PHYSICO-MECHANICAL PROPERTIES AND DIMENSIONAL STABILITY OF NATURAL FIBRE COMPOSITES FABRICATED FROM POLYETHYLENE WASTE AND WALNUT SHELLS

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Abstract
Within the framework of the study, a series of composites were produced with different shares of finely ground walnut shells (10%, 25% and 40% mass). Polyethylene obtained from selective packaging waste collection was used as a matrix, and the preparation process was in two stages – mixed and injection. The produced materials were analyzed for their physical properties (density, moisture content), mechanical properties (hardness, Young's modulus, DMA), and resistance to environmental factors (swelling and water absorption, TGA). The particle size distribution of the filler and morphological properties of the composites (SEM) was also investigated. The addition of the plant filler increases the hardness and considerably improves the stiffness of the composite. The absorptivity of the described NFCs is comparable to that of natural-filled composites containing additives that slow down the swelling process.

1 Introduction

The growing interest in thermoplastics reinforced with natural fibres that has been observed in the past three decades [1] is primarily conditioned by economic and environmental factors. These materials, apart from the desired aesthetics, are characterised by an unconventional combination of low density and high resistance to atmospheric factors, such as water or UV radiation, which are typical of a polymer matrix, and a relatively high hardness and stiffness owing to the vegetable filler [1-3]. Products made from wood polymer composites (WPCs), which have been sold in the U.S.A. for over 30 years and in Europe for over a dozen years, have become well established on the world market because they have filled the gap between traditional raw materials and the expensive solutions of next-generation materials. WPC production, which totalled 1500 000 million tons in 2010, is rapidly growing and is likely to reach 5 million tons in 2015, according to predictions [4].

The increase in the price of wood and its wastes that has been recorded in recent years has made scientists and producers turn to plant raw materials whose price is not dependent on political or economic situations, as is the case for wood. Fibres used as a filler in natural fibre composites (NFCs) can be obtained from stems, leaves, fruits or all three elements together and from woody parts, seeds and husks. In the literature, we can find descriptions of composites filled with fragments of plants, such as cotton, jute, sisal, kenaf, bamboo, banana

tree, rice, sugar cane, corn, coconut tree, pineapple or ramia [5-8]. The properties of composites reinforced with plant fibres, along with health, environmental and financial concerns, support their use as substitutes not only for wood fibres but also for synthetic ones. Taking into consideration the two fundamental criteria of filler selection, i.e., availability and price, the use of waste biomass in the form of walnut shells from the food-processing industry seems well justified. The world's yearly walnut crop ranges between 1 200 000 and 1 500 000 tons, with China, the U.S.A, Iran, Turkey, Ukraine and Romania ranking among the largest producers [9]. According to Food and Agriculture Organization data, the U.S.A, Mexico and China are the leading exporters of shelled nuts, and the main importers are Spain, Italy and Germany; as for unshelled nuts, the main exporters are the U.S.A, Mexico and France [9]. The amount of shell waste generated in the sugar, bakery, cosmetic, pharmaceutical and distilling industries is difficult to estimate, but the shell is known to account for 45-75% of a nut's weight. This study assesses the possibility of physical modification of polymers with a plant filler. Polyethylene obtained from selective packaging waste collection was used as a matrix, while ground-to-flour walnut shells served as a filler. Within the framework of the study, mixtures were selected that permitted the production of composites suitable for construction applications and for use in the outer elements of buildings.

2 Materials and testing methods

2.1 Materials

For the matrix, a highly transparent white packaging foil was used that was made of high-density polyethylene (HDPE) by MARINK Co., which served as a substitute for packaging waste materials, while food-processing industry waste in the form of walnut shells (*Juglans regia species*) served as a filler. The shells were ground using a KSW3306 CLATRONIC grinder. The measured properties of HDPE show an MFR (190, 2,16) of 0,88 g/10 min.

2.2 Characterisation of the filler

The particle size distribution was defined via air stream sifting in conformity with the norm EN 933-10 [10], and the determination was performed at the Research Institute of Roads and Bridges.

2.3 Processing

The manufacturing process was run in two stages. In the first stage, the substrates were mixed, while in the second stage, the samples were shaped via injection. The composite components were mixed in a Farrel Bridge mixer from David Bridge and Co. The mixture was then rolled in an LWII roller from Veb Erste Maschinenfabrik at 120°C to ensure homogenisation. The obtained materials were crumbled with the use of an industrial mill. The obtained granular dumbbells were shaped into a standard form using a BOY 22A injector from the DR BOY company. During the injection moulding process, the temperatures in the individual cylinder zones ranged between 165 and 180°C, with an injection pressure of 950-1068 bar and a clamping pressure of 900-1068 bar. Descriptions of all the composite mixtures and the HDPE sample are listed in Table 1.

2.4 Characterisation of the composites

2.4.1 Physical properties

The density of the samples was fixed using a RADWAG 180/W scale equipped with a set for determining the solid body density in conformity with EN ISO 1183-1 [11]. The humidity content was estimated on the basis of the mass difference of the sample obtained during drying for several consecutive days at 103°C until a solid mass was formed, in conformity with ISO 16979 [12].

2.4.2 Mechanical properties

The Brinell hardness was determined in accordance with the norm EN 1534 [13] using the Vickers-Brinell tester from the VEB Werkzeugmaschinen-Kombinat "Fritz-Marx Stadt"

company. Because of the specificity of the equipment's design, the nominal load of 2884 N was achieved after only 3 s; for each type of material, 20 tests were carried out on average. The mechanical properties at static stretching were determined with the use of a Zwick Z005 in conformity with the norms EN ISO 527-1 [14] and EN ISO 527 [15]. Measurements were performed using an extensometer. The assumed length of the measured distance was 50 mm, while the stretching speed was 10 mm/min. The mechanical properties upon bending as a function of temperature were determined with the use of a TA-Instruments-DMA Q800. The examination was carried out with temperatures ranging between -100 and 120°C using a dual cantilever grip and a bending frequency of 1 Hz.

2.4.3 Swelling and water absorption
The swelling in the length, width and thickness and the absorption after immersion in water were calculated basing on the size difference and the mass of composites placed in water at room temperature for a period of 1, 2, 4, 7, 17 and 28 days. The examination was performed in conformity with the norm EN 317 [16].

2.4.4 Thermal properties
A thermogravimetric analysis (TGA) was carried out using a TA-Instruments-TGA Q500. Each of the materials was tested in an atmosphere of oxygen and nitrogen. During the analyses, gas flow rates of 30 ml/min in the chamber and 70 ml/min in the oven were used; the samples were heated up to 600ºC at the speed of 10ºC/min.

2.4.5 Morphological properties
Microscopic observations were performed with the use of a TM 3000 scanning electron microscope. Microstructure images were performed for composite sections sputter-coated with gold and palladium. A hundred-fold magnification was applied during the observation at an acceleration voltage of 15 kV.

3 Results and discussion
NFC properties, like those of WPCs, depend on the size of the filler's grains. Thus, the distribution of the size of the grains of the ground walnut shells was determined, as shown in Fig. 1. The obtained results make it possible to state that 80% of the particles of the applied filler have a grain size ranging between 32 and 420 µm.
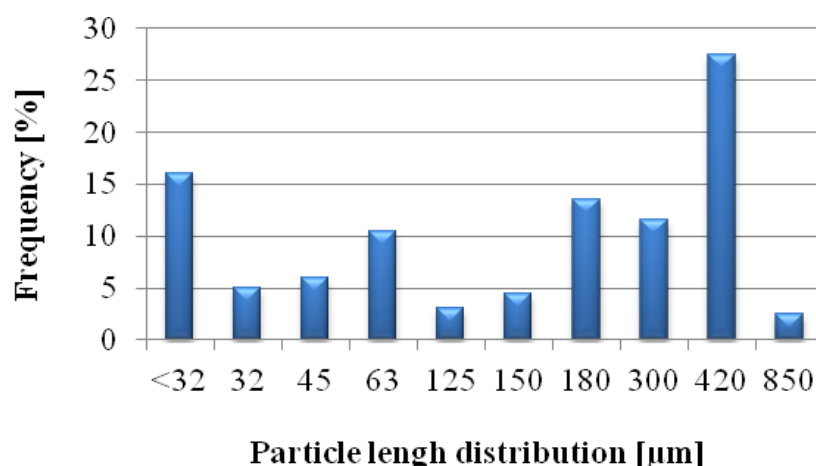

Figure 1. Particle size distribution of walnut shell flour

The low density of the used materials is essential in many applications, and so the influence of the amount of filler on the NFC density was estimated compared with the density of the applied HDPE (Tab. 1). The composite density ranges between 0.98 and 1.06 g/cm^3 and is

higher than the matrix density by only 4–13%, which qualifies the obtained NFCs as light materials.

As a result of the introduction of a hydrophilic filler into the hydrophobic matrix, there is trapped water in the filler of the obtained NFCs whose content is presented in Table 1. As in the case of density, the moisture content in all the composites grows along with the increasing amount of filler, reaching a max. of 1.68% in sample OW40. The introduction of some amount of water along with the natural filler is unavoidable, and its quantity depends on the filler type, origin and storage conditions; however; it should be kept in mind that the composites showing a high moisture content absorb more water while being used, which negatively affects their mechanical properties and durability [1].

Sample name	Filler portion, % mass	Density, g/cm^3	Moisture content, %	Hardness HB, kG/mm^2	E, GPa
HDPE	-	0,94 (0^a)	0 (0)	37 (2)	0,93 (0,08)
OW10	10	0,98 (0,001)	0,52 (0,02)	39 (2)	1,11 (0,062)
OW25	25	1,02 (0,01)	1,26 (0,02)	45 (3)	1,45 (0,159)
OW40	40	1,06 (0,013)	1,68 (0,05)	43 (4)	1,75 (0,085)

Table 1. List of compositions and the test results
[a] The values in parentheses are standard deviations.

Hardness values of the investigated materials are listed in Table 1. The nutshell flour filler increases the NFC hardness by 5–22%, depending on the participation of the plant filler. The highest value of the parameter was found in composite OW25; the introduction of larger amounts of the filler does not guarantee improved hardness.

Young's longitudinal modulus of elasticity (E), calculated from the ratio of the stress and the corresponding elongation [17], provides information on the material's stiffness. The used filler substantially increases the stiffness of composite materials, which linearly grows along with the increasing participation of the nutshell flour. In the composite with the highest share of the filler (OW40), an 89% increase in Young's modulus was recorded compared with the HDPE sample.
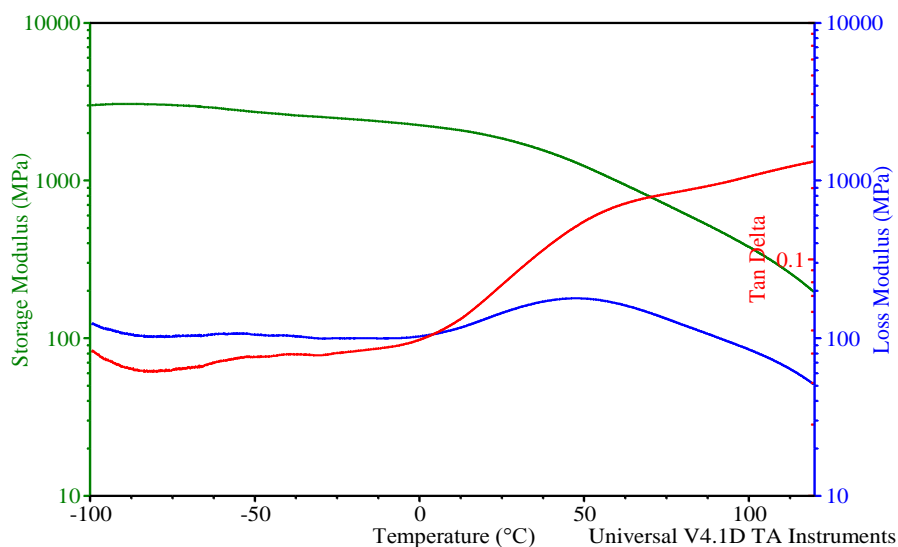

Figure 2. DMA cures of OW40 composite

A dynamic mechanical analysis (DMA) is carried out to define the physico-mechanical properties of plastics that condition the materials' reaction to vibrations that occur as the result of long-lasting and changeable in time strain during heating (Fig. 2). The examination makes it possible to determine the storage modulus E' for the energy absorbed and returned by the material by the elastic properties of the material, the loss modulus E'' showing a dispersed energy in the material (viscous properties) and the loss tangent tgδ, which is the ratio of the dispersed energy in the polymer in the form of heat to the max. elastic energy accumulated in the polymer during strain [18]. The examined materials were characterised using DMA, and the individual values read from thermograms for the selected temperatures are listed in Table 2.

Sample name	T_α [°C]	E' [MPa]		
		-30°C	20°C	50°C
HDPE	70	1715	1103	603
OW10	70	1917	1242	703
OW25	71	2270	1643	980
OW40	74	2532	1951	1232

Table 2. Specification of T_α and E' values determined for different temperatures of use

An analysis of the modulus E' value confirmed that adding natural fibres to a polymer increases the stiffness of NFCs. The storage modulus (E') grows along with the increase in the composite participation in the filler, e.g., the ambient temperature of E' in composite OW40 is 77% higher than the value determined for the HDPE sample. A determination of the peak T_β, corresponding to the relaxation of macroparticles during glass transition, is very difficult for some materials and is encumbered with considerable errors. In the literature, it has been stated that the determination of the transition β for HDPE, usually occurring at approximately -60–10°C, is quite often impossible [19]. The produced materials show transition T_β at -50°C. The transition temperature α – T_α, corresponding to melting of the crystalline phase in the matrix, exhibits higher values in composite materials than in the polyethylene itself. This behaviour is caused by the change of the matrix crystallisation course due to the application of a filler.

The examination of swelling and absorption is based on the determination of the percentage increase in the mass and size of samples subjected to water action for a given period of time. These results are especially useful for materials in applications in which water interaction may condition the stability and durability of the material. The results of absorption and the increase in length, width and thickness after 1 and 28 days of immersion in water are listed in Table 3.

Sample name	Water absorption, %		Length swelling, %		Width swelling, %		Thickness swelling, %	
	1 day	28 days	1 day	28 days	1 day	28 days	1 day	28 days
HDPE	0,0 (0[a])	0,0 (0)	0 (0,1)	0,2 (0,1)	0 (0,1)	0,4 (0,2)	0,1 (0,1)	1,4 (0,1)
OW10	0,0 (0)	0,3 (0)	0 (0)	0,3 (0)	0 (0)	0,4 (0)	0,1 (0,1)	2 (0,3)
OW25	0,1(0)	0,8 (0)	0 (0)	0,5 (0,1)	0,1 (0,1)	0,7 (0,1)	0,2 (0,2)	2 (0,4)
OW40	0,3(0)	1,1 (0)	0,1 (0)	0,5 (0)	0,1 (0,1)	0,5 (0,1)	0,2 (0,2)	2 (0,4)

Table 3. Swelling and water absorption of composites after 1 and 28 days of immersion
[a] The values in parentheses are standard deviations.

The combination of a hydrophilic filler and a hydrophobic matrix gives the obtained composite the ability to absorb water. Water penetration into the composite is possible

because of the pores present in the filler, empty spaces at the component boundaries and microfractures in the matrix, giving the materials a porous nature [20]. The amount of absorbed liquid is generally conditioned by the participation of the plant filler and the exposure time to water action. The highest mass increase of 1.1 % was recorded in sample OW40 following 28 days of immersion, which resulted in the change of sample size. The length and width of the sample grew by 0.5%, while the thickness grew by as much as 2%. The water absorption index for the produced NFCs following 24 h of exposure is similar to that in the composites manufactured from HDPE recyclate with 30, 40 and 50% wood flour that was additionally modified with an absorption-limiting additive, as presented in the paper of Adhikary et al [20]. It is worth mentioning that some changes in the size were also recorded in the pure polymer for which the absorption value was close to zero.

A thermogravimetric analysis was carried out to assess thermal stability of the materials. The analysis is based on the measurement of a sample mass subjected to the action of increasing temperature. Mass loss, recorded using an ultra-sensitive scale, is the result of chemical changes occurring in the material and the formation of degradation products [21]. Fig. 3 shows the thermographs of HDPE, composites and walnut shell flour.

The moisture content in the filler was 4%, while the per cent share of inorganic parts and dust, determined by an analysis of air, was greater than 3,5%. The temperature of the degradation process in OWD 10, carried out in an atmosphere of nitrogen, is approximately 300°C, while in an atmosphere of oxygen, it reached 250°C; the higher the filler share in the composite, the lower the temperature. The number of peaks read from the mass loss curves (DTD), indicating the speed of changes occurring in the material, provides indirect information about the degree of homogeneity of its constitution. For each composite and the filler itself, 4 peaks were observed on the DTG curves. The peak at approximately 230°C corresponding to lignin degradation [7] is notably visible only in walnut shell DTD. The peaks occurring at approximately 480°C, read from composite DTD and sample PE, correspond to chemical changes connected with polymer decomposition. The maxima in the region of 100°C correspond to water evaporation, those at 300°C correspond to hemicellulose decomposition and those of 350°C correspond to the decomposition of α-cellulose [7].
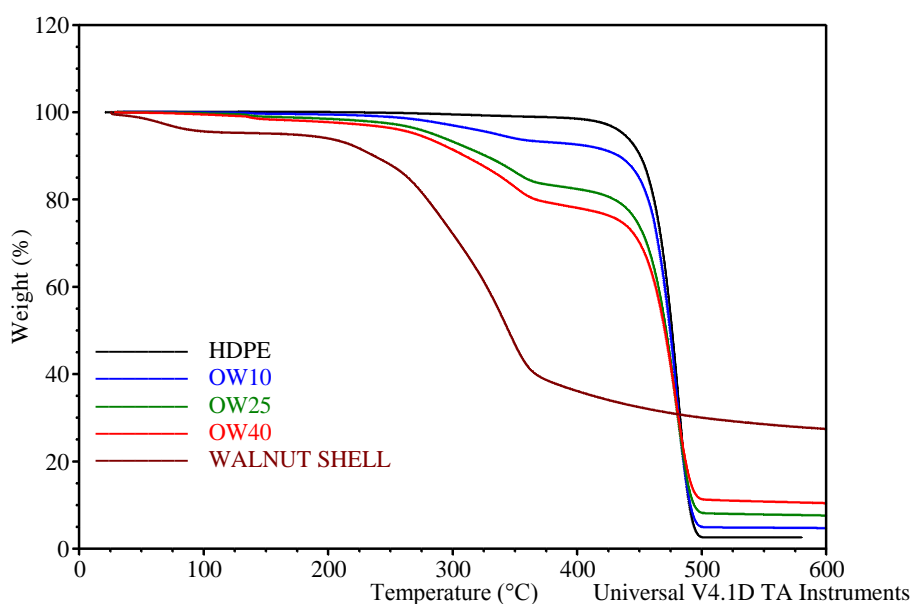

Figure 3. TGA curves of HDPE, composites and walnut shell flour

Microscopic observations made it possible to assess the homogeneity of the filler and also, indirectly, the wetting degree of the filler by the polyethylene matrix (Fig. 4).
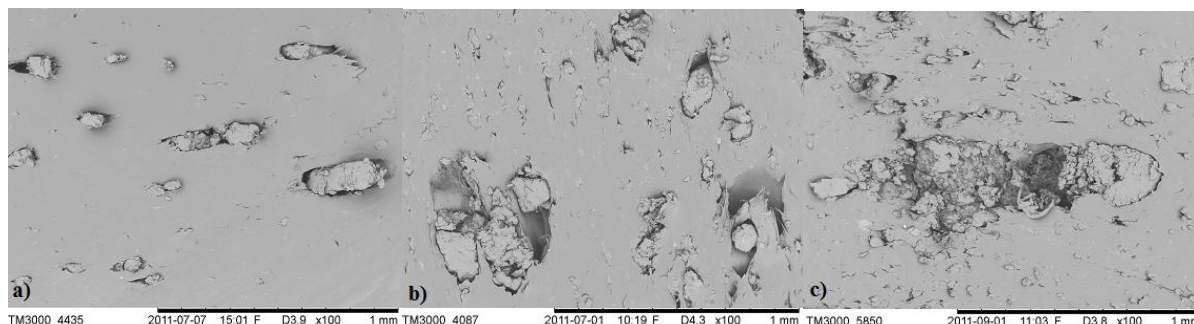

Figure 4. SEM imagines of composites a) OW10, b) OW25 and c) OW40

The analysis of the SEM images confirms the occurrence of filler particles of different sizes, and the increase in the filler's share is favourable to the formation of agglomerates. The presence of agglomerates and large particles limits the contact surface of the components and negatively affects the quality of their connection. The porosity of composites is conditioned not only by the pores present in the filler and the insufficient wetting of its surface by the polymer but also by the voids formed in the material during processing as the result of water evaporation. A decrease in the amount of water trapped in the filler is confirmed by the thermogravimetric analysis and the moisture content examination. A greater number of empty spaces in composites of a higher degree of filling not only worsens their mechanical properties, i.e., hardness, but also shortens their exploitation time due to the material's increasing absorptivity.

4 Conclusions

Within the framework of the study, a series of composites were produced with different shares of finely ground walnut shells. Waste raw materials were used for the preparation of the composites, and the preparation process was carried out with the use of the instruments and technologies applied in polymer processing. The produced materials contain no refining additives that could increase the price of the product or make its neutralisation more difficult.

The addition of the plant filler increases the hardness of the polymer matrix and considerably improves the stiffness of the composite. The density of the composite is simultaneously increased. The absorptivity of the described NFCs is comparable to that of natural-filled composites containing additives that slow down the swelling process. The thermal properties of the composites allow them to be safely used at the ambient temperature.

The prepared materials can be successfully used in the construction and furniture industries or as elements of road infrastructure and gardening architecture. The analysis performed on the investigation results makes it possible to state that commercial utilisation of this type of NFC most often occurs for mixtures with filler proportions of 25–40% wt. After use, the composites can be recycled or neutralised by burning for energy recovery.

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