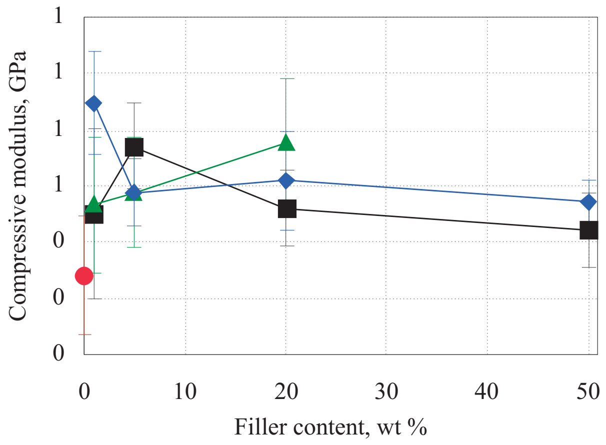

Fig. 3. The influence of the FA content and FA grain size (designations as in Fig. 2) on the compressive modulus

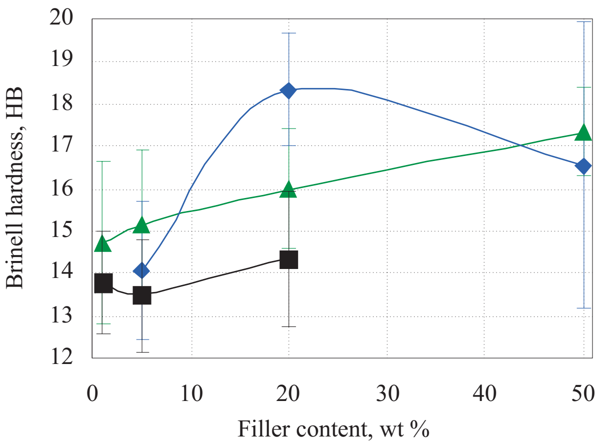

Fig. 4. The influence of the FA content and FA grain size on the average Brinell hardness (designations as in Fig. 2)

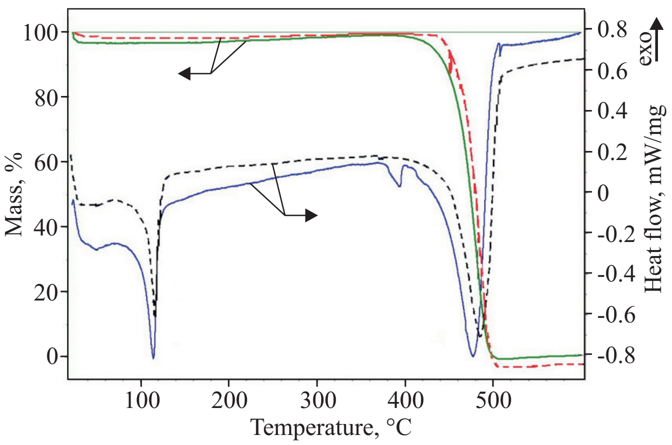

Fig. 5. TG and DSC thermograms with registered transitions registered for PE-LD (green — TG, blue — DSC) and PE-LD + 5 % FA (15—30 μm, red — TG, black — DSC) samples

obtained for the sample with 20 wt % of the 15—30 μm FA fraction. The increase of this sample's *HB* compared to pure PE-LD was 30 %. The most predictable increase in *HB* was obtained after using FA with the smallest particle size 0—15 μm. The least satisfactory effect was observed in the composite with the 30—60 μm FA fraction where *HB* even decreased or remained on the same level depending on FA content. The relation between *HB* and FA content in this case is nearly proportional. However, in the samples containing FA of bigger granulation, a maximum or a minimum hardness value can be observed. Basing on the dispersion of the measurement values, it can be concluded that there is a relatively uniform distribution of the filler in the samples.

Thermal properties

Figure 5 shows the results of the thermal research on PE-LD + FA samples obtained using DSC and thermogravimetry (TG) techniques. In the thermogram of pure PE-LD the melting temperature (T_m) of the polymer can be read at 115 °C. In the temperature of about 400 °C the reactions of polymer decomposition begin, wherein the first effect in the process occurs at the temperature of 394 °C, at which there also starts a slight mass loss. Next, there is a second, much clearer endothermic effect of absorbing large amounts of heat, accompanied by rapid mass loss. The total decomposition of the polymer occurs at 500 °C. Fig. 5 shows also an exemplary DSC and TG thermogram of PE-LD containing 5 wt % of the 15—30 μm FA fraction. Analyzing the thermograms of PE-LD + FA samples it can be concluded that the additive does not significantly change T_m of PE-LD, which means that the crystalline structure is not destroyed. A very small increase in T_m is observed in the samples containing FA larger then 15 μm, however the increase by about 0.7 °C lays within the measurement error. The most obvious differences occur in the area of polymer degradation. The specimen containing the smallest FA particles behaves virtually the same as pure PE-LD, whereas the samples containing larger particles (>15 μm) exhibit increased thermal resistance. What is interesting, the small melting peak at 394 °C diminishes after adding 5 wt % of the 15—30 μm FA fraction, and disappears totally in the case of the composite with 5 wt % of largest particles (30—60 μm). In addition, the decomposition of the composites (the mass loss) begins at the temperature of about 20 °C higher than in pure PE-LD.

Flammability test

The combustion of polymers follows according to the fixed pattern. First, the polymer is preheated in the presence of a flame source. During preheating, the polymer decomposes releasing gaseous hydrocarbons into the atmosphere around the flame source. These hydrocarbons become ignited at the appropriate temperature and combust releasing heat. Although most of this heat is lost to the surroundings, a part comes back to the polymer and causes pre-heating, decomposition, ignition, and combustion of the polymer. Then, the cycle continues. Disturbing this cycle would relatively inhibit combustion, thus different methods have been employed to increase either the ignition time, or the time before which the polymer begins to generate fire on its own without an external heat source (auto-combustion) [13] or to reduce the flame propagation rate (spread of fire). Disrupting the fire cycle can be achieved in three ways: modifying the polymer to produce less flammable gases, inhibiting burning or extinguishing flame and reducing the feedback heat from the flame to the decomposing polymer. Therefore, many flame retardants have been developed [13]. Basing on the knowledge that the glow time of pure PE-LD lasts 18 s, burning time is 50 s and flame propagation rate is equal to 257 s, whereas in the filled PE-LD those combustion processes occur with retardancy increased even by 100—600 % [14, 15], the flame test has been performed. There are many test methods to examine the flammability of a polymer. Most of these methods are not quantitative in the sense that a prescribed heat flux is not provided or the test method does not produce data useful for a prediction of the ignition time and hence the aspect of flammability hazard to determine the tendency to ignite and sustain burning. If the test results in the ignition and rapid combustion of the sample, apparently the material is a flammability hazard. On the other hand, if the test results in no ignition, it does not mean that the material meets fire safety standards. The test results can be affected by environmental conditions, sample size, and flame exposure size [16].

Samples with dimensions 10 × 10 × 0.1 cm obtained by hot pressing at about 260 °C were successively placed in the furnace and subjected to a flame of propane-butane flame source. The measurement of the temperature during the test was enabled by an infrared camera, whose principle of operation is based on the infrared radiation emitted by objects. It should be noted that the distance between the flame face and the samples in all cases was 15—20 cm, so there was no direct contact with the flame itself. Fig. 6 shows the results of fire tests carried out on each sample. Observation and analysis of the conducted experiment allows concluding that the addition of FA created some sort of a barrier, so that the modified material is burned slower compared to the pure PE-LD (Fig. 6a) and the flow was observed at the temperature over 150 °C. Such a hypothesis is also confirmed by examination of the composite films after the experiment, because it is clear that the structure of the areas, where due to an uneven distribution of FA, and thus bigger amounts of it, did not tear. However in the areas where there was less FA, the polymer melted and the surface of the composite film was severely damaged (Fig. 6b). It follows, that the samples with added filler have a higher thermal resistance in extreme conditions, which is in accordance with the results of DSC and TG.

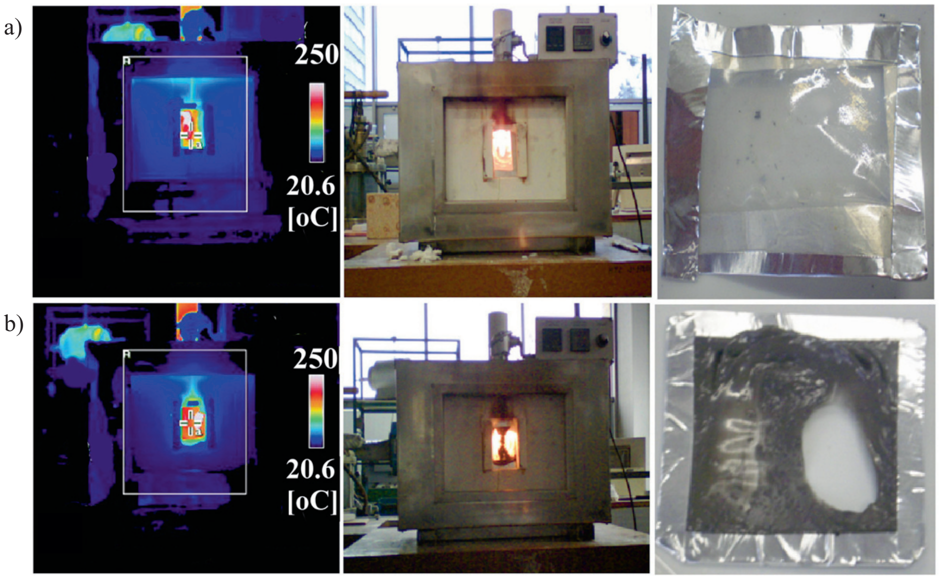

Fig. 6. Results of the fire test carried out and the view of the sample for: a) pure PE-LD; b) exemplary sample of PE-LD + 50 % FA (15—30 μm)

CONCLUSIONS

In this study the waste filler, FA, was added to the low-density polyethylene in the amount of 1, 5, 20 or 50 wt %. During the injection molding process no major problems were encountered, although the addition of FA increases the viscosity of the mixture processed. Only the 50 wt % content of 30—60 μm FA fraction disables producing a sample in the process of injection molding. Generally, the technological line did not require additional changes in the instrumentation. Analysis of the tensile strength of the studied samples proved that FA does not significantly affect the mechanical properties of the matrix when the filler content is less than 20 wt %. Higher FA content introduces major changes in the composite structure, leading to reduction of the tensile strength. The presence of the FA in PE-LD greatly increases the Young's modulus in the obtained composite materials. There is also a tendency to reduce the elongation at break, ε, with increasing the FA content. The thermal analysis of the composites showed that the addition of FA increases the thermal resistance. The temperature of their decomposition is by 20 °C higher than that of pure PE-LD. The flame tests show the increase of the melting temperature of the composites to above 150 °C. Concurrently, the time after which the polymer at high temperature reached the flow state increased together with FA content. It can be stated that the addition of FA in order to modify PE-LD is a reasonable and effective solution. Thus, with the acceptable mechanical properties and processability, there are no objections to substitute even 20 wt % of the polymer mass by FA.

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