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THE PROPERTIES OF A POLYPROPYLENE MATRIX COMPOSITE WITH ANTHRACITE FILLER

The article presents the results of research concerning the effect of anthracite dust with 10%, 20%, 30%, 40% and 50% content in composites with a polypropylene matrix on selected properties. Hardness was examined with the Shore's D method; stiffness, tensile strength as well as (MFR) Melt Flow Rate and (MVR) Melt Volume Rate of the investigated material were evaluated; wettability of the obtained material was also determined. Surface and volume resistivity were also investigated; the thermal properties of the filler were determined by thermogravimetric analysis (TGA). It was found that the investigated polypropylene composites filled with anthracite dust are hydrophobic materials and the composite hardness and stiffness are growing along with the volumetric increase of anthracite. It was noted that anthracite reinforces the material to a limited extent.

Keywords: Polymer composites, Polypropylene, Anthracite, Shore's method, Tensile strength

1. Introduction

The increased interest in polymer materials, in terms of new applications, forces research over the improvement the materials' properties by modifying them. The fillers introduced into the polymer matrix modify practically all physical properties of the created composites, often also influencing their chemical properties. They improve mechanical, tribological, rheological, thermal, dielectric, chemical and processing properties, and also reduce the shrinkage value and most often increase viscosity of the material, limit the expansion of the plasticised material stream and improve the process of heat dissipation during cooling, thus affecting the content of the crystalline phase in the polymers capable of crystallisation [1-6].

In the recent years, carbon fillers have been successfully used in the form of carbon fibres, graphite, carbon nanotubes, carbon black (formless carbon), powdered fossil carbon (hard coal in its pure form, shungite, anthracite). The advantageous properties of carbon materials in combination with the appropriate polymers and modification possibilities have made them an important component of polymer composites applied in the automotive, mining and chemical industries. Carbon fillers enhance polymers' resistance to heat, environmental factors and UV radiation. Depending on the carbon filler type, it is possible to achieve the desired volume and surface resistivity and magne-

tostrictive properties of polymers, preponderantly for polyolefin-matrix composites. In addition to improving electrical properties, carbon fillers are expected to improve mechanical properties, in particular abrasive wear resistance and hardness. The interaction of polymers with fillers, apart from the phenomena occurring on the surface, also affects the density of the matrix particles in the area of filler particles. The volumetric content of the filler plays an important role; too high a filler content does not always enhance the abrasive wear resistance. When we want to modify the dielectric characteristics, graphite or carbon black are normally used, which increase the electrical conductivity [7-13]. Investigations into polymer composites with fillers in the form of powdered hard coal, shungite and anthracite prove that they meet the objectives set for them. Shungite, as a polypropylene filler, exhibits good adhesion with its macroparticles and increases its electrical conductivity. The addition of about 4% wt. of shungite improves the tensile strength and tensile stress at break. The strength declines with the increase in the filler content (for 5% wt. of shungite, the composite strength is 25% lower than for pure PP). Shungite influences positively the growth in the value of the elasticity coefficient, as well as the stiffness of the material, causes a decrease in impact strength and a decrease in relative elongation at maximum stress and at stress at break, reduces the flow rate value and contributes to the growth in the crystallisation and melting temperature [7,9,11]. Investigations

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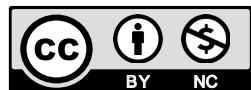
were also conducted into pure hard coal with a different carbonisation degree. The addition of this filler to polyamide has influenced the increase of viscosity. Polyethylene with a carbon filler does not significantly changes the tensile strength, but it reduces deformation and impact strength, enhances hardness and reduces electrical resistance of composites. Additionally, the introduction of about 7% wt. of carbon filler to thermoplastic materials inhibits expansion of the stream related to the Barus effect. Growth in the abrasion resistance of the cast polymer graded composites with an epoxy resin matrix with added powdered ortho-coking coal and anthracite dust was also observed [14-17].

The article presents the results of the tests of hardness, tensile strength and Young's modulus, density, mass and volume flow rate, wettability, resistivity and thermogravimetric analysis (TGA) of the manufactured polypropylene matrix (PP) composites filled with anthracite dust with a varied percentage content of 10%, 20%, 30%, 40%, 50%.

2. Experimental

2.1. Materials

The investigations were carried out with the samples of the MOPLEN H548R polypropylene (PP) matrix composite (a homopolymer with high Melt Flow Rate (MFR) – 23 g/10 min (low viscosity) and good stiffness – modulus of elasticity – 1650 MPa) with the addition of 10%, 20%, 30%, 40%, 50% of anthracite dust. Anthracite dust with a moisture content of 3.5%, 0.99% of sulphur and 24.1% of ash and was used. The bulk density of anthracite dust is 0.5225 g/cm^3. Before the filler was introduced into the polymer matrix, it was dried at 100°C.

PP/anthracite blends were extruded using a Göetffert counter rotating twin-screw extruder, diameter at the exit. The following conditions were selected for extrusion: zone I temp. of 200°C, zone II temp. of 220°C, zone III temp. of 230°C, head temp. of 240°C, revolutions of 6-8 rpm. As a result of extrusion, a granulate was obtained from which test pieces were prepared (in the form of 1A type "paddles" as per PN-EN ISO 527-2:2012 standard) by injection moulding using the Battenfeld Plus 35/75 injection moulding machine with a Unilog B2 control system, with a ratio of L/D 17. The marking of the samples is shown in Table 1.

TABLE 1

Marking of the samples of the produced composite PP/anthracite

Marking of the samples	H1	H2	H3	H4	H5	H6
Content of anthracite [%]	0	10	20	30	40	50

2.2. Methods

The distribution of the anthracite dust grain size was carried out by laser diffraction on a Beckman Coulter LS 13320 apparatus, according to ISO 13320:2009.

The hardness of the examined samples was determined using the Shore scale D method according to PN-EN ISO 868:2005, with the use of an electronic hardness tester from Zwick at 22°C; measurement readings were taken after 15 seconds. Before the test, the samples were conditioned at the test temperature for 24 hours.

The tensile strength of the composites and pure polypropylene was tested with a Zwick/Roell Z020 testing machine at a stretching rate 5 mm/min at room temperature. This experimental speed was chosen due to the high content of filler in the samples. It was expected that the samples would be characterized by high stiffness and low value of the relative elongation at break. Testing at higher speed could negatively affect the reliability of obtained results. The tensile stiffness modulus was determined in accordance with PN-EN ISO 527-1:2012 and PN-EN ISO 527-2:2012 on Instron TT-CM 80 testing machine equipped with an Instron mechanical extensometer at room temperature at a test rate of 1 mm/min.

The density of the samples was determined by the immersion method in accordance with PN-EN ISO 1183-1:2019-05 using a Mettler-Toledo XS 105 scale equipped with a density determination attachment. The test was performed with the A method – the immersion method with the samples cut out from the test pieces; distilled water was used as a test fluid.

The Melt Flow Rate (MFR) was established as per PN-EN ISO 1133:2006 using a Zwick-Roell Mflow capillary plastometer. The measurements were taken at a test load of 2.16 kg at 230°C on granulates. The time of sample conditioning at the measurement temperature without the test load applied was 5 minutes with a nozzle diameter of 2.095 ± 0.005 mm. In addition, the value of the Melt Volume Rate (MVR) was determined.

The wettability of the composite was determined on the basis of water wetting angle determination carried out using the G-10 apparatus from Krüss GmbH. Deionised water with the surface tension of 72.8 mJ/m^2 was used for measurements.

The volume and surface resistivity were determined using the Keithley Instruments Inc. model 8009 electrometer in line with ASTM D257-14 and IEC 60093:1980 methodology. The measurements were carried out at a test voltage of 300V.

A thermogravimetric analysis (TGA) was carried out using the Mettler-Toledo XS 105 thermobalance at a heating rate of 20°C/min. A gas flow rate of 60 ml/min was used during the test. The samples were heated to 600°C in the atmosphere of pure nitrogen and above 600°C to 900°C in the atmosphere of pure oxygen to remove carbon black.

The filler's microstructure and the fractures of the examined composites, formed after a static tensile test, were observed with a Zeiss SUPRA 35 scanning electron microscope, using the accelerating voltage of 15 kV. The samples were sputtered with gold.

3. Results and Discussion

It was calculated as a result of analysing the grain size distribution of anthracite dust that over 70% of the filler particles

have the dimensions between 12 and 40 μm. The grain size distribution of the filler and its surface morphology is a parameter affecting the properties of composites by determining the surface area of the matrix-filler connection. The filler applied, in the form of anthracite dust, shows a flaky structure (Fig. 1), with a well-developed and heterogeneous morphology of the external surface of single grains with visible discontinuities (Fig. 2). The heterogeneous structure influences a favourable combination of components and better adhesion of anthracite dust to the polypropylene matrix.
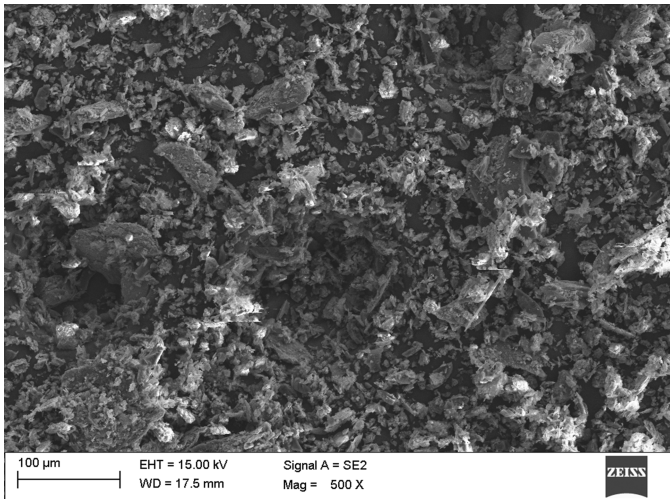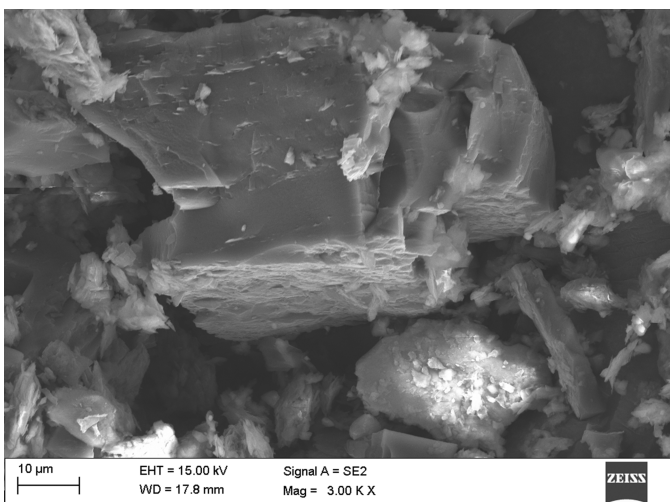

Fig. 1. Microstructure of anthracite dust

Fig. 2. Surface morphology of a single grain of anthracite dust

It was found as a result of Shore D hardness tests that the introduction of powdered anthracite into the polypropylene matrix has largely increased the hardness of the tested material. The hardness of PP/anthracite composites is rising along with the growing filler volume (Table 2). A similar effect is described in literature, when filler content increases, the hardness of composite increases [5,6,18,19]. This is caused by the phenomenon of blocking the movement of polymer chains and the related elastic and permanent plastic deformation caused by

large-sized anthracite particles distributed in the polymer matrix (Fig. 1). Moreover, the filler particles themselves are distinct for much higher hardness (about 350HV) than polypropylene (calculated as about 20-30HV). As the filler content is growing, up to 40%, a clear increase in the sample hardness to 75.3°ShD is observed, in comparison with the value of the matrix hardness of 69.5°ShD. Noteworthy is a relatively small hardness difference observed between H5 and H6 samples, containing 40% and 50% of anthracite dust respectively (Table 2). This effect is probably caused by exceeding the optimum filler content to effectively counteract the permanent deformation of the sample. Therefore, it can be concluded from the above that if it is necessary to improve the material stiffness and hardness, only the introduction of the filler to the mass content in the material of approx. 40% will be effective. Above this content, due to the higher price of anthracite compared to polypropylene, it is not economically justified.

The results of hardness tests were reflected and confirmed in the characteristics of the material determined during tensile testing. Here too, as in the case of hardness testing, with the increase in the filler content, the stiffness of the material and its resistance to deformation has improved [19]. By heightening the amount of filler particles in the material, difficult deformation of polymer chains is seen. At the time of applying a tensile load to the sample, in order to initiate its elastic deformation, it is necessary to initiate the movement of the chains making up the polypropylene. Similarly to the hardness of the investigated materials, the presence of anthracite inclusions dispergated in the matrix blocks the possibility of their movement, which leads to a noticeable increase in material stiffness. For the H6 blend, the stiffness modulus is 2956 MPa, twice as high (2.04) as for the unfilled polypropylene, which has a stiffness of 1446 MPa (Table 3). Szeluga et al. also describe the impact of natural hard coal microparticles on the increase of polymer composites stiffness modulus [20]. It should be noted that the values of the tensile stiffness modulus achieved by the examined materials are similar to the values of this parameter for polymer materials, classified as engineering materials. This means that the materials developed can be successfully used in applications where stiffness is a determining factor in the use of a given material. At the same time, along with the growing filler content in the material, due to its limited coherence with the polymer matrix, the strength of the material deteriorates. This is in accordance with results described in literature, e.g. in the case of PP/shungite or PE/ash from bituminous coal composites [6,7]. This effect is observed for samples with the filler content of 10%, 20% and 30%, for which R_m is 27.2 MPa, 25.2 MPa and 22.9 MPa, respectively. For the samples containing 40% (22.7 MPa) and 50% (22.1 MPa) of anthracite dust, their strength is within the error limits of the method identical to that of a sample containing 30% of filler (Table 3). This means that anthracite has a reinforcing effect on the material. This is most probably associated with the presence of sufficient adhesion forces at the boundary of polymer-filler phases, to transfer part of the load to the filler inclusions. It can be confirmed by appraising the results of the investigations that

with the growing content of anthracite powder in the material, the value of the quotient of the material strength and the matrix content grows. This denotes that the filler introduced, contrary to expectations [16,17] improves the mechanical properties of the material. No decrease of tensile strength value with increase of filler content in sample (reduction in amount of base material,) means that dust causes a slight sample strengthening. This effect doesn't allow to state that anthracite can be treated as an effective reinforcement for polypropylene – the strengthening effect is not strong enough, however, based on research results it can be determined. Due to the limited adhesion of the material to the anthracite particles, it is not possible to transfer stresses from the polymer matrix to the filler as efficiently as in the case of typical reinforcements, e.g. glass or carbon fibres or graphene fillers [21-23]. For example hybrid polypropylene composites with 10 wt % basalt fibers and 10 wt % carbon fibers are characterized by more ten two and a half times increase in strength [21]. For this reason, no increase in material strength above the value of this parameter characteristic for an unfilled matrix (30.9 MPa) is observed. From this point of view, the adhesion of polymer matrix to filler is limited. However, treating anthracite dust as filler, it can be stated that its adhesion to matrix is sufficient. It should be emphasized that original assumption of introducing anthracite into polypropylene was not to determine its impact on the mechanical properties of the resulting composite. The authors assumed that samples would exhibit properties similar to those typical for plastics, in which fillers reduce strength value and decrease flexibility. The investigated carbon filler begins to clearly reveal its effect only after exceeding 30% in the polymer, when the increase in the filler content reduces the negative effects associated with the reduction of the active cross-section of the polymer responsible for transferring the applied stresses. In such a situation, the filler particles have an opposite effect at the same time: first of all, they reduce the material's cross-section and form a kind of an internal notch, reducing the active cross-section of the load-bearing material, additionally concentrating the stresses in their vicinity. However, the limited adhesion forces present at the boundary of phases enable to transfer loads partially to the filler particles and to enhance the material strength. Nevertheless,

it can be concluded that the tensile strength (yield stress) values obtained do not exclude the possibility of the technically rational use of these materials, even in more responsible applications. The observed effect of limited reinforcement of the material is attributed to a highly hydrophobic character of the filler, confirmed by the tests described below. Consequently, it was possible to partially bind the polymer particles to the anthracite surface and to strengthen the material. Microscope observations of the PP/anthracite fractures formed during the stretching process have confirmed the cracking of the composite at the filler-matrix boundary. This mechanism is related to the growth in strength properties. Anthracite dust remains embedded in the matrix and is visible as dispergated, non-homogeneous particles (Fig.3).
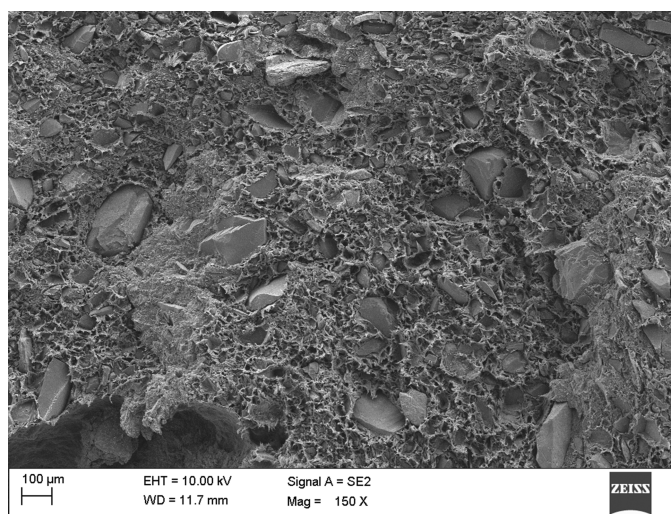

Fig. 3. Microstructure of composites fracture after stretching, samples H5

The rheological properties of the material obtained were influenced by introducing a carbon filler in the form of powdered anthracite into the polypropylene. Viscosity is influenced by increasing the filler content in the material, causing growth in viscosity [7,24]. The parameter is evaluated on the basis of (MFR) Melt Flow Rate and the (MVR) Melt Volume Flow Rate. This is due to the inability to plasticise and thus to radically increase the susceptibility to deformation under the load, which is as a result of a lowering value of internal friction of anthracite. During the tests performed in a capillary plastometer, the plasticised polypropylene was flowing through the device nozzle under a load applied with a 2.16 kg piston. As the content of the carbon filler grew in the material, the polymer flow was limited by a rising number of anthracite inclusions. The presence of solids in the molten polymer made it necessary for the plasticised material to overcome the effects caused by the presence of small solid inclusions, which hindered its flow. For deformation, i.e. for infinitesimal movement of layers, it was necessary to overcome the heightening internal friction by the applied load, which was caused by the increase in viscosity. It should be highlighted here that the evaluation of changes in rheological properties values based on the analysis of the melt

TABLE 2

Hardness of matrix and PP/anthracite composite

Marking of the samples	H1	H2	H3	H4	H5	H6
Hardness [°ShD]	69.5	72.1	72.6	73.5	75.3	75.8

TABLE 3

Stiffness modulus (Young's modulus), tensile strength and elongation at break of the pure PP and investigated PP/anthracite composite

Marking of the samples	H1	H2	H3	H4	H5	H6
Stiffness Modulus, E [MPa]	1446	1746	1883	2223	2532	2956
R_m [MPa]	30.9	27.2	25.2	22.9	22.7	22.1
Elongation at break, ε_r [%]	258.2	8.7	5.9	4.3	3.5	2.9

flow rate (MFR), which is usually sufficient, may not be reliable. Considering a significant difference in the density of the polymer material (0.8642 g/cm^3) and the filler (2.02 g/cm^3), along with the growing percentage content of anthracite dust in the material, which is obvious, the density of the investigated composite grows markedly (Table 4). This makes it difficult to assess the impact of the filler on the viscosity of the material. In the case of the investigated materials, it is much more advantageous to evaluate changes in the melt volume flow rate value, which is independent from variations in the examined material's density. For the H6 blend containing 50% of the filler, its MFR is 8.13 g/10 min, more than three times (3.04) lower than that of the base polymer of 24.73 g/10 min. The MVR flow rate is more than four times (4.02) lower for the H6 sample (8.57 cm^3/10 min) than for the PP matrix (34.41 cm^3/10 min). The values are given in Table 4. A ratio of the observed differences between the melt flow rate and the melt volume-flow rate is almost identical to the ratio of the density differences of the tested materials (0.72 to 0.75).

TABLE 4

Values of density and MFR and MVR parameters of polymer matrix and PP/anthracite composite

Marking of the samples	H1	H2	H3	H4	H5	H6
Density, [g/cm^3]	0.8642	0.8866	0.9832	1.0277	1.0880	1.2060
MFR, [g/10 min]	24.73	22.54	17.09	15.95	12.03	8.13
MVR, [cm^3/10 min]	34.41	29.57	22.49	16.07	12.89	8.57

There is no difference in electronegativity in the polypropylene between the carbon atoms forming the main chain; in addition, the insignificantly small dipole moments between carbon and hydrogen atoms cancel out each other as a result of their spatial symmetry. This makes polypropylene non-polar and hydrophobic. Investigations of surface wettability of the examined composite have revealed that with the rising content of crushed anthracite in the sample, its hydrophobicity, evaluated on the basis of the wetting angle, is rising. The water wetting angle grows linearly (Fig. 4) from 87.77° for H1 (0%) to 114.52° for H5 (40%). Similar results were obtained in work describing PP/shungite composites, where the wetting angle increased linearly from 98° for pure PP to 109° for 30% shungite content [7]. This is a consequence of specific properties of anthracite. In the case of carbon, its hydrophobicity depends on multiple factors. Especially on the content of oxygen in the mineral, carboxyl hydrocarbon groups and the grain size.
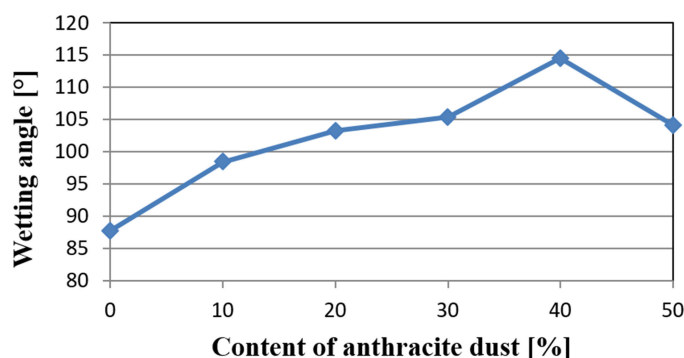

Fig. 4. Influence of anthracite content on the value of wetting angle of composite with water

The anthracite applied in the experiment is a carbon variety characterised by the highest degree of carbonisation with a very low hydrophilic ash content. Moreover, carbon in the form of larger grains has a more hydrophilic character, which is also related to the roughness of the surface, which favours the adhesion of the liquid to the surface. For this reason, the introduction of anthracite filler with a small size of a single grain into the polymer matrix has supported the growing hydrophobicity of the composite along with the growth of the filler content in the material to 40% of the volume in the composite.

An anthracite filler was introduced into the polypropylene matrix to enhance the electrical properties of the material obtained in this way [16,17,25]. It was assumed that anthracite, due to its specific properties, i.e. very high carbon content and low content of impurities, could contribute to the reduction of the resistance value of the polymeric material containing it. Improved results are presented in article [25]. In the paper [25] are described investigations of electrical properties of segregated composites with an ordered distribution of anthracite filler particles in a polypropylene and polyethylene matrix. The perlocation nature of conductivity was found. In segregated composites, electrical conductivity has improved in comparison with conventional composites.

Surface and volume resistivity have declined by introducing anthracite dust into the polymer material. Surface and volume resistivity values for PP are, respectively, 1.17E+17 Ω and 1.12E+15 Ωm. The presence of anthracite with 50% content of H6 reduces the surface and volume resistivity to 1.77E+15 Ω and 4.62E+13 Ωm (Table 5). The values examined for the samples are indeed 10 to 100 times lower than those for an unmodified material, but they are still relatively high and do not allow to clas-

TABLE 5

Effects of anthracite content on surface and volume resistance

Marking of the samples	H1	H2	H3	H4	H5	H6
Surface resistance (ASTM D257/IEC 60093) U=300V [Ω]	1.17E+17	4.84E+15	1.86E+15	9.28E+14	6.15E+14	1.77E+15
Volume resistance (ASTM D257/IEC 60093) U=300V[Ωm]	1.12E+15	7.67E+13	2.64E+13	1.00E+13	2.44E+12	4.62E+13

310

sify the obtained materials as semiconductors (conventional limit value of 10^7 Ωm). It is most probably caused by the unfavourable geometric form of particles of the applied filler, which is shown in a SEM image (Fig. 1). A decrease in the volume and surface resistivity deteriorates the electroinsulating properties of composites, but enables to improve antielectrostatic properties [7].

A thermogravimetric analysis of the applied filler showed that it is possesses excellent thermal resistance and a low content of volatile compounds. Its intensive decomposition begins only at temperatures exceeding 600°C, which is characteristic for carbon. The filler is very stable until the decomposition temperature is reached. The graph shows a slight loss of sample weight from about 100°C (Fig. 5), which is caused by evaporation of moisture from the sample and small amounts of volatile organic compounds present in the anthracite. Despite this phenomenon, it can be concluded that thermal stability is one of the advantages of anthracite as a filler of polymer materials and can be successfully used to modify polymers to improve their mechanical properties.

4. Conclussion

1. The conducted investigations have shown unequivocally that the introduction of a carbon filler into a polypropylene matrix has a significant influence on the properties of the material obtained in this way.

2. The investigated composites are hydrophobic in their character and are characterised by high viscosity compared to an unfilled polymer. As the anthracite content is rising in the polymer matrix, the density of the investigated composite is falling.

3. It was found out that with the increase in the volume content of powdered anthracite in the material, its stiffness, evaluated on the basis of hardness values and modulus of elasticity, is growing. This is often observed as a result of introducing hard filler particles into the polymer matrix.

4. In was additionally found that anthracite at 30% volume shows a limited tendency to reinforce the material, which prevents a radical deterioration in the strength of the material as is the case for other fillers. With the enhanced resistance of the material to deformation, it is feasible to use it to produce elements of structural nodes, for which high stability during work is required. This is an unquestionable advantage of the developed material.

5. The anthracite dust in examined samples showed limited strengthening effect – the absence of a clear reduction in tensile strength of samples with the highest contents of described filler.

6. Despite very good electrical properties of the anthracite dust (derived from high carbon content) introduced into the polypropylene matrix, it was not possible to significantly improve the electrical properties of the achieved composite. The polymer used as a matrix of the material in the investigations was distinct for its low viscosity, which facilitated its processing, but at the same time has increased the tendency to surround and separate from each other the particles of the conductive filler (encapsulated them in polymer). The anthracite particles separated from each other by layers of an insulator – polypropylene – could not have created the efficient ways of transporting electrical charges.

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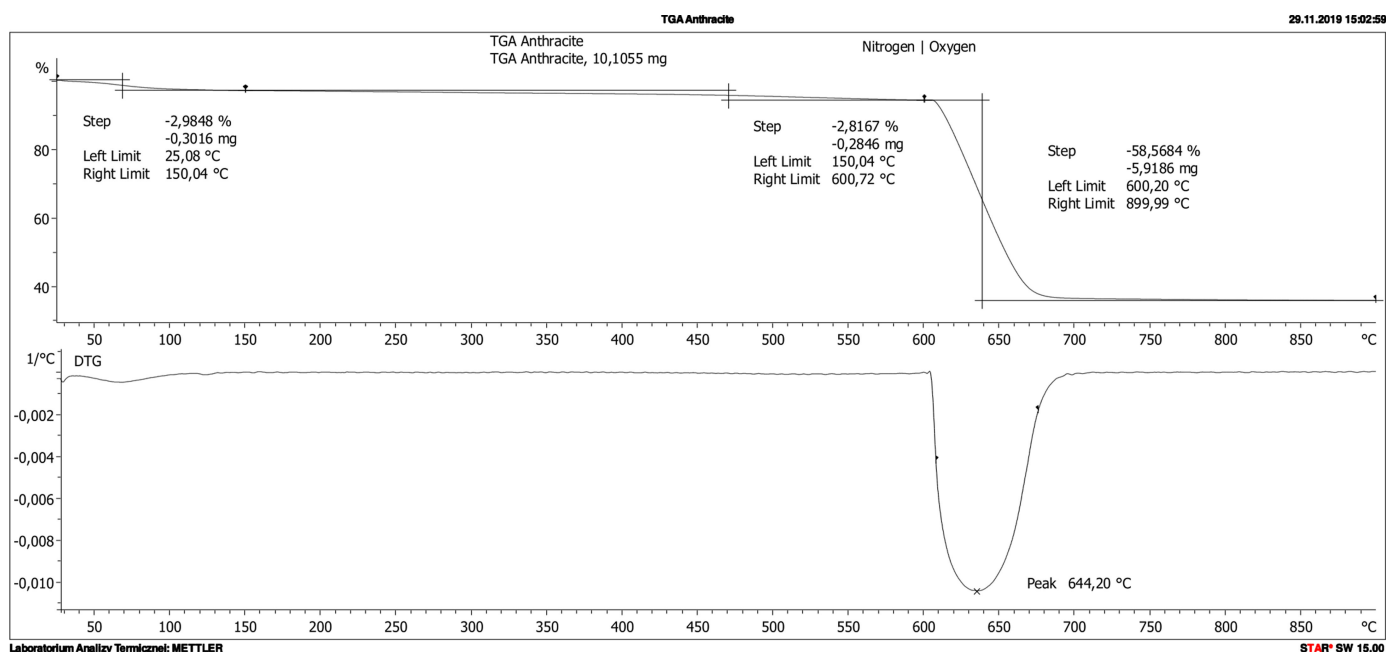[2] E.K. Sichel (Ed.), Carbon black polymer composites, Marcel Dekker, New York (1989).

Fig. 5. Thermogram of the anthracite dust

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