

A. WŁODARCZYK-FLIGIER^{1*}, M. POŁOK-RUBINIEC¹, B. CHMIELNICKI²**POLYPROPYLENE-MATRIX POLYMER COMPOSITES WITH NATURAL FILLER**

Polymer composite materials based on the Moplen HP400R polypropylene matrix with a filler from walnut shell flour with 30, 40 and 50% content and 200-315 μm and 315-443 μm fraction were produced by the injection method. The effect of filler content was analysed on the processing properties of the composites such as: MFR Melt Flow Rate and the MVR Melt Volume-flow Rate, as well as the temperature of the filler flour decomposition using the TGA thermogravimetric analysis method. The following was also determined: density, hardness, tensile strength and stiffness modulus of elasticity of the materials in question. The obtained composite material was characterised by low density, which increased with the rising filler content. It was found that the applied natural filler has increased the hardness and stiffness modulus of the composite and decreased the tensile strength.

Keywords: WPC composites, processing of composites, natural filler, properties

1. Introduction

In the recent years, interest in polymer composite materials has increased, which has resulted in intensified research on these materials. The polymer composites production technology is one of the fields of chemical technology. The components added to polymers in processing can be divided into two groups: fillers and auxiliary agents (dyes, plasticisers, stabilisers, porophors, flame retardants, etc.) [1,2]. The fillers introduced into polymers are in the solid state, in a specified quantity and size. The aim of their introduction into polymers is to reduce the costs of the material and to obtain the expected mechanical, thermal and other properties [1,3]. The modification of polymers results in achieving the polymer composites characterised most often by lower water absorption, higher resistance to deformation under load at elevated temperature, higher impact strength or a lower thermal expansion coefficient [2]. Different types of polymers have started to be used and compared as a basic component, and various types of fillers of different origin, different percentage content or different fractions [4,5].

One way of utilising natural raw materials (including wood) as an alternative to traditional fillers is to use them as fillers for the production of WPCs (*Wood Plastic Composites*). The definition of WPC composite materials in various articles combines the criteria that these materials must meet. According to this

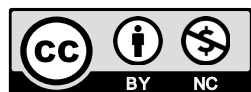
definition, “WPCs are thermoplastically processable composites consisting of plant fragments, polymeric material and auxiliary agents in varying degrees of fraction”. One of the reasons for manufacturing such materials was the growing fabrication cost of the products from typical polymer materials. The largest group, both in Poland and in other countries, comprises the materials reinforced with wood, due to its high availability, as well as the diversity of species. The still growing interest in polymer-wood composites derives from the good properties of the products obtained from them, by combining the beneficial properties of both the matrix and the filler [6-9].

The development of new polymer composites allows to extend their application in various fields of economy. It is very important to search for new competitive organic and inorganic fillers, as well as to introduce various types of filler modifications as well as other additives. Another crucial aspect is the development of effective technologies for the fabrication of new polymer composite materials with functional properties suitable for a specific application [10]. The advantage of WPC composites over typical polymers is that their appearance is similar to wood, while maintaining high resistance to environmental factors, characteristic for polymers, and reduced sensitivity to microbiological degradation, as is the case for natural raw materials [11]. Currently, alternatives to commonly used wood flour fillers applied in WPC composites are being searched for. Such fillers

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include walnut shell flour allowing to reduce water absorption and improving functional properties. This would allow their use, among others, as garden elements (terrace boards, balustrades, playgrounds, roof coverings, etc.) [12,13]. In countries suffering from a shortage of wood due to climate conditions, shells of various species of nuts are not applied in industry and are used as fuel. Shells account for 25-67% of the total nut weight and are recovered as waste in the food or cosmetic industry [14]. In recent years, nut shells have been crushed in many countries, providing a lower process cost than in the case of wood. This is a major advantage for the use of nut flour as a filler in WPC materials. In addition, nut shell flour has a relatively low price of about 5 cents/kg less than the cheapest wood flour – pine flour. Due to these characteristics, research over WPC composites filled with nut shell flour becomes a response to the real needs of consumers.

The article presents the results of investigations into: density, (filler density), hardness, tensile strength, tensile stiffness modulus, MFR Melt Flow Rate and the MVR Melt Volume-flow Rate, TGA thermogravimetric analysis of the manufactured polymer composite materials with a polypropylene matrix with a filler from walnut shell flour with different percentage content and different fraction.

2. Experimental

2.1. Materials

The investigations were carried out on polymer composite materials based on the Moplen HP400R polypropylene (produced by Lyondellbasell in Poznań) matrix with the filler from walnut shell flour with 30, 40 and 50% content and fractions of 200-315 μm and 315-443 μm (Table 1). The PP polypropylene used as a matrix is a homopolymer designed for injection, characterised by low viscosity and good stiffness.

TABLE 1

Marking of the investigated materials

Flour from walnut shells, fraction μm	The content of flour in the composite, %			
	0	30	40	50
Marking of the investigated materials				
200-315	E1	E2	E3	E4
315-443	F1	F2	F3	F4

The walnut shells used as a filler to produce polymer composite materials were crushed, before extrusion, in two stages: initially in a hammer mill SchutteBuffalo and then in a turbine mill (Institute of New Chemical Syntheses. Division of Inorganic Chemistry "IChN" in Gliwice-Poland). After crushing, the flour was sieved through sieves of different mesh size in order to obtain different size of flour grains.

Then, the flour was dried at a temperature of about 80°C for about 4 hours and mixed with polyolefin granulate. Such blends were subjected to one homogenising extrusion using a Goöttfert counter rotating twin-screw extruder at a ratio of

L/D = 25, equipped with an extrusion head for extruding a bar with \varnothing 3 mm diameter at the exit.

The extrusion process conditions selected for the PP/nut shell flour composite blends: zone I temperature: 180°C, zone II temperature: 200°C, zone III temperature: 210°C, head temperature: 215÷220°C, number of rotations: 2-4 rpm.

After extruding, the granulate was injected, and the final result were test samples in the form of a standardised A1-type test piece according to PN-EN ISO 527-1. The injection process was carried out with a Battenfeld Plus 35/75 injection moulding machine equipped with a Unilog B2 control system with the L/D ratio of 17.

The density was measured for all the polymer composite materials, the MFR Melt Flow Rate and the MVR Melt Volume-flow Rate were determined, and the temperature of flour decomposition was established by the thermogravimetric analysis. In addition, tensile strength, tensile stiffness modulus and hardness of the materials obtained were determined.

2.2. Methods

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

Density was examined using the immersion method in accordance with PN-EN ISO 1183, using the following measurement conditions and parameters: 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 natural filler bulk density tests were carried out in accordance with APrPN-ISO60 standard.

The hardness of the examined polymer composite materials was tested with the ball method at the ambient temperature of 22°C under a test load of 358 N in line with the guidelines of PN-EN ISO 2039-1 standard. The test was performed using a Zwick hardness tester.

A static tensile test was performed on a universal testing machine manufactured by Zwick/Roell Z020 according to PN-EN ISO 527-1:1998, at a test speed of 5 mm/min at the ambient temperature of 22°C.

The tensile stiffness modulus was measured in an Instron TT-CM 80 testing machine in accordance with PN-EN ISO 527-1 and PN-EN ISO 527-2 standards, using the following conditions and parameters of measurement: the piece type: 1A. The pieces were injected from the previously prepared granulate, the temperature of the test: 22°C, humidity: 50%, test speed: 1 mm/min. an Instron mechanical extensometer was used in the tests.

The MFR Melt Flow Rate and the MVR Melt Volume-flow Rate were determined in accordance with PN-EN ISO 1133 using the following measurement conditions and parameters: test temperature: 230°C, test load: 2.16 kg, time for pre-conditioning of the samples at the measurement temperature without the ap-

plied load: 5 min., nozzle diameter: $2,095 \pm 0,005$ mm, apparatus: Zwick-Roell Mflow plastometer.

The decomposition temperature of the walnut shell flour was determined using the TGA thermogravimetric analysis. The investigations were carried out with the following parameters: Mettler-Toledo thermobalance, heating rate: $20^{\circ}\text{C}/\text{min}$. up to 600°C , the measuring cell was flushed with nitrogen, above 600°C nitrogen was changed to pure oxygen, the flow rate of gases through the measuring cell: $60 \text{ ml}/\text{min}$.

The image of microstructure of the matrix and filler powders and the image of the materials produced after a static tensile test, sputtered with gold, were made using an electron scanning microscope, ZEISS Supra 35. An accelerating voltage of 10 kV was applied.

3. Results and discussion

Walnut shell flour, due to its favourable structure, is a promising filler for WPC polymer composite materials. Nut shells are made up of woody plant cells, the so-called sclerenchymatic tissue, with practically no natural polymers: lignin and cellulose.

Sclerenchymatic cells have thickened, woody walls and are the hardest plant tissues. In the case of many plant species they are additionally saturated with suberin. This substance, composed mainly of long-chain fatty acids and their esters with aliphatic alcohols, exhibits strong hydrophobic properties, which additionally protects the shell against biodegradation and moisture absorption. The hydrophobic character of the shell surface is a significant difficulty in decomposition of this plant tissue by the enzymes of microorganisms and in its assimilation. As a consequence, walnut shell flour has a significantly higher resistance to biodegradation and lower water absorption than leaf and coniferous tree flour. In addition, it should be noted that natural polymers such as lignin and cellulose, which occur in different amounts in wood depending on the wood species, can be easily degraded by other environmental factors, e.g. UV radiation, which leads to greying of the wood and colour change. The absence of lignin and cellulose in shells brings another important advantage from the thermoplastic processing point of view, namely the improvement of the thermal resistance of the filler.

The size distribution (Fig. 1) of the walnut shell flour grains, used as a filler, is one of the parameters influencing the mechanical properties of the produced composites.

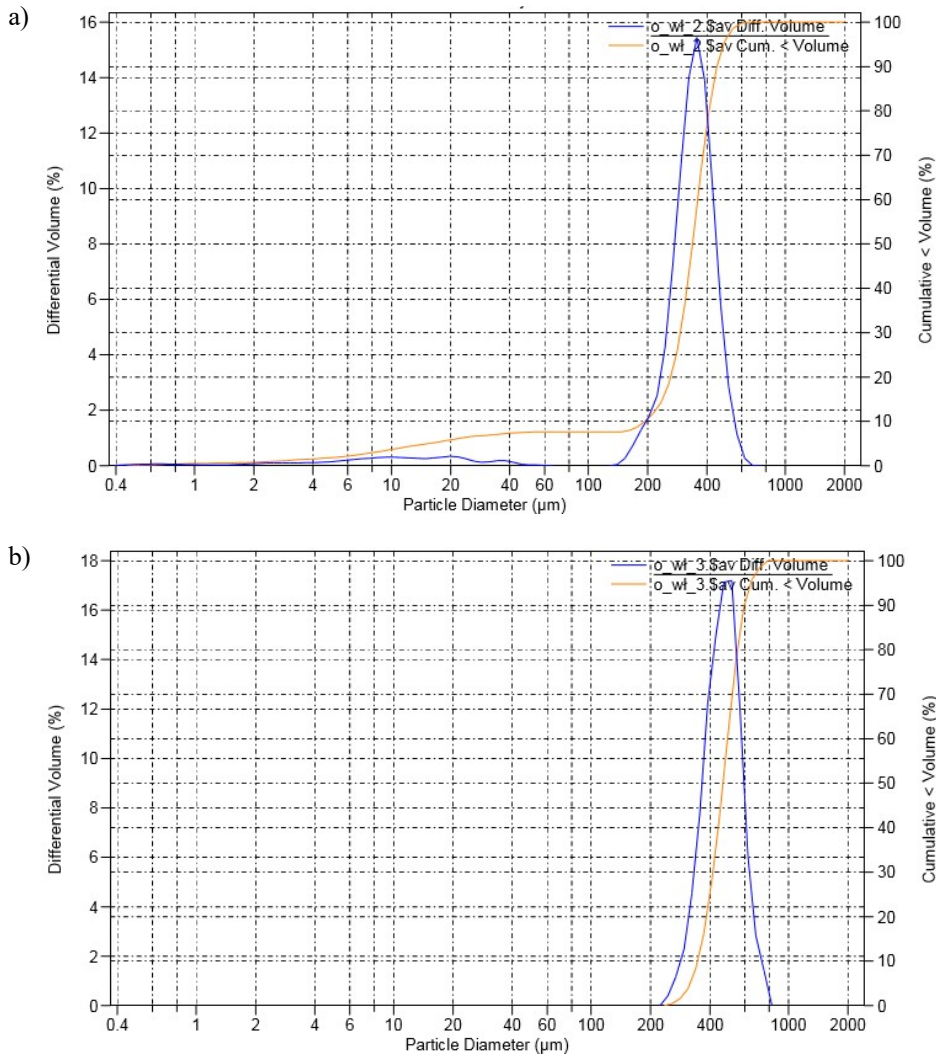


Fig. 1. Particle size distribution: a) material E, b) material F

The investigations performed into the shape of grains of the crushed walnut shell flour (Fig. 2), used as a filler in the composite, show a non-uniform and well-developed external surface in the loose state, and inside the grains, discontinuities are visible (Fig. 3). This most probably results from the structure of walnut shells. These discontinuities allow the polymer to fill the voids, which influences the connection between the filler and the matrix.

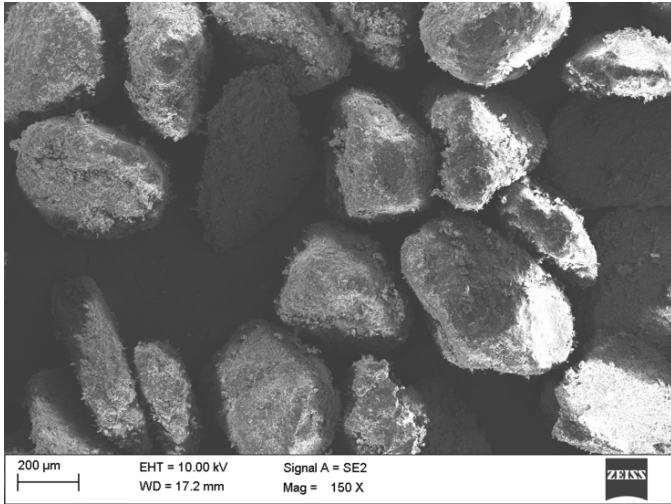


Fig. 2. Shape of walnut shell flour grains

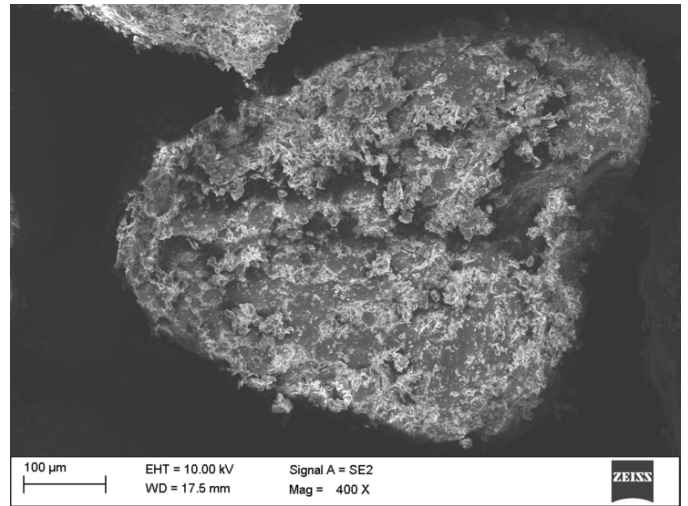


Fig. 3. Single walnut shell flour grain

In the case of the investigated walnut shell flour, its intensive thermal degradation occurs only above approximately 230°C. A slight loss of mass is observed on the thermogravimetric curve (Fig. 4), occurring from about 50°C until the beginning of intensive thermal decomposition of the filler, which is connected with the release of moisture from the material and of natural essential oils it contains. For this reason, it is advantageous during processing to use systems to degasify the plasticised

polymer mixed with the filler. For the traditional wood flour, the decomposition temperature is significantly lower. For fillers made of coniferous trees with a high content of lignin and cellulose, as well as resins, it can only be about 170°C, as is the case with pine wood. For flours from hard deciduous trees, e.g. oak, due to their more favourable composition resulting from a lower content of natural polymers, the temperature of their thermal degradation may reach even 200°C. Such low temperatures of natural filler decomposition significantly limit the possibility of using composites, thus dictating the type of the polymer matrix. For traditional WPC composites, only polyolefins may be used as the matrix: polyethylene and polypropylene, softened poly (vinyl chloride) and biodegradable polymers, e.g. polylactide (PLA), to a lesser extent, due to their high material price and a narrow area of potential applications. The mentioned polymers can be processed at relatively low temperatures to ensure that no filler degradation occurs. The investigations of walnut shell flour car-

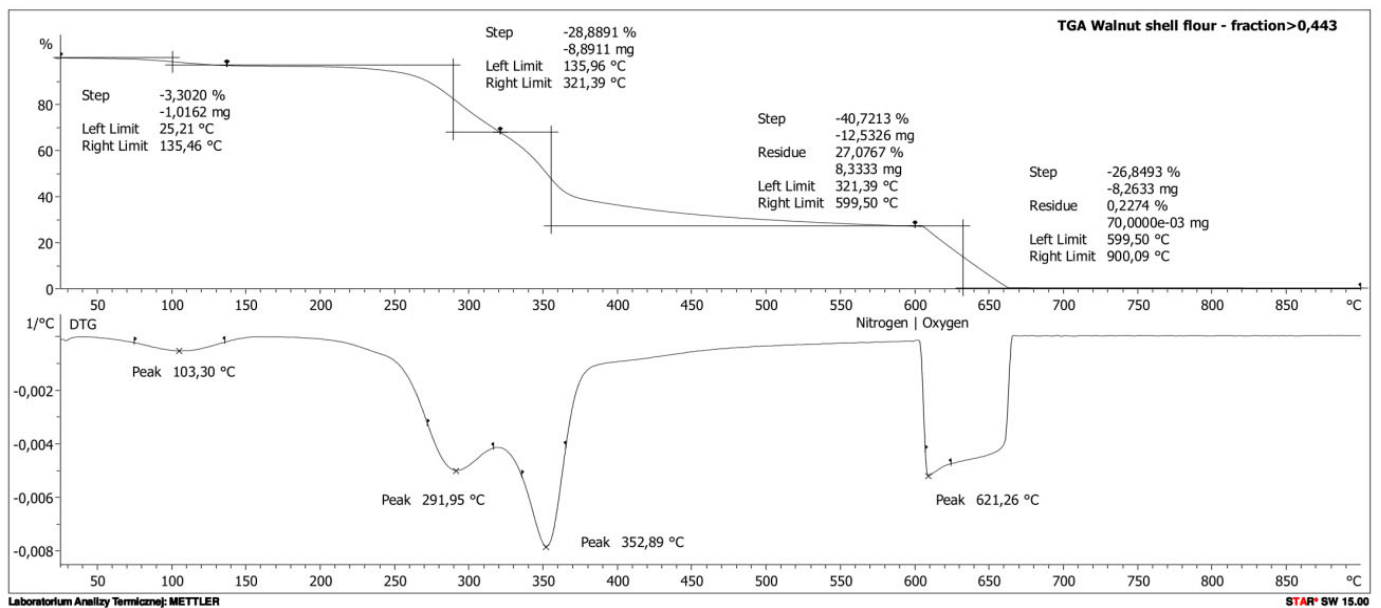


Fig. 4. TGA curve of walnut shell flour decomposition

ried out showed that this filler has a significantly higher thermal resistance than traditional wood flour, which makes it possible to use it in compositions with other polymers, as well as to process it at a higher temperature with the polymer matrices used so far. This will allow to facilitate and increase the production efficiency of components from WPC composites.

It can be observed on the obtained thermogravimetric curve that the thermal decomposition of the filler, initiated at the temperature of about 230°C, progresses up to the temperature of 600°C. At this temperature, the measuring cell was started to be flushed with pure oxygen to remove the carbon black residue produced during the sample calcination. When the heated sample was started to be flushed with oxygen, the sample residue was then completely oxidised after reaching the temperature of approx 660°C. This proves the absence of mineral contaminations in the sample and its completely organic character.

The filler bulk density for the 200-315 µm fraction is 0.4681 [g/ml] and for the 315-443 µm fraction 0.6160 [g/ml].

The higher the filler content in a composite material, the higher its density (Table 2). Similar results were obtained in the case when wood flour was used as filler [15,16]. Samples containing 50% of walnut shell flour have a density of more than 1 g/cm³. Such growth in the value is caused by the high density of nut shells [15]. The density of the investigated composites is also determined by the porosity of the material, resulting from the presence of pores occurring in the natural filler, as well as free voids between the matrix and the filler. The characteristic structure of the flour, which is free of cellulose and lignin, means that it has a much heavier specific weight than other parts of the wood.

The introduction of a natural filler into polypropylene has influenced the rheological properties of the composite produced. The higher the flour content in the matrix, the higher its viscosity, evaluated with MFR and MVR. The both rates of the composite depend on the material temperature and pressure obtained during processing, as well as on the distribution of PP molecular weight and the presence of a filler in the matrix. The addition of walnut shell flour to the polymer matrix makes it more difficult for the composite to flow, which reduces the MFR and MVR values of the material compared to the polypropylene matrix material itself (Table 2). The value of the melt mass and volume-flow rate decreases with the increasing percentage content of a filler in the matrix. During the tests performed in a capillary plastomer, the plasticised PP flowed through the device nozzle under a load applied by a 2.16 kg piston. For the movement of the polymer layers, the applied load had to overcome the growing internal friction, which resulted in an increase in viscosity. It can be noticed that the introduction of the flour, consisting of

a finer fraction, into the polymer, has a slightly greater influence on the increase in viscosity of the material, evaluated based on MFR and MVR values. The samples of the investigated F-series materials filled with flour with the particle size of 315-443 µm are distinct for a slightly higher value of the both indices characterising rheological properties of the composite. This is caused by lower fragmentation of the filler, which translates into fewer points disturbing the polymer flow. The plasticised material, when flowing through a plastometer nozzle in the case of E-series materials, containing a more fragmented flour, must overcome a greater number of internal obstacles, which increases the value of internal friction, counteracting deformation of the liquid. Despite the identical filler content in the both samples, the F-series materials contain fewer flow disturbing elements due to the statistically larger volume of a single particle. This effect will most probably be maintained until a certain limit size of filler particles is exceeded, above which there will be a mechanical blocking of the flow of the plasticised material through the nozzle of the measuring device.

It can be concluded according to the investigations carried out that when using the examined composites, the polymer grades with low viscosity, selected according to the specific application, should be employed for their production. The low viscosity of the plasticised composite material will enable the injection processing of the material. However, in the case of this method, for fabrication of products from polymer composites, it will be important to choose the appropriate size of the natural filler fraction. If a coarse-grained filler flour is used, especially when the injected elements are of low thickness, the injection holes in the mould may become clogged and defects in the form of incomplete injection mould filling may occur.

By introducing the walnut shell flour into the PP matrix, a noticeable increase in the hardness of the examined composite was seen. Along with the growth of the filler content in the matrix, the hardness of the produced material rises markedly. Compared to the PP matrix itself, its hardness is 58.1 HB, where in the case of 30% content of flour with a smaller fraction, the hardness grew to 62.7 HB, and in the case of flour with a larger fraction, the hardness rose to 68.8 HB. This effect is caused by blocking the movement of polymer chains and the related elastic and permanent plastic deformation caused by the filler particles distributed in the polymer matrix. The ball, which is a penetrator in the test, by acting on the material, causes its deformation, which is a measure of the material hardness in a pressed ball (Brinell) test. In order for this to happen, the polymer must be deformed, i.e. there is a series of chain shifts in the polymer. When the moving polymer chains encounter on their way rela-

TABLE 2

Density and values of the MFR (Melt Flow Rate) and the MVR (Melt Volume-flow Rate) of the investigated material

Material	E1	E2	E3	E4	F1	F2	F3	F4
Density [g/cm ³]	0,8642	0,9665	0,9778	1,0103	0,8642	0,9667	0,9743	1,0355
MFR [g/10 min]	24,73	14,32	8,44	5,21	24,73	14,51	12,00	5,78
MVR [cm ³ /10 min]	34,41	16,98	11,08	5,52	34,41	17,27	13,75	6,95

Mechanical properties of the investigated composite materials

Material	E1	E2	E3	E4	F1	F2	F3	F4
Hardness HB	58,1	62,7	72,0	78,6	58,1	68,8	73,0	78,4
Stiffness modulus [MPa]	1446	2139	2199	2336	1446	2067	2124	2393
Tensile strength [MPa]	30,85	21,61	19,58	16,39	30,85	21,12	19,05	16,29

tively large grains of the filler, their further movement requires avoiding such an obstacle, which is practically impossible due to the complex molecular structure of the polymer. In this situation, the investigated material, moving under the influence of the deepening penetrator, starts to influence the filler inclusions, attempting to force their movement together with the polymer. However, due to considerable sizes of the filler flour particles, energy is dissipated due to the distribution of the load applied to one side of the inclusion on the whole surface. The filler particles themselves are much harder than polypropylene. With the increase of filler content in the matrix up to 50%, a significant increase in the hardness of the investigated materials is observed. On the other hand, there are no clear differences in hardness between the samples containing 40% and 50% of different fractions (Table 3).

Strength properties are conditioned by the interaction of the filler with the polymer matrix. This is important when one of the composite components is hydrophilic and the other hydrophobic [17-19]. This occurs mainly in the case of a polymer composite, where the matrix is a polymer from the polyolefin group.

After introducing the examined filler in the form of walnut shell flour into the polymer matrix, its strength properties have changed. Similar results were obtained in the case when wood flour was tested as filler [18,20-22], and also in the case of PE matrix and filler of walnut flour [16]. Along with the increase in the content of the flour in the composite, the tensile strength value has decreased [18] and its stiffness grew. A 50% content of the filler in the matrix caused a decrease in composite strength to approx. 16 MPa in both cases of the fraction size. It is possible that it stems from incomplete wetting of the filler flour by the matrix particles, which is also visible on the images from the scanning microscope (Fig. 5), where small voids are visible at the interface of the filler particles and PP matrix particles. When the natural filler does not show adhesion to the polymer matrix or its value is low, the material reinforcement effect caused by the presence of the filler cannot occur. The load applied to the sample in this situation is not transferred from the matrix to the filler particles. The matrix material has to oppose it only. However, due to the presence of discontinuities in it, in the form of filler inclusions, the actual cross-section of the composite is reduced, which leads to a decrease in the strength of the investigated material. In the case of the examined samples, the strength of the material is linearly dependent on the filler content. However, it causes an increase in the stiffness modulus of the composite, which corresponds to the results of the material hardness test. The stiffness modulus of a composite material with 50% filler content, for 200-315 μm fraction, is rising to 2336 MPa, and for

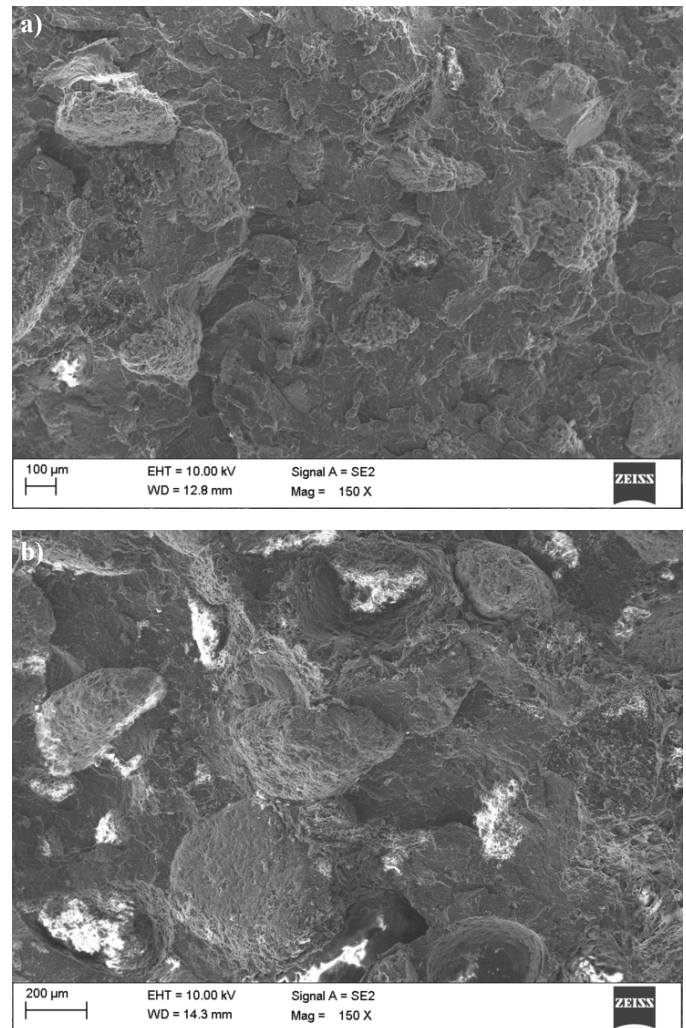


Fig. 5. The microstructure of the composite fracture after stretching: a) material E, b) material F

larger filler particles, it grows to 2393 MPa. As the percentage content of the filler in the material matrix is growing, the deformation of polymer chains becomes more difficult. At the time of applying the 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 filler inclusions dispersed in the matrix is blocking their movement, leading to a major increase in material stiffness. Mechanical properties of the manufactured composites depend to a large extent on the ability of the flour filler to blend into the matrix microstructure. Microscope observations on fractures after stretching showed that in all the studied materials, the presence of cracks was ob-

served in the composite at the filler-matrix boundary, the presence of pores, a different size and shape of filler particles, as well as the presence of agglomerates from the filler flour. The filler particles are not deformed during the manufacturing process.

4. Conclusion

It can be concluded based on the investigations of the produced polymer composite materials that the use of walnut shell flour is technically reasonable and that the research pursued responds to the users' real needs. This material, due to the specific structure of the filler, exhibits a number of beneficial properties, superior so far to the wood flour from coniferous trees commonly used in the manufacture of composites. First of all, it is possible to process the composite at a much higher temperature, which facilitates the production process by reducing the flow resistance of the material. A higher decomposition temperature of the investigated flour also allows to apply, as a composite matrix, other polymers than those used until now, which will enable to enhance the functional properties of the products made of them. The investigations of the produced polymer composite materials have confirmed a regularity described in many articles, claiming that growth in the flour content in the matrix causes a decrease in certain strength properties of composites. The composites produced are characterised by a significant increase in hardness and stiffness along with an increase in the filler content in the PP matrix and a decrease in tensile strength. A small effect of the filler fraction size on the studied properties was also observed. A low density of the material depends, in particular, on the material porosity.

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