The effect of natural fillers on the mechanical properties and flammability of low-density polyethylene

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Abstract: The effect of 10-40 wt% natural fillers (pumpkin husks, bean sorting waste, pine sawdust) on the mechanical properties and flammability of LDPE was examined. As the filler content increased, the hardness slightly increased and the tensile strength and relative elongation decreased. The tensile modulus more than doubled (pumpkin husks, pine sawdust). The linear combustion rate increased unfavorably, but the assumed flammability class HB40 was achieved, except for LDPE filled with 40 wt% pine sawdust (HB75). At the same time, the temperature in the combustion area decreased in the vertical flammability test.

Keywords: polyethylene, natural fillers, tensile properties, flammability.

Wpływ napełniaczy naturalnych na właściwości mechaniczne i palność polietylenu małej gęstości

Streszczenie: Zbadano wpływ naturalnych napełniaczy (łuski dyni, odpady sortownicze fasoli, trociny sosnowe) stosowanych w ilości 10-40 % mas. na właściwości mechaniczne i palność LDPE. Wraz ze wzrostem zawartości napełniacza nieznacznie zwiększała się twardość, a zmniejszała wytrzymałość na rozciąganie i wydłużenie względne. Moduł sprężystości przy rozciąganiu zwiększył się ponad dwukrotnie (łuski dyni, trociny sosnowe). Niekorzystnie wzrosła liniowa szybkość spalania, ale uzyskano zakładaną klasę palności HB40, poza LDPE z dodatkiem 40 % mas. trocin sosnowych (HB75). Jednocześnie obniżyła się temperatura w obszarze spalania w pionowym teście palności.

Słowa kluczowe: polietylen, napełniacze naturalne, właściwości mechaniczne przy rozciąganiu, palność.

Polymers and polymer composites used in mass production, those based on polyolefin polymers, are modified to reduce their unfavorable impacts on the natural environment [1–4]. Despite the mastered processes of material, raw material, and energy recycling, a significant part of polyolefin waste, polyethylene, and polypropylene, remains in landfills and outside them, and their decomposition takes an exceptionally long time [4-6]. It creates ecological threats related to the long-term exclusion of land from use and contamination of soil and groundwater, and it is economically ineffective and socially unacceptable. Products of its decomposition also accumulate in living organisms, posing threats to their health and life [1, 3, 4].

The current ecological trends and environmentally friendly lifestyle, called „The 4R", derived from the English words "Reduce, Reuse, Recycle, Repair", as well as the EU strategy for the circular economy, have increased interest in degradable and biodegradable polymer composites. In many applications, traditional polymer composites are replaced by biocomposites containing fillers of plant origin [1, 4, 6–8]. WPC composites containing fillers in the form of wood powders have been on the market for many years, used primarily as garden elements, construction joinery, elements of sorting equipment, and even vehicle parts, and their production processes and properties are already relatively well known [1, 2, 6].

Most recent research regards composites containing kenaf, sisal, jute, flax, hemp, bamboo, cotton, and coconut fibers [1, 2, 4, 7]. Attempts to obtain partially degradable biocomposites based on polyethylene and waste from the food industry in the form of sunflower husks, nut shells, pistachios, and bran are being made [1, 2, 7, 9, 10]. This is due to the temperature limits for processing composites with natural fillers to approximately 200°C. It narrows the choice of materials to thermoplastic polymer composites, such as poly(vinyl chloride), polystyrene, polypropylene, and polyethylene, which are produced and used in higher quantities. In many literature references [1, 2, 6] one can find information that composites with natural

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fillers up to 30 wt% have comparable properties to the material constituting the matrix, good processability, and appearance. In the case of intended reduction of their production costs, especially using recycled materials, filler surface modifications are not often used [2, 9, 10]. Unfortunately, the negative effect in this case is usually a deterioration of mechanical properties and flammability [8–14]. For most natural fillers, research concerns the introduction of micrometer-sized particles into polyethylene. Tests on the properties, including flammability, of polyolefin composites filled with particles of the order of millimeters are studied rarely. Therefore, this area of research needs further exploration.

The aim of the work was to obtain composites based on polyethylene and selected, unmodified natural fillers in the form of pumpkin peels, waste from sorting beans and pine sawdust with a surface appearance like organic materials, with a maximum 30% reduction in tensile strength and a minimum flammability class of HB40. Moreover, the aim was to determine the dependence of selected mechanical properties and flammability on the type and content of natural fillers in low-density polyethylene.

EXPERIMENTAL PART

Materials

The polyethylene Malen E FABS 23-D022 (BasselOrlen Polyolefins Ltd, Poland) was used as a raw material. It has a melt flow rate MFR of 1.95 g/10 min. (190°C; 2.16 kg), a density of 923 kg/m^3, an elastic modulus of 250 MPa, a yield point of 10 MPa, and it is intended for the injection molding process and film extrusion. The natural additives to LDPE (hereinafter referred to as A) were pumpkin husks (B) and bean sorting waste (C). For reference wood post-production, in the form of pine sawdust (D) was also introduced into LDPE. Those additives had particle sizes in the range of 0.8–1.6 mm. With a filler content of 10–40 wt% a small deterioration in the mechanical properties and ignition and combustion resistance of polyethylene was expected, while obtaining favorable features such as odor and appearance like natural materials.

Fig. 1. The appearance of obtained samples

Samples preparation

After grinding and drying for 24 hours at 40°C, the fillers were introduced into the polyethylene in the mechanical mixing using a frame mixer. Samples in the form of classic tensile test blades were obtained using a laboratory Allrounder 320 C500-170 injection molding machine (Arburg, Loßburg, Germany). The temperature in the individual heating zones of the plasticizing system of the injection molding machine was 30, 160, 170, 180 and 180°C, the nozzle temperature was 200°C, the injection pressure was 90 MPa, the injection mold temperature was 23°C, the mold cooling time was 20 s, and the total cycle time was process 34 s. The samples with a filler content of 20 wt% are presented in Fig.1.

Methods

Hardness was determined according to the PN-EN ISO 868 standard using a Shore hardness tester model AFFRRI ART 13 with a test head according to the D scale. Tensile properties were determined in accordance with the PN-EN ISO 527 standard, using a Zwick/Roell Z010 testing machine (Ulm, Germany) with a head with a maximum tensile force of 10 kN. The crosshead speed was 50 mm/min. Vertical and horizontal flammability tests were carried out in accordance with the PN-EN 60695-11-10 standard, using a universal stand for testing polymers flammability [9]. The ignition source was a 50 W gas burner powered by propane. The sample burning time and the length of the burned surface were measured. The temperature of the sample combustion area was measured with a V20 thermal imaging camera from Vigo System S.A. (Ożarów Mazowiecki, Poland).

RESULTS AND DISCUSSION

Because of undertaken research on modified polyethylene samples, the data were obtained and presented in Table 1. It allows to determine hardness dependency on the type and content of the filler. There were no statistically significant dependences of hardness based on the type of filler used in the case of bean waste (C) and pine sawdust (D). Within the increase in the content of pumpkin husk (B), the hardness of polyethylene increases in comparison to unmodified LDPE by almost 16%, reaching a value of 57.3°Sh at 40 wt% of its content. No change in hardness for bean waste (C) was observed, with the hardness of polyethylene increased slightly after the introduction of pine sawdust (D), up to 52.3°Sh with its 40 wt% content in PE.

The dependence of LDPE tensile properties, such as tensile strength, tensile modulus, and elongation at the

T a b l e 1. Shore D hardness test results

Type of filler	Filler content, wt%				
	0	10	20	30	40
B	49.4	51.2	52.3	55.0	57.3
C	49.4	47.4	47.8	48.6	49.1
D	49.4	50.0	50.9	52.6	52.3

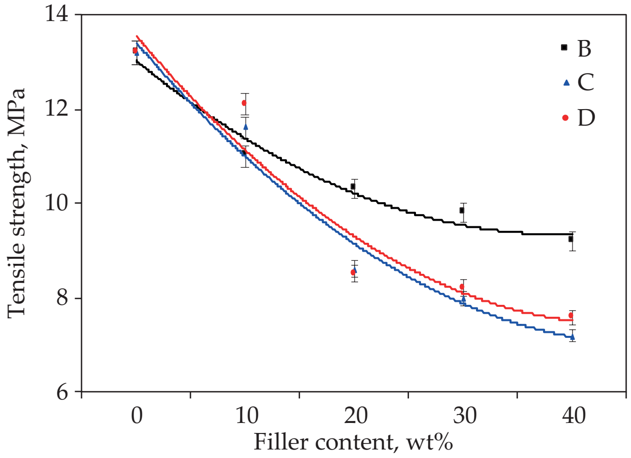

Fig. 2. The effect of filler type and content on LDPE tensile strength

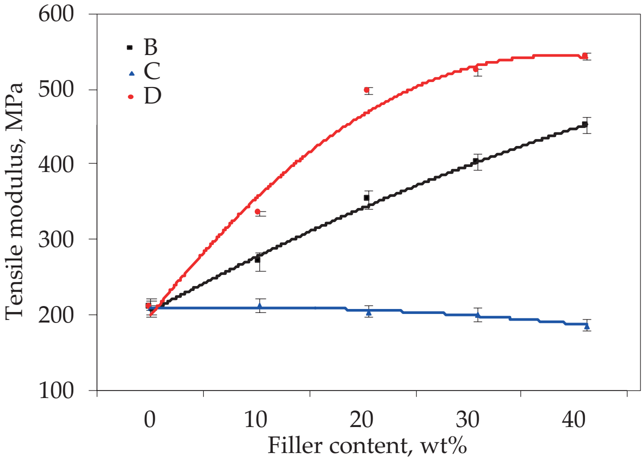

Fig. 3. The effect of filler type and content on LDPE tensile modulus

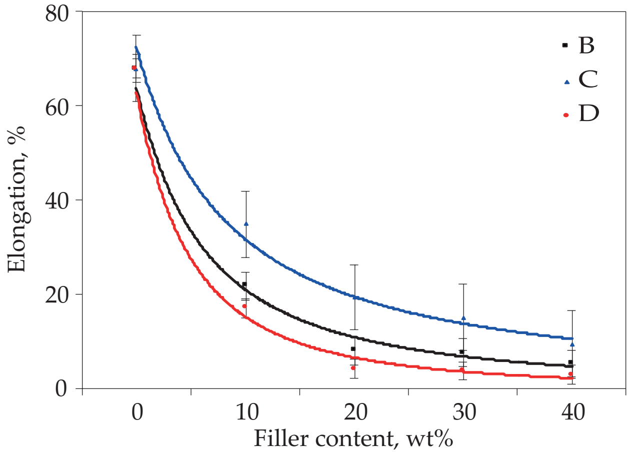

Fig. 4. The effect of filler type and content on LDPE elongation at maximum tensile stress

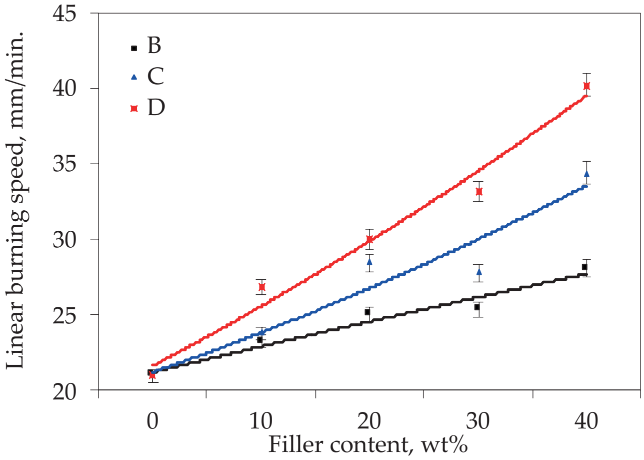

Fig. 5. The effect of filler type and content on linear burning speed

maximum tensile stress, on the type and content of the filler were determined.

In conclusion, LDPE tensile strength is influenced by both the type of filler and its content, which can be seen in Figure 2. The introduction of natural fillers resulted in a decrease in tensile strength compared to pure LDPE, which is in line with expectations. The strength of LDPE filled with pumpkin husks decreased the least by almost 30% compared to pure polyethylene (curve B). The strength was reduced to a slightly greater extent by the introduction of bean waste (curve C) and pine sawdust (curve D), by 45% and 42%, respectively.

The introduction of pine sawdust and pumpkin husks into LDPE resulted in the expected increase in the tensile modulus, as seen in Fig 3. This was observed especially in the case of pine sawdust, where the tensile modulus increased from 209 MPa (pure LDPE) to 543 MPa with 40 wt% filler content and to a slightly lesser extent in the case of pumpkin peels, which increased by 116% compared to pure LDPE. The introduction of bean waste had

T a b l e. 2. Flammability horizontal tests results

Filler	B			
Filler content, wt%	10	20	30	40
Burning time of the measuring section, s	193	181	178	160
The length of the burnt part, mm	75	75	75	75
Linear burning speed, mm/min	23.3	25.0	25.3	28.1
Flammability class in horizontal test	HB40	HB40	HB40	HB40
Filler	C			
Filler content, wt%	10	20	30	40
Burning time of the measuring section, s	189	158	162	131
The length of the burnt part, mm	75	75	75	75
Linear burning speed, mm/min	23.8	28.5	27.8	34.4
Flammability class in horizontal test	HB40	HB40	HB40	HB40
Filler	D			
Filler content, wt%	10	20	30	40
Burning time of the measuring section, s	167	150	136	112
The length of the burnt part, mm	75	75	75	75
Linear burning speed, mm/min	26.9	30.0	33.1	40.2
Flammability class in horizontal test	HB40	HB40	HB40	HB75

negligible effect on the modulus, causing only a slight decrease (approximately 11% at the highest filler content) compared to unfilled LDPE. This may be related to the large particle sizes, which were in the upper size range of the obtained fraction, and with a weak bond to the polyethylene matrix. It resulted in large flexibility of the matrix during tension and showing minimal transfer of loads in a structural transition area within a grain boundary. A similar correlation can be found also for other natural additives used in widespread research [14–17].

Figure 4 shows the relative elongation at the maximum tensile stress. As expected, the decrease in flexibility, particularly in high at low filler contents and milder at higher filler contents are visible. The highest relative decrease in elongation was observed in the case of pine sawdust (95%) and pumpkin husks (92%) introduced into polyethylene, slightly smaller in the case of bean waste introduced into polyethylene (86%). The effect of introducing fillers with large particle sizes is often typical and is well-known in the literature [15–17].

The flammability tests in the presence of an ignition source in a horizontal test of modified polyethylene samples are presented in Table 2, including the established flammability class. For all samples, burning in the entire measuring section, dripping of burning drops and ignition of the cotton indicator are present. All tested types of modified polyethylene, regardless of the additives, the HB40 flammability class was obtained, except for polyethylene with 40 wt% pine sawdust content, for which the lower HB75 flammability class was established. However, the introduced fillers changed the linear burning rate of polyethylene, where for unmodified polyethylene it was 21 mm/min. The combustion rate increased to the greatest extent after the introduction of pine sawdust (D), to 26.9 mm/min with 10 wt% of it and to 40.2 mm/min with 40 wt% of it. The combustion rate increased to a slightly lesser extent after the introduction of the remaining fillers, as shown in Figure 5.

Figure 6 shows an analysis of the temperature field in the burning sample, performed to determine changes in the maximum temperature in the burning area (area 1) and the temperature recorded along a straight line running through the longitudinal axis of the sample during the burning process (Fig. 6, area 2). The maximum temperature in the area where the sample is burning 10 s after removing the ignition source has the highest value in the case of sample B (215°C), and a lower value in samples C (206°C) and D (213°C). The maximum temperature for unmodified polyethylene A is lower and amounts to 192°C, which may be caused by faster dripping of the molten material and, as a result, cooling of the burning sample. Differences in the combustion rate and temperature in the burning area are visible Figure 7, in the temperature change curves recorded along a straight line running through the longitudinal axis of the sample, with a shift in the maximum temperature peaks of the curves obtained for filled polyethylene can be seen. Both

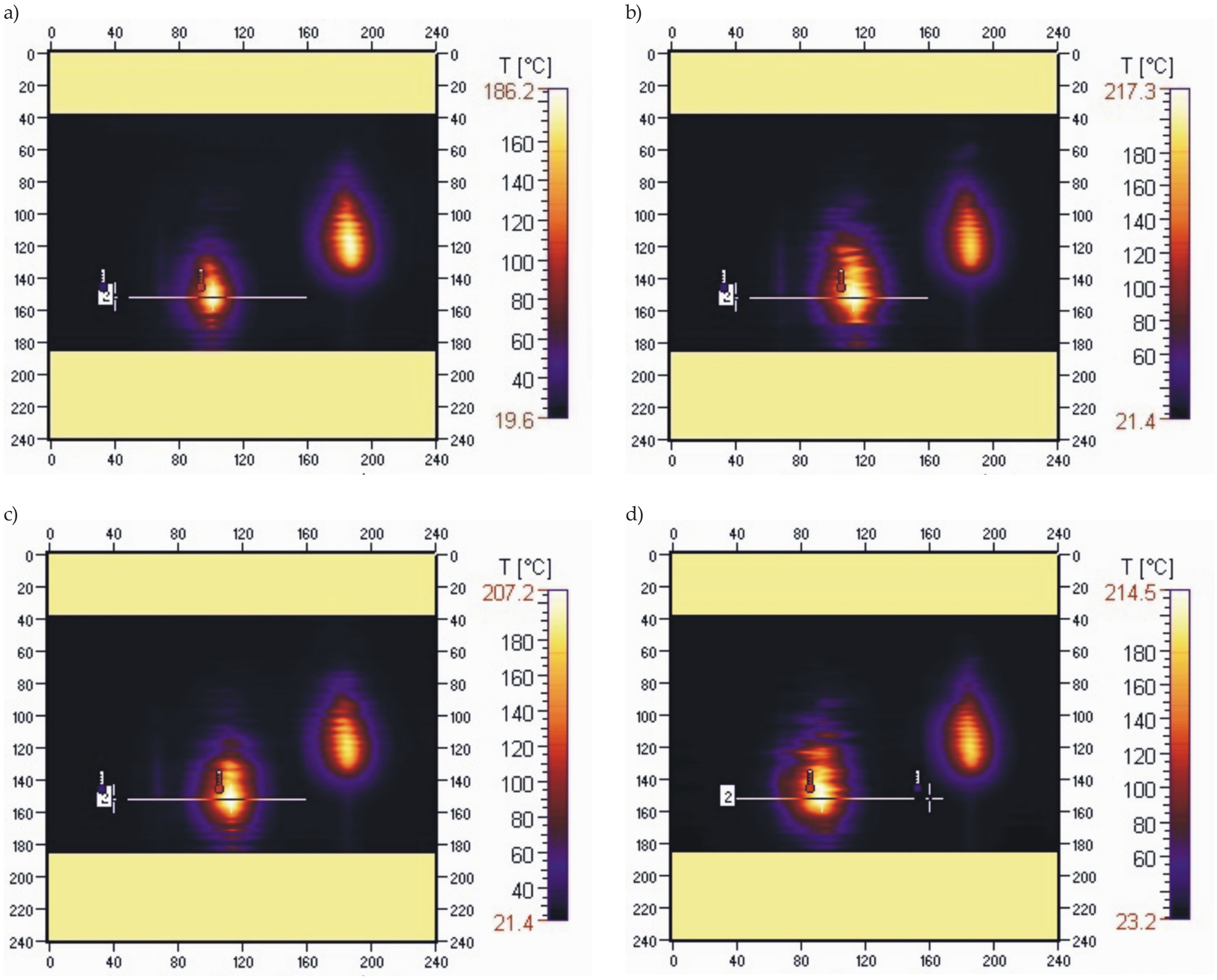

Fig 6. Thermograms recorded 10 s after subtraction of the ignition source in the horizontal test: a) sample A, b) sample B with 20 wt% filler content, b) sample C with 20 wt% filler content, b) sample D with 20 wt% filler content

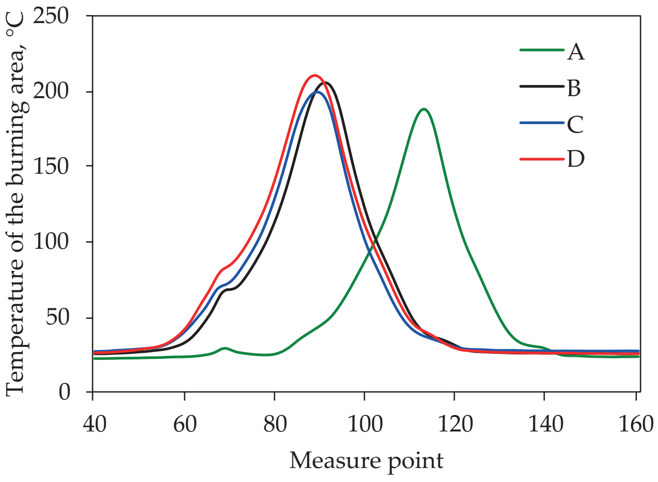

Fig. 7. Temperature along the burning sample of the horizontal test 10 s after subtraction of the ignition source

the combustion temperature of samples with natural fillers is higher and the shift of the curves for LDPE filled towards the beginning of the coordinate system established at the place where the sample was attached indicates a higher combustion rate.

In all tested cases, immediately after the ignition test (within 9–16 s), the flame covered the entire length of the sample, which made it impossible to precisely determine the combustion rate and the flammability class. An analysis of changes in the temperature of the burning area conducted in a vertical burning test of unmodified polyethylene samples and those containing 20 wt% of natural fillers, showing thermal images of the burning area recorded 40 s after the removal of the flame source (Fig. 8). The maximum temperature in the area of sample burning in the vertical test after 40 s since subtracting the ignition source has the highest value in the case of sample A (223°C), slightly lower for sample C (219°C) and B (217°C) and significantly lower for sample D (202°C). In this case, the faster dripping of molten polyethylene

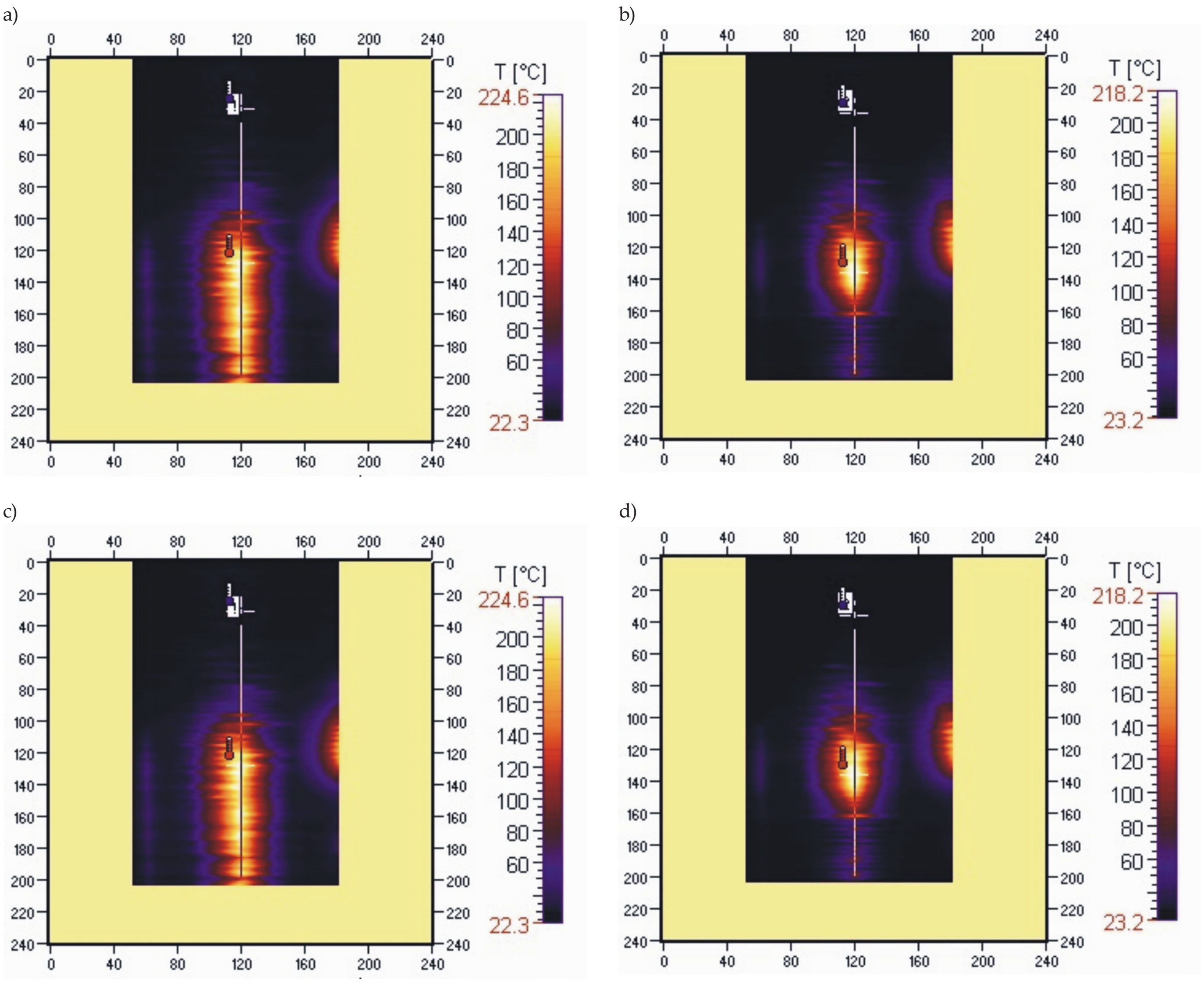

Fig 8. Thermograms recorded 40 s after subtraction of the ignition source in the vertical test: a) sample A, b) sample B with 20 wt% filler content, c) sample C with 20 wt% filler content, d) sample D with 20 wt% filler content

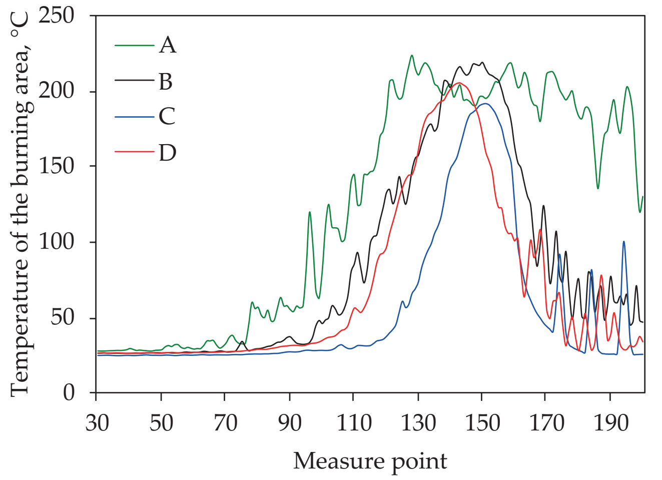

Fig. 9. Temperature along the burning specimen of the vertical test 40 s after subtraction of the ignition source

a larger area of the sample covered by the flame resulting in the temperature increase for the burning area (Fig. 8a).

The introduced additives disturb the flow of molten polyethylene and detachment the entire fragments of burning material observed, which reduces the generation of heat in the burning area. This is reflected in a reduction in temperature and a reduction in the area covered by the flame (Fig. 8 b, c, d). This is also visible in the temperature curves along the sample (Fig. 9), where the high flame temperature area is much larger in the case of polyethylene and much smaller at lower temperature values for samples containing natural fillers.

CONCLUSIONS

The impact of the introduction of natural fillers in the form of pumpkin husks, bean waste and pine sawdust on the mechanical properties and flammability of polyethylene was demonstrated. Once the pumpkin husks content is increased, the hardness of polyethylene increases as well, by almost 16% compared to unmodified LDPE. No change in hardness was observed in the case of bean waste, but the hardness of polyethylene increased slightly after the introduction of pine sawdust. The introduction of natural fillers resulted in a decrease in the tensile strength compared to unmodified LDPE, which is in line with expectations. The strength of LDPE modified with pumpkin peels decreased the least, by almost 30% compared to unmodified polyethylene. The introduction of bean waste and pine sawdust reduced the strength to a slightly greater extent by 45% and 42%, respectively. The introduction of pine shavings and pumpkin peels into LDPE resulted in an expected more than doubling of the longitudinal modulus of elasticity. The introduction of bean waste had a small impact on the value of the module, causing only a slight decrease, around 10%. The relative elongation at the maximum value of tensile stress, as expected, was reduced compared to unmodified polyethylene by approximately 90%. To improve the strength properties, it would be advisable to use surface modification of the fillers to increase their adhesion to the polyethylene matrix.

The introduction of the above-mentioned fillers resulted in obtaining a HB40 flammability class, i.e., the same as for unmodified polyethylene, except for polyethylene with 40 wt% pine sawdust content, for which a lower HB75 flammability class was established. A significant increase in the combustion rate was found in the horizontal test of filled samples, which is an unfavorable effect. When pumpkin husk was used as a filler, this increase was about 44% compared to unmodified polyethylene, while the introduction of bean sorting waste resulted in about 64% increase in the combustion rate and an almost twofold increase in pine sawdust (over 91%). The maximum temperature in the burning area increased slightly by 7–12% compared to unfilled polyethylene. The burning process was slightly different in a vertical arrangement, where the results were significantly influenced by the process of melting and dripping or detaching burning fragments of material. Here, the highest temperature in the burning area was recorded for unmodified polyethylene, while the lower one for polyethylene containing natural fillers. The introduction of these fillers resulted in the detachment of entire burning fragments of the material, which in the case of pumpkin husks and bean sorting waste resulted in a slight temperature reduction (1.7–2.6%), while pine sawdust caused a significant temperature reduction by almost 10% compared to pure polyethylene. Obtaining a higher flammability class would be possible if the filler particles were better bonded to the polyethylene matrix using surface modification, which, however, would increase the costs of producing the cheap composites. However, even in non-structural products made of this type of material, it would be advisable to additionally introduce flame retardants. The added value obtained in the manufactured materials is an attractive appearance and smell (temporary) as well as accelerated degradation, especially in the case of thin-walled products, which, however, requires further research.

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