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INVESTIGATION OF PROPERTIES OF MOLDED PARTS MADE OF POLYETHYLENE WITH ADDITION OF ASH FROM BITUMINOUS COAL

The aim of the conducted research was to determine the effect of filler in the form of microspheres from fly ash being a product of bituminous coal combustion on the functional properties of polyethylene. Comparative analysis of unfilled polyethylene and polyethylene with additions of 5, 10 and 15% (wt.) fly ash from bituminous coal was carried out. Tests of the mechanical properties were performed: tensile strength, hardness determined by the Shore method and the ball indentation method. Color and gloss analysis was also performed. On the basis of the conducted tests, it was found that the modification of polyethylene with fly ash from coal combustion has a significant impact on the functional properties of the tested materials. The molded parts from unfilled polyethylene exhibited the lowest value of hardness, while the largest value of hardness was obtained by parts made of polyethylene with 15 wt.% filler content. The content of fly ash from bituminous coal combustion also affects the tensile strength and elongation of the tested materials. As the filler increases, its tensile strength decreases. As a result of the addition of the filler, changes in the coordinates describing the color, as well as a reduction in the brightness value and a reduction in the gloss degree for the angles of incidence of 60° and 20° were noted. The presented research results indicate that producing polyethylene composites with the addition of microspheres from fly ash originating from bituminous coal combustion gives the possibility to obtain composites with significantly better mechanical properties as compared to unfilled polyethylene. The use of fly ash from the combustion of bituminous coal as a filler results in obtaining an inexpensive filler compared to fillers used in industry today. At the same time, it contributes to reducing the amount of waste generated from the combustion of bituminous coal. The test results give the possibility to use the composites produced in various industries as a raw material for the production of various engineering elements.

Keywords: polymer composites, polyethylene, fly ash, hardness, tensile strength, color, gloss

BADANIA WYBRANYCH WŁAŚCIWOŚCI WYPRASEK WTRYSKOWYCH Z POLIETYLENU Z DODATKIEM POPIOŁU Z WĘGLA KAMIENNEGO

Celem przeprowadzonych badań było określenie wpływu napelnacza w postaci popiołów na właściwości użytkowe polietylenu. Wykonano analizę porównawczą nienapelnionego polietylenu oraz polietylenu z dodatkiem 5, 10 i 15% popiołów lotnych pochodzących ze spalania węgla kamiennego. Przeprowadzono badania właściwości mechanicznych: wytrzymałości na rozciąganie, twardości metodą Shore'a oraz metodą wciskania kulki. Dokonano również analizy barwy i połysku. Na podstawie przeprowadzonych badań stwierdzono, że modyfikacja polietylenu popiołami lotnymi pochodzącymi ze spalania węgla kamiennego ma istotny wpływ na właściwości użytkowe badanego tworzywa polimerowego. W badaniach twardości najmniejszą wartość zarejestrowano dla nienapelnionego polietylenu, natomiast największą dla kompozytu z 15% dodatkiem napelnacza. Zawartość popiołów lotnych ma również wpływ na wytrzymałość na rozciąganie i wydłużenie badanych tworzyw. Wraz ze wzrostem zawartości napelnacza maleje jego wytrzymałość na rozciąganie. Na skutek dodatku napelnacza odnotowano zmiany we współrzędnych opisujących barwę, a także zmniejszenie wartości jasności oraz zmniejszenie stopnia połysku dla kąta padania światła 60° i 20°. Przedstawione wyniki badań wskazują na to, iż wytwarzanie kompozytów polietylenu z dodatkiem popiołów lotnych pochodzących ze spalania węgla kamiennego daje możliwość uzyskania kompozytów o znacznie lepszych właściwościach mechanicznych w porównaniu do nienapelnionego polietylenu. Zastosowanie popiołów lotnych pochodzących ze spalania węgla kamiennego jako napelnacza umożliwia pozyskanie taniego napelnacza w porównaniu do napelnaczy używanych w przemyśle obecnie. Równocześnie przyczynia się do zmniejszenia ilości odpadów powstałych podczas spalania węgla kamiennego. Wyniki badań dają możliwość zastosowania wyprodukowanych kompozytów w różnych gałęziach przemysłu jako surowca do produkcji różnorodnych elementów inżynierskich.

Słowa kluczowe: kompozyty polimerowe, polietylen, popioły lotne, twardość, wytrzymałość na rozciąganie, barwa, połysk

INTRODUCTION - AIM OF RESEARCH

The production of composites is one of the most intensively developing methods of the physical modification of polymers, due to the possibility of designing

new materials with specific physical properties and structures. The leading objective of producing new composite materials is to improve the mechanical prop-

erties, heat or chemical resistance, and sometimes improve the processing properties or reduce the price [1-6]. High density polyethylene (partially crystalline, thermoplastic) is used to make composites with a polymer matrix. It belongs to the class of hydrocarbon materials from the polyolefin group. It is characterized by a high molecular weight, very good tribological properties and low abrasiveness. It is a material that is used in many industries and applications. Polyethylene is used, for example, to produce duct insulation, canisters, orthopedic prostheses, syringes and various types of packaging, e.g. for cosmetics, bottles and foil [7, 8]. Work [9] presents the results of investigations of waste plastics from packaging materials and other uses recovered in large quantities. An investigation was conducted to produce a new building material from fly ash and polyethylene. The work was carried out with two typical coal fly ashes and polyethylene bags. The tensile strengths and chemical resistance of the materials, in addition to the effect of temperature were examined. Characterization of these materials was also studied by means of XRD, IR and SEM techniques. The tensile strengths of the materials range from 0.92 to 2.62 kP/mm². When the ratio of fly ash was low, better results were obtained. High chemical resistance of the obtained composites was also found. The author of work [10] presents the industrial advantages of using ashes as fillers. The advantages of using these agents in various industries was described. For example, compounds of up to 50% fly ash were extruded and compression molded into building materials like roof shakes and lumber. The ash adds stiffness and reduces the cost. Compounds of 15÷30% fly ash are in prototype testing for injection-molded car trim. Besides adding stiffness, fly ash raises the "recycled" content of auto parts. The authors of work [11], in order to improve the interaction between the inorganic filler and the organic matrix, surface treated fly ash cenospheres with a silane coupling agent and HDPE-g-dibutyl maleate was used as a compatibilizer. The tensile and thermal properties of the composites were measured. The results reveal that both the surface modification of cenospheres accompanied by compatibilization led to substantial improvement in the mechanical properties and thermal stability of the composites. The effect of fly ash as a filler on the mechanical properties of HDPE is described in study [12]. Three different particle sizes of fly ash were used. The concentration of fly ash was varied up to 40% by weight. The composites were prepared using a twin screw extruder and then test specimens were prepared by injection molding. The tensile, flexural and impact properties were tested. The microstructure was investigated by means of scanning electron microscopy (SEM) of the fractured samples. Both the tensile and flexural strengths and moduli were found to increase with fly ash addition. The tensile elongation drastically reduced at fly ash concentrations greater than 10%. With an increasing fly ash concentration the impact resistance decreased up to about 15% fly ash concentration and

then did not reduce significantly on further addition. The composites with the smallest sized fly ash particles proved to be better in enhancing strength and relative elongation. The modulus and impact resistance did not seem to depend much on particle size. Study [13] presents the effect of particle size variation of fly ash as a filler with different concentrations (5÷40 wt.%), on various properties of recycled polyethylene terephthalate (RPET). The mechanical, rheological, electrical and thermal properties of the composite material were evaluated and the microstructure was investigated by scanning electron microscopy (SEM). It was seen that micro particle inclusion increased the mechanical properties of the system. By means of SEM it was observed that good dispersion and also very good interaction of the fly ash particles and the polymer matrix occurred.

The authors of work [14] in an effort to utilize fly ash (FA) beneficially, developed composites from an ethylene-octene random copolymer (EOC) and unmodified as well as surface-modified class-F fly ash (MFA) by twin screw extrusion. An addition of 20 wt.% MFA to EOC improves its tensile strength by 150%, moreover, MFA contributes to improving the values of stress (100% increase) and strain (300% increase) of EOC. The thermal stability of the EOC matrix is appreciably improved by the addition of either FA or MFA, while the melting behavior is not considerably influenced by either. Fractographic study reveals improved adhesion between the EOC and MFA particles up to a filler content of 20%, beyond which the adhesion between EOC and MFA is weakened, causing a reduction in the mechanical properties. The 'flammable' nature of EOC changes to 'self-extinguishing' on the addition of even 10 wt.% FA or MFA, as ascertained from the study.

In work [15], the authors investigated recycled high-density polyethylene (RHDPE)/coir fiber (CF)-reinforced biocomposites. Samples were fabricated using the melt blending technique in a twin-screw extruder and the test specimens were prepared in an automatic injection molding machine. Variation in the mechanical properties, crystallization behavior, water absorption, and thermal stability with the addition of fly ash cenospheres (FACS) in RHDPE/CF composites was investigated. It was observed that the tensile modulus, flexural strength, flexural modulus, and hardness properties of RHDPE increase with an increase in fiber content from 10 to 30 wt.%. Composites prepared using 30 wt.% CF and 1 wt.% MA-g-HDPE exhibited optimum mechanical performance with an increase in the tensile modulus to 217%, flexural strength to 30%, flexural modulus to 97%, and hardness to 27% when compared with the RHDPE matrix. The addition of FACS results in a significant increase in the flexural modulus and hardness of RHDPE/CF composites. Dynamic mechanical analysis tests of RHDPE/CF/FACS biocomposites in the presence of MA-g-HDPE revealed an increase in storage (E') and loss (E'') moduli with a reduction in the damping factor ($\tan \delta$), confirming a strong bond between the fiber/FACS and MA-g-HDPE in the RHDPE matrix. Differential scan-

ning calorimetry, thermogravimetric analysis thermograms also showed improved thermal properties in the composites when compared with the RHDPE matrix. The main motivation of this study was to prepare a value added and low-cost composite material with optimum properties from consumer and industrial wastes as the matrix and filler.

The current paper presents the results of investigations on the effect of filler additive in the form of fly ash originating from bituminous coal combustion in pulverized coal boilers, on the properties of polyethylene injection molded parts. The tests included determining the hardness by the Shore method and the ball pressing method, testing the tensile strength, as well as color and gloss measurements.

MATERIALS, EQUIPMENT AND RESEARCH METHODOLOGY

High density polyethylene (HDPE) with the commercial name Hostalen GC 7260 (for injection molding applications), manufactured by Lyondell Basell Industries Holdings was used in the examinations. As a filler, fly ash was used as a product of bituminous coal combustion in pulverized coal boilers in the Połaniec Power Plant Enea S.A. Before processing, the polyethylene was dried in a Zelmet dryer with a KC-100/200 heat chamber at the temperature of 70°C for 4 hours. The fly ash was covered with a silicone preparation. The composites were prepared by the extrusion method. The samples for testing (in the form of paddles for the tensile strength test) were injected using a Krauss Maffei KM65 - 160 C4 injection molding machine with a 30 mm diameter screw and an L/D ratio = 23, as well as a mold closing force of 650 kN. Optimal properties of the test samples were obtained with the following injection parameters:

- injection temperature 205°C,
- mold temperature 40°C,
- injection velocity 45 cm³/s,
- injection time 0.45 s,
- injection pressure 60 MPa,
- holding pressure 30 MPa,
- holding time 28 s,
- cooling time 15 s.

A type D hardness tester was used to test the hardness using the Shore method. The test consisted in measuring the resistance which the test material exhibits when plunging a cone of a fixed shape and dimensions in to the material. The pressure on the test sample was 50 N. The distance between the measurements was a minimum of 6 mm, and a minimum of 12 mm from the edge of the sample. The result was read after 1 s, unless further penetration of the cone was observed, then the reading was carried out after 15 s. Hardness was expressed in Shore D units [16].

Determining the hardness by the ball indentation method consisted in pressing a 5 mm diameter ball made of hardened steel and polished surface under the

action of total load F into the test sample. The initial load was 9.81 N. The load was selected so that the depth of the recess was in the range of 0.15÷0.35 mm. The depth of the impression was read after 30 s from the beginning of the measurement [16].

A 20 kN universal testing machine Hegewald&Peschke Inspekt 20 was used to conduct static tensile testing. Specific samples were used for the test in accordance with the PN-EN ISO 527-3: 1998 standard. The following parameters were determined during the static tensile test: yield strength, stress at break and tensile strength [17]. For the color analysis, an X-Rite spectrophotometer was used. Color analysis was performed using the CIELab method, which determines the color based on the measurement of three chromaticity coordinates: L^* , a^* , b^* . Coordinate L^* denotes brightness, where $L^* = 0$ means black and $L^* = 100$ means white. Co-ordinate a^* is the proportion of red/green, where $+ a^*$ means red, and $- a^*$ means green. Coordinate b^* is the ratio of yellow/blue, where $+ b^*$ means yellow, and $- b^*$ means blue [16].

For the gloss analysis, an Elcometer 406 Statistical Glossmeter was used with the light source directed to the surface to be tested at a given angle, and the receptor which is located on the mirror reflection of the incident light beam. The tests were carried out at two light reflection angles: 60° and 20° [16].

INVESTIGATION RESULTS

Figures 1-4 shows the dependence between the strain and stress on the tested samples with different ash content from bituminous coal.

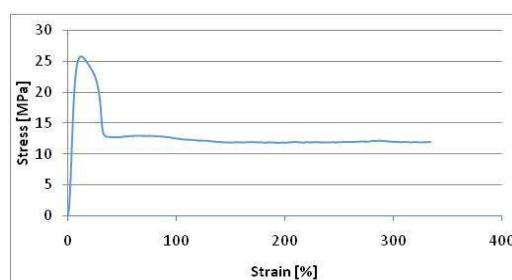


Fig. 1. Relations between strain and stress for HDPE

Rys. 1. Zależności odkształcenia do naprężenia dla HDPE

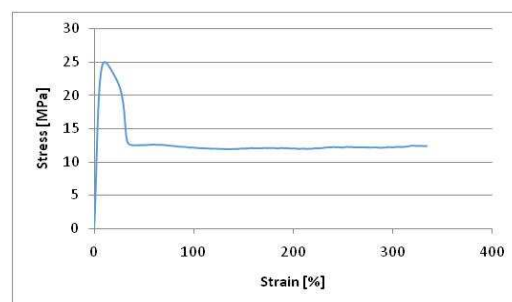


Fig. 2. Relations between strain and stress for HDPE + 5% ash from bituminous coal

Rys. 2. Zależności odkształcenia do naprężenia dla HDPE + 5% popiołu z węgla kamiennego

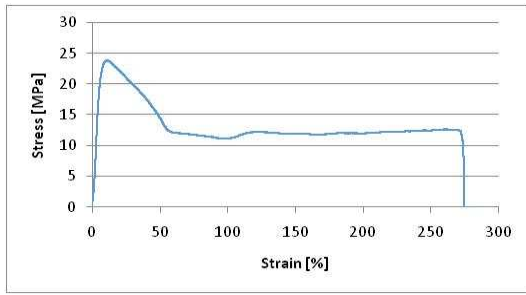


Fig. 3. Relations between strain and stress for HDPE + 10% ash from bituminous coal

Rys. 3. Zależności odkształcenia do naprężenia dla HDPE + 10% popiołu z węgla kamiennego

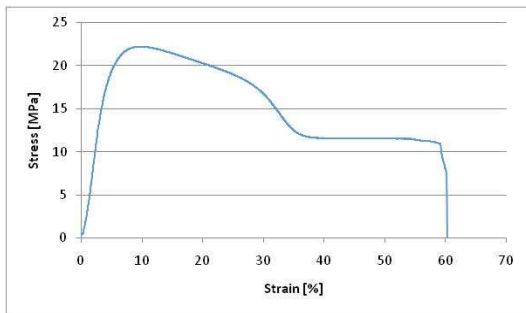


Fig. 4. Relations between strain and stress for HDPE + 15% ash from bituminous coal

Rys. 4. Zależności odkształcenia do naprężenia dla HDPE + 15% popiołu z węgla kamiennego

The above graphs show that as the content of bituminous coal ash in the polyethylene increases, the tensile strength of the molded parts decreases slightly. Parts from HDPE with a 5% ash content had a 3% lower tensile strength than unfilled parts, and successively, parts with 10% ash - 8% lower and with 15% ash - 18% lower than the unfilled samples. The samples from HDPE without filler and with a 5% ash content do not break, and those samples had much higher elongation at break than the samples with greater amounts of filler (higher than 300%). Higher amounts of ash additions reduced the elongation of molded parts from polyethylene. Parts with a 15% ash content exhibit the smallest elongation value, only 60%.

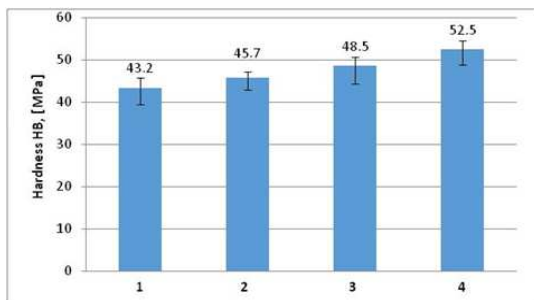


Fig. 5. Changes in HB hardness value of individual samples: 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 5. Zmiany wartości twardości HB poszczególnych próbek: 1 - HDPE, 2 - HDPE + 5% popiołów z węgla kamiennego, 3 - HDPE + 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

Figure 5 is a graph showing the change in the hardness value of individual samples determined by the ball indentation method. The hardness of the material linearly increases with the content of bituminous coal ash.

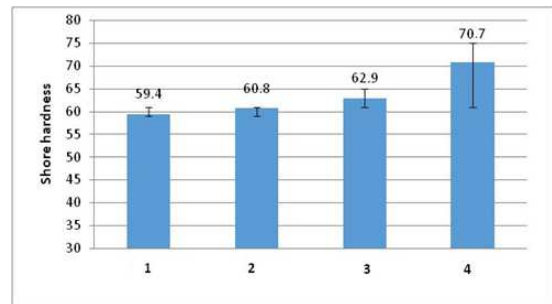


Fig. 6. Changes in Shore hardness value of individual samples: 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 6. Zmiany wartości twardości Shore'a poszczególnych próbek: 1 - HDPE, 2 - HDPE + 5% popiołów z węgla kamiennego, 3 - HDPE + 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

Figure 6 is a graph showing the change in the hardness value of individual samples determined using the Shore method. The hardness of the molded parts increases with an increase in the content of bituminous coal ash.

Figures 7-9 present the results of measuring the color of molded parts made of polyethylene and its composites. The results of the analysis of L^* , a^* , b^* color attributes for composites with different contents of bituminous coal ash are presented.

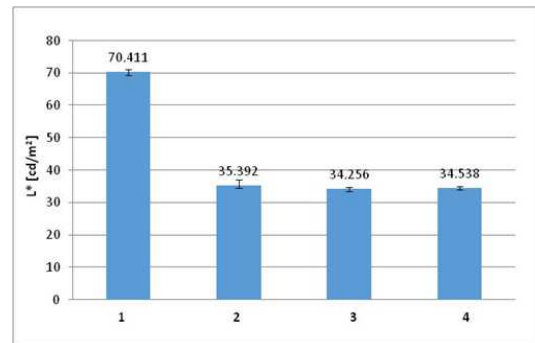


Fig. 7. Color attribute L^* : 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 7. Atrybut barwy L^* : 1 - HDPE, 2 - HDPE + 5% popiołów z węgla kamiennego, 3 - HDPE + 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

From Figures 7, 8 and 9, it can be deduced that as the filler increases, the brightness value decreases. In the case of coordinate a^* , the proportion of green color decreases and with the addition of 15% ash it turns red. Co-ordinate b^* , however, turns from blue into yellow, along with a 5% increase and more in the filler additive content. From the results of the L^* coordinate test, it can be seen that for unfilled HDPE, the brightness value is much higher than in the case of filled materials.

Coordinate L^* only for the filled materials decreases slightly. In color attribute a^* for unfilled HDPE in relation to the materials with different contents of ash from bituminous coal, the share of green color is clearly visible. Nonetheless, in the material with the content of 15% ash, only the share of red color is visible. In the b^* attribute, only the unfilled HDPE has a blue color share. The remaining samples containing 5, 10 and 15% bituminous coal ash have a yellow fraction, which increases with an increase in the filler.

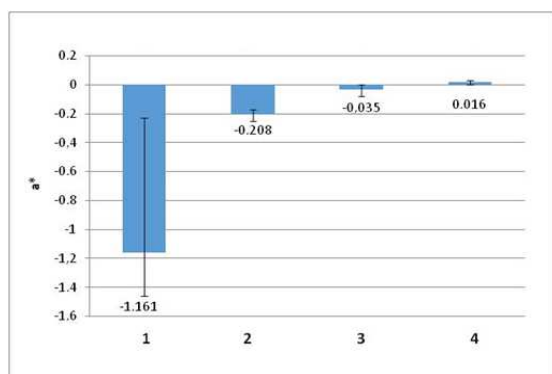


Fig. 8. Color attribute a^* : 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 8. Atrybut barwy a^* : 1 - HDPE, 2 - HDPE+ 5% popiołów z węgla kamiennego, 3 - HDPE + 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

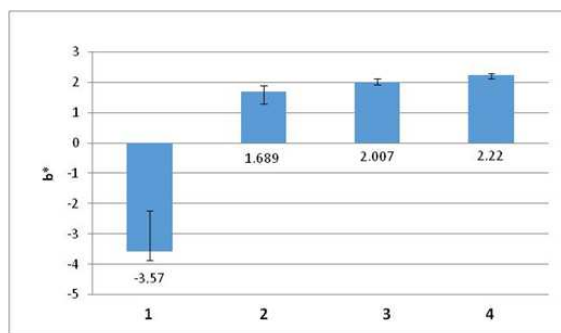


Fig. 9. Color attribute b^* : 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 9. Atrybut barwy b^* : 1 - HDPE, 2 - HDPE + 5% popiołów z węgla kamiennego, 3 - HDPE + 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

Figures 10 and 11 present the results of measurements of the gloss of polyethylene molded parts with different contents of bituminous coal ash as well as the average values of gloss measurement. The results of the gloss tests for light reflection angles of 60° and 20° for the samples with different contents of bituminous coal ash are presented.

Based on the analysis of the data presented in Figures 10 and 11, it was found that as the amount of ash from bituminous coal increases, the gloss at the angles of incidence of 60° and 20° decreases (molded parts become more mat).

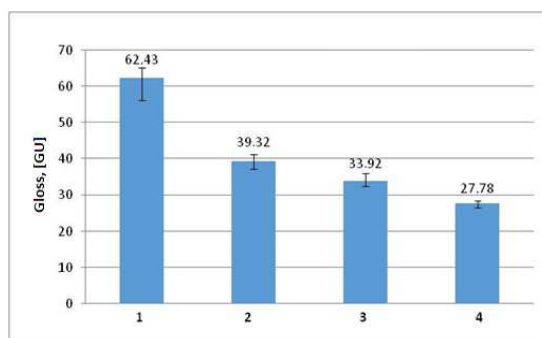


Fig. 10. Gloss of tested samples for angle of incidence 60° : 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 10. Połysk badanych próbek dla kąta padania światła 60° : 1 - HDPE, 2 - HDPE+ 5% popiołów z węgla kamiennego, 3 - HDPE+ 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

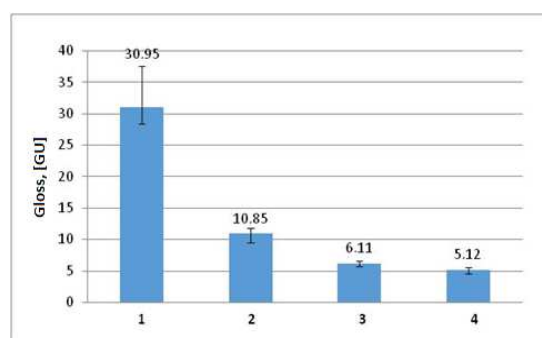


Fig. 11. Gloss of tested samples for angle of incidence 20° : 1 - HDPE, 2 - HDPE + 5% bituminous coal ash, 3 - HDPE + 10% bituminous coal ash, 4 - HDPE + 15% bituminous coal ash

Rys. 11. Połysk badanych próbek dla kąta padania światła 20° : 1 - HDPE, 2 - HDPE + 5% popiołów z węgla kamiennego, 3 - HDPE + 10% popiołów z węgla kamiennego, 4 - HDPE + 15% popiołów z węgla kamiennego

SUMMARY

Summarizing the analysis of the conducted tensile strength tests, it can be concluded that with an increase in the content of bituminous coal ash in composites, the tensile strength decreases. Samples from unfilled HDPE and HDPE with 5% filler content were characterized by greater maximum elongation than the samples with larger amounts of filler.

On the basis of the conducted hardness tests by the ball indentation and Shore methods, it can be stated that with an increase in bituminous coal ash, the hardness of polyethylene molded parts increases.

From the conducted gloss studies, it can be clearly stated that with an increase in ash from bituminous coal, the gloss level is reduced. In the color test, significant changes in both the brightness and shade of the examined composites were found. The change in the value of coordinates a^* , b^* , and lightness L^* , as well as the gloss value can be explained by the different structure at different filler content, as indicated by changes in the mechanical properties of the composites.

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