





Polypropylene matrix composite with charcoal filler

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ABSTRACT

Purpose: The aim of the article is to present the thermal, electrical and mechanical properties of the produced polymer composites with a filler in the form of charcoal powder.

Design/methodology/approach: The tests were carried out on samples of pure polypropylene (PP) and polymer composites, the matrix of which is polypropylene (PP), and the filler was charcoal powder with a volume fraction of 10%, 20%, 30%, 40% and 50%. The tested polymer composites in the form of granules were produced by extrusion, and then standardised test profiles were made by injection moulding.

Findings: The hardness of the tested composites was determined by the Shore D method, the grain size distribution of the filler used was determined using the laser method and its thermal stability was tested using the TGA thermogravimetric analysis. The volume and surface resistivity were also determined and the density was determined. It was found that the charcoal powder used as a filler is characterised by high thermal stability – up to 600°C – and with an increase in its volume share in the polymer matrix, the hardness and density of the produced composites increases.

Practical implications: The tested composites can be used as structural composites for complex elements requiring high hardness and strength.

Originality/value: The research results indicate the possibility of using charcoal as a filler in polymer matrix, which, due to its low production cost, may be an alternative to expensive carbon fillers.

Keywords: Composite, Polymer composites, Charcoal filler, Thermogravimetric analysis, Resistivity

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PROPERTIES

1. Introduction

Specific processing and functional properties of polymer materials have contributed to their wide application in many branches of industry such as: automotive and aviation, pharmaceutical, packaging, textile, construction, chemical and cable industries. The most commonly employed thermoplastics include polyethylene, polypropylene and poly(vinyl chloride). Polymer composites, defined as multifunctional and versatile materials, are becoming increasingly important among construction materials and are now applied in nearly all areas of life [1-3].

Composites are heterogeneous materials consisting of a polymer phase-matrix and dispersed types of other auxiliary substances-fillers, among which active fillers such as different coal particles deserve special attention. The phase of a continuous character is represented by a composite matrix, while the filler is the dispersed or reinforcing phase, which usually has greater rigidity and mechanical strength than the polymer phase. The polymer matrix is designed to combine all the components of a composite as a whole and is responsible for transferring stresses between fillers and determines the method of processing the composite. A filler is a solid particle with a proportion of more than 10% by weight in a polymer matrix. In the case of materials processed by injection or extrusion, the filler content can reach up to 60%, and in the case of resins up to 90%; it has been found that at such a filling level, macromolecular material becomes more a filler binder [2-6]. The use of fillers does not guarantee that we will achieve an improvement in all properties, there is no filler with a comprehensive effect, the improvement of some properties causes deterioration of others. The filler, which is to fulfil specific tasks, should indicate: low absorption and water content, low specific weight, chemical inertness to the polymer and hardener in the case of hardenable materials, good wettability and thermal resistance, allowing it to be processed with the plastic. The most common undesirable side effects of using fillers are: sedimentation (may cause heterogeneity of the material), agglomeration – reduces the value of mechanical properties, deterioration of processing properties, increase in density, increase in moisture absorption, which affects the deterioration of dielectric properties. The effects of the interaction of fillers with a polymer matrix should be determined individually for each type of composite and tested using experimental methods [6-11].

Active fillers, which improve mechanical, tribological, rheological, thermal, dielectric, chemical and processing

properties, are of significant importance in the modification of polymeric materials. For several years, among construction materials, interest has been gained in composites based on polymeric materials with the addition of fillers in the form of powders and dusts, fibres and nano-additives. Carbon fillers, which include various types of carbon black and graphite, as well as hard coal, shungite, anthracite, are very popular, they are an alternative to expensive fillers made of carbon nanotubes [7-10]. Carbon fillers are an important component of polymer composites, due to their favourable properties and the possibility of modification, which – in combination with appropriate polymer matrices – have a positive effect on the improvement of electrical properties, resistance of polymers to environmental factors and UV radiation. Particularly good results were obtained in the case of carbon fillers in polyolefin matrices, and materials of this type can be used as: shields against the effects of electric and magnetic fields, sensors for measuring various physical quantities, thermistors, protective coatings against the accumulation of electrostatic charges and heating elements emitting infrared radiation. It was found that the use of carbon black evenly distributed in the polypropylene matrix significantly increases the value of the longitudinal stiffness modulus and causes a slight increase in the mechanical strength of the material. Literature data confirms that composites with a polypropylene matrix with a carbon black content of up to 9% can be used as materials for the production of multiple chemical sensors. The materials with the best electrical characteristics were obtained from PP and PE composites, in which the carbon black content was close to the percolation threshold [8-18]. The use of carbon fillers also increases the hardness and abrasion resistance of polymer composites, as well as the strength properties. The addition of shungite and anthracite in polypropylene matrices increased the hardness and stiffness of the tested composites. The addition of shungite improves electrostatic properties, and the composites are hydrophobic [14-19].

2. Experimental procedure

Prepared for the tests was a polymer composite with a polypropylene matrix with the addition of a filler in the form of a charcoal powder with a percentage share of 10% (G2), 20% (G3), 30% (G4), 40% (G5) and 50% (G6). A sample containing 100% polypropylene was designated G1. The matrix is made of MOPLen H548R polypropylene (PP), it is a homopolymer with high fluidity, which is

characterised by good stiffness and low viscosity. The filler used in the form of charcoal was created as a result of pyrolysis of wood from deciduous beech trees. The charcoal before extrusion was ground twice to the smallest grain on a finger mill called MUT at the New Chemical Synthesis Institute, Inorganic Chemistry Division "IChN" in Gliwice, Poland, and then sieved through screens with different mesh sizes. The obtained charcoal powder was dried for several hours at 100°C and mixed with polypropylene granules. The PP/charcoal blends obtained in this way were homogenised using a Göetffert counter-rotating twin-screw extruder, with an L/D25 ratio, equipped with a bar extrusion head with an exit diameter of \varnothing 3 mm. The following extrusion parameters were used: 1st zone temp. 200°C; 2nd zone temp. 220°C; 3rd zone temp. 230°C; head temp. 240°C; turnover: 6-8 rpm. A granulate was obtained by grinding the extruded rod with a laboratory "Metalchem" granulator, and then by injection, samples were prepared for testing in the form of standard A1 type "paddles" in accordance with PN-EN ISO 527-2:2012. The injection process was performed on a Battenfeld Plus 35/75 injection moulding machine with the Unilog B2 control system, with an L/D17 ratio.

The analyses of measurement of the charcoal powder grain size were performed by laser diffraction on a Beckman Coulter LS 13320 apparatus, according to ISO 13320:2009.

The decomposition temperature of the charcoal powder was determined using the TGA thermogravimetric analysis. The investigations were carried out with the following parameters: Mettler-Toledo XS 105 thermobalance, heating rate: 20°C/min., the flow rate of gases through the measuring cell: 60 ml/min. The samples were heated to 600°C under a pure nitrogen atmosphere, and to remove the carbon black in an atmosphere of pure oxygen in the temperature range of 600-900°C.

Density was examined using the immersion method in accordance with PN-EN ISO 1183. The following measurement conditions and parameters were used: test method: A (immersion method), test liquid: distilled water; the material cut out from the injected test pieces was examined, the determination was carried out using the analytical balance Mettler-Toledo XS 105 with an attachment for density testing.

The Shore D scale method according to PN-EN ISO 868:2005 was used to determine the hardness of the tested composites. The samples were conditioned at a temperature of 22°C before the hardness measurement. The test was performed on an electronic hardness tester (durometer) by Zwick, at a temperature of 22°C. Measurement readings were taken after 15 s.

On a Keithley Instruments Inc., Model 8009 electrometer, the surface and volume resistivity of the PP/charcoal composites tested were determined using a test voltage of 300 V. The tests were carried out in accordance with the research methodology according to ASTM D257-14 and IEC 60093:1980.

The image of microstructure of the filler powders, sputtered with gold, were made using an electron scanning microscope, ZEISS Supra 35, using the accelerating voltage of 15 kV.

3. Results and discussion

The study of the thermal properties of fillers used in polymer composites is necessary to determine the effect of materials reinforcing polymer matrix on the thermal stability of composites. The thermal stability of charcoal was investigated by TGA thermogravimetric analysis in nitrogen and pure oxygen atmosphere. The distribution curve of the tested charcoal powder is shown in Figure 1. Charcoal is characterised by a single-stage decomposition process that takes place above 600°C, a phenomenon typical of carbon fillers. In the temperature range of 25°C-600°C, the charcoal powder filler is very stable. One can observe (Fig. 1) a slight loss of mass at the temperature of approx. 80°C, this phenomenon is related to the evaporation of moisture and volatile organic compounds that occur as components of charcoal. As a result of the thermogravimetric analysis, it was found that the charcoal powder is characterised by good thermal properties and a low content of volatile compounds.

The parameter that also affects the mechanical properties of the produced PP/charcoal composites is the grain size distribution of the charcoal powder, which determines the size of the contact surface of the filler-matrix components.

Based on the laser analysis (Fig. 2) and the grain size distribution of the ground charcoal powder, it was calculated that more than 75% of the filler particles used have dimensions in the range of 0-20 μ m. Based on the analysis of the SEM images, it was noticed that the charcoal powder is uniformly distributed in the polypropylene matrix (Fig. 3). No agglomerates of the tested filler were found in any of the tested samples, which could adversely affect the strength of the produced composites. Moreover, it was found that the individual filler grains showed a heterogeneous and well-developed outer surface with a preserved partial structure of

the wood cell walls (Fig. 4). The heterogeneous and discontinuous grain morphology of the charcoal powder has a positive effect on the adhesion and better combination of components in the polymer composite. Polypropylene,

especially with a low viscosity at the processing temperature, fills the voids in the grains of the charcoal powder, thanks to which it adheres better to it, creating a kind of mechanical bond.

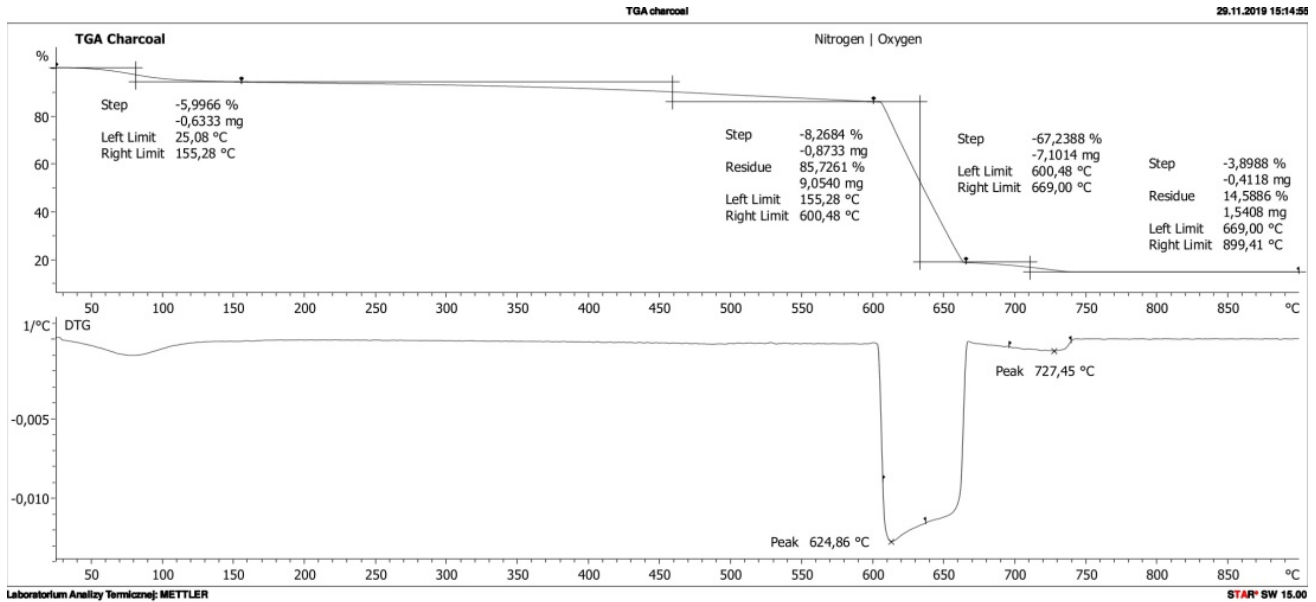


Fig. 1. Thermogram of the charcoal powder

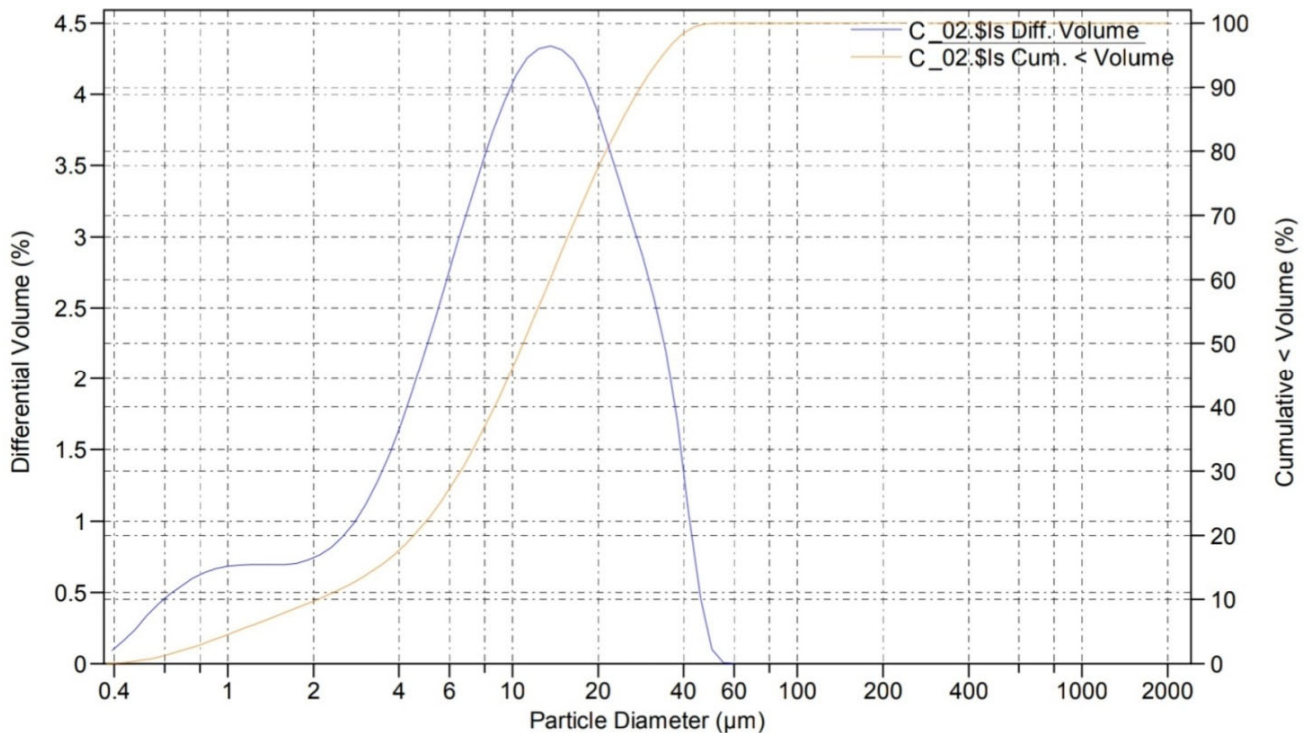


Fig. 2. Particle size distribution

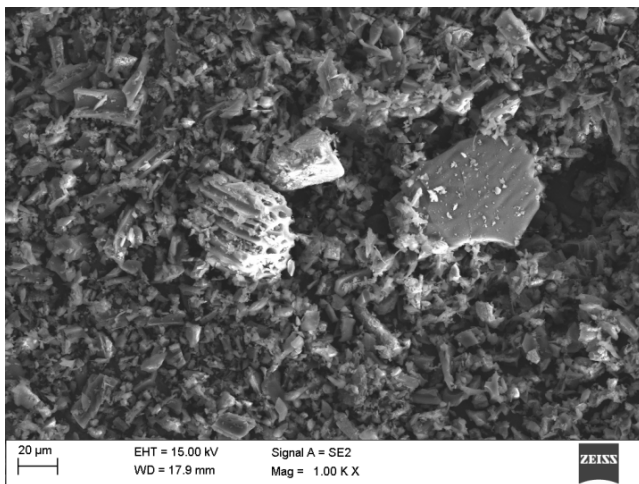


Fig. 3. Microstructure of charcoal powder

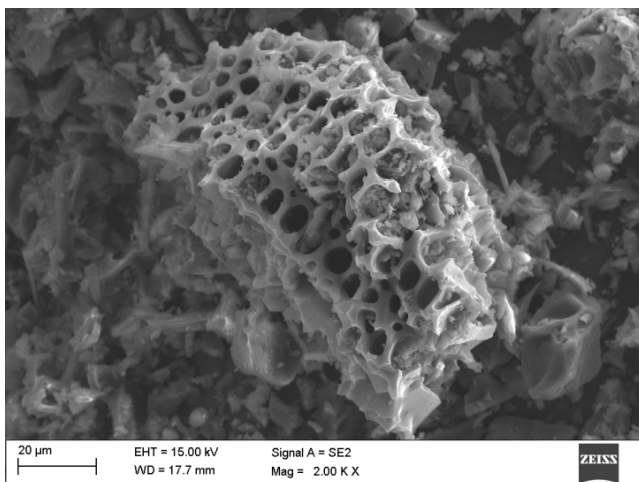


Fig. 4. Surface morphology of a single gran of charcoal powder

The higher the filler content in the composite material, the higher its density (Tab. 1), similar trends have been found in many scientific publications [6-19]. The composite with 50% charcoal powder has a density of 1.35 g/cm^3 , while pure PP has a density of 0.8642 g/cm^3 .

A significant increase in density is related to a higher density of the filler, approx. 1 g/cm^3 . The density test results obtained for the described samples correspond to the theoretical calculations, which confirms the lack of gas inclusions in the material, which could indicate degradation of the material or its porosity caused by the emission of volatile compounds from the filler.

An important property of the produced polymer composites is the hardness, which was determined by the Shore D method. With the increase of the percentage content of the filler in the polymer matrix, the hardness of the produced composite increases. The hardness of the polymer matrix is 69.5°ShD , along with an increase in the volume fraction of charcoal powder to 50% (G6), the hardness increases to 76.7°ShD (Tab. 1).

Table 1.

Density and hardness of matrix PP and PP/charcoal composite

Marking of the samples	Density, g/cm^3	Hardness, $^\circ\text{ShD}$
G1	0.8642	69.5
G2	0.8822	72.1
G3	0.9328	72.7
G4	1.0160	74.0
G5	1.0736	75.0
G6	1.3500	76.7

Such a large increase in hardness with a maximum filler percentage of 50% may indicate that this is the optimal content in the case of improving the hardness of the produced composites. The 50% filler content will not affect the permanent deformation of the sample. A slight change in hardness was noticed in the case of samples with the content of G2 10% (72.1°ShD) and G3 20% (72.7°ShD), which is probably related to a slight influence of this content on the hardness of the PP/charcoal composite produced.

The volume and surface resistivity of the produced PP/charcoal composites were also tested, due to the filler used in the form of charcoal powder, which is to improve the electrical properties of the polymer composite. Charcoal has a three times higher energy value than wood and shows strong absorption, due to its highly developed surface, and is characterised by a low tar content. The introduction of charcoal powder into the polypropylene matrix resulted in a decrease in volume and surface resistivity (Tab. 2), which decreased the electrical insulating properties of the produced composites. The produced PP/charcoal composites can be used wherever an increase in anti-electrostatic properties is needed – e.g. in electronics or components working in potentially explosive areas. It is worth noting that the tests showed a much greater impact of the filler introduction on the volume resistance value than on the surface resistance.

Table 2.
Effects of charcoal content on surface and volume resistance

Marking of the samples	Surface resistance (ASTM D257/IEC 60093)	Volume resistance (ASTM D257/IEC 60093)
	U=300 V, Ω	U=300 V, Ωcm
G1	1.17E+17	1.12E+15
G2	6.64E+14	4.06E+15
G3	6.41E+14	1.89E+08
G4	1.01E+15	5.00E+07
G5	1.61E+15	5.12E+07
G6	1.69E+15	3.77E+08

This is probably due to the formation of percolation paths deep inside the material, which allowed the flow of electric charges. However, the effects associated with the flow of a plasticised composite during the formation of samples prevented the formation of this type of electrical connections on the surface of the samples.

4. Conclusions

It was found that, due to its thermal stability, the tested charcoal powder can be successfully used as a filler for polymer matrices in order to modify and improve the mechanical properties of the resulting polymer composites. A typical tendency was observed in the case of introducing hard particles of filler into the polymer matrix, related to an increase in the hardness of the produced material with an increase in the volume fraction of the filler in the matrix.

The introduction of charcoal powder into the polypropylene matrix increased the electrostatic properties, but worsened the electrical insulating properties.

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