THE INFLUENCE OF MALEIC ANHYDRIDE ADDITION ON THE MECHANICAL PROPERTIES OF PP/BUCKWHEAT HUSK COMPOSITES

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Abstract
Composites filled with 10, 30, 50% of buckwheat husk and wood flour were prepared by extrusion and injection moulding, equivalent samples with addition of compatibilizer (polypropylene-graft-maleic anhydride/MAPP) were prepared. Samples have been tested to obtain tensile strength, Young modulus, elongation at yield point and at break, during the static tension test. To evaluate the morphology of the composites the SEM images of the samples containing 10 and 50% filler were made. Despite the use of buckwheat husk the mechanical properties of the obtained composites are not worse than the reference samples made from wood-polymer composite. The structure of the husk filled material confirmed the effectiveness of the used maleic anhydride addition.

1. Introduction

The subject of presented work deals with the use of the natural filler obtained from the agri-food industry wastes as a reinforcement for polymer composites. Using of these composites provides a number of advantages. The combination of the thermoplastic matrix with the reinforcing phase is responsible for the increase in the flexural rigidity, low specific gravity of the filler allows to obtain composite with low density. Some of the fillers normally used for the preparation of natural fibers composites require expensive treatment to form fine flour suitable for processing, the proposed buckwheat waste in a form of husk reduces the costs associated with fibers preparation. In addition, the use of natural filler reduces the price of the finished material.

Buckwheat husk attributed to many health-promoting properties, and therefore is used as a filling for therapeutic mattresses and pillows. Husk absorbs moisture, does not heat up, and inhibits the growth of harmful organisms, i.e. mold, dust mites. A buckwheat husk characterized by a high content of hydrogen atoms and has a calorific value allowing its use as biofuel granular, pellets or briquettes, low sulfur content in the chemical composition makes the combustion not harmful to the environment.

The aim of the work is to prepare composite, develop the guidelines for processing and examine the characteristics of polypropylene-buckwheat husk composite. The standard WPC material obtained with the same processing methods was prepared as a reference composite. These studies also evaluate the impact of PP-graft-maleic anhydride (MAPP) addition.

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2. Experimental

2.1. Materials

The base polymer used in this study was isotactic polypropylene HP525J (Basell Orlen Polyolefins), the MFI rate of this resin was 3 g/10min (230°C/2,16kg), which makes that polymer suitable for injection molding. The main investigated filler was buckwheat husk (BH) obtained from the Polish cultivation. The supplied material is a waste product from the processing of buckwheat grains. Buckwheat husk can be characterized by dark brown color, irregular shape and intensive odor (Fig. 1). Preparing the filler for processing consists of grinding in high speed mill and drying for 24 hours in 80°C in cabinet dryer. The wood flour (WF) was used as a second referenced filler, the used material was Lignocel C120 (J. RETTENMAIER & SÖHNE GmbH) obtained from the conifer trees, the particle size range between 70-150 μm. The compatibilizer used during the tests was the Orevac CA100 (ARKEMA) which was the functionalized polypropylene-grafted-maleic anhydride (MAPP) induces polarity of polypropylene which enhanced the adhesion to fibers.

Figure 1. The buckwheat husk sheels before milling.

2.2. Composite preparation

Four types of samples was prepared for the study, first group was filled with buckwheat husk, second filled with wood flour and the corresponding samples with the addition of MAPP. To obtain the necessary samples all four types of composite mixtures were extruded and injection molded.
The first step of preparation consist of material milling was prepared using the high speed mill (Retsch ZM200), matrix polypropylene and natural filler were grinded separate. After that the matrix compound and the appropriate filler was mixed together using the rotational mixer (Retsch GM200). The concentration of natural filler was 10, 30 and 50% by weight. The received mixture was dried before next preparation step using the cabinet dryer, 24 hours at 80°C. In order to investigate the effect of the compatibilizer the polypropylene matrix was blended with the compatibilizer, the concentration of MAPP was 5%. The extrusion process was performed using the twin-screw extruder (ZAMAK EH16D), the extrudate was cooled in a water bath and granulated in a low-speed mill. The prepared pellets were dried before injection molding for 24hours in 80°C. The final shaping process was performed on the injection molding machine (ENGEL ES 80/20 HLS), two types of samples was prepared, dumpbell samples for mechanical tests and rectangular bars for flammability measurements.

2.3. Material characterization

The static tension test was conducted using the universal testing machine (INSTRON 4481) the measurements were performed according to ISO 527-2 standard. The used sample (Fig. 2) type was 1BA, test speed was 10 mm/min.

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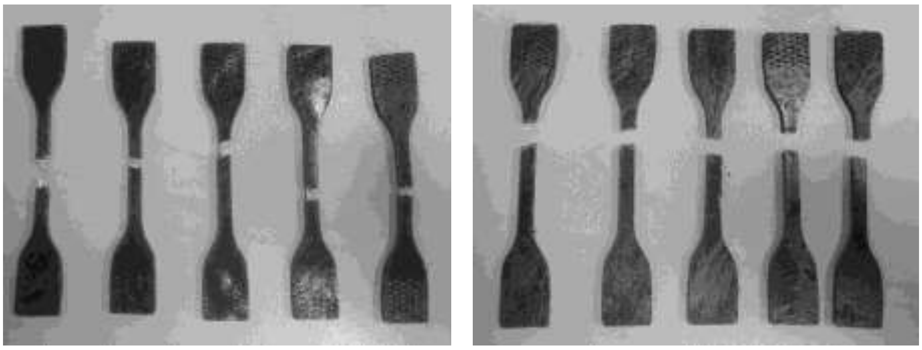

Figure 2. Dumpbell samples after static tensile test.

The microstructural analysis of the fracture surface of the composites was carried out using a scanning electron microscope - Carl Zeiss EVO 40. The samples were initially freeze-fractured under liquid nitrogen and then the fractured surface was coated with a fine layer of gold before observation. For the SEM investigation the samples with filler content 10 and 50% were selected, both with buckwheat husk and wood flour and corresponding samples with maleic anhydride.

3. Results

The results of mechanical test are collected in the Table 1. The results analysis relates mainly to the effectiveness of MAPP modification conducted for both fillers.

Table 1. Mechanical properties from static tension test.

Specimen Type	*Yield stress* (MPa)	*E modulus* (MPa)	*Elongation* (%)	*Elongation at break* (%)
Pure PP	36 ±4	1600 ±180	10 ±4	530 ±78
MAPP	31 ±5	1550 ±55	7 ±3	510 ±75
PP10WF	29 ±1,3	1730 ±175	4,8 ±0,45	43 ±20
PP30WF	26 ±0,5	2520 ±95	2,5 ±0,25	4 ±0,75
PP50WF	25 ±1,2	3050 ±345	1,8 ±0,2	2,5 ±0,4
MAPP10WF	32,5 ±0,8	1820 ±65	4,5 ±0,45	12,5 ±3,5
MAPP30WF	35,5 ±0,8	2190 ±235	3,5 ±0,3	5,5 ±0,5
MAPP50WF	38,5 ±1,0	2830 ±170	3 ±0,2	3,5 ±0,4
PP10BH	23 ±1,0	1365 ±60	5 ±0,5	11 ±0,6
PP30BH	18,5 ±0,8	1570 ±145	3 ±0,5	11,5 ±0,5
PP50BH	20 ±0,75	1690 ±175	2,5 ±0,35	4,5 ±1,0
MAPP10BH	30 ±0,5	1315 ±155	6,5 ±0,9	60 ±35
MAPP30BH	29 ±1,2	1620 ±195	3,5 ±0,2	5 ±1,0
MAPP50BH	36,5 ±3,5	2420 ±390	2,5 ±0,2	2,6 ±0,2

The tensile strength of unmodified samples filled with buckwheat husk decreases with the increasing content of the filler, for the husk content of 50% the decrease was approx. 40%. For samples modified with maleic anhydride the decrease of R_m was observed only for small filler contents, for the samples with the maximum 50% of filler the tensile strength was similar to pure PP. The tensile strength changes of the samples filled with wood flour are similar to the samples filled with buckwheat husk.

The improvement of Young modulus was observer for the samples containing 30% and 50% of both natural fillers. The results for the wood flour were significantly better, which can be explained by more fibrous morphology and smaller size of the wood particles. Nevertheless the reinforcing effect for the buckwheat husk composites was at very high level. The highest Young's modulus is obtained

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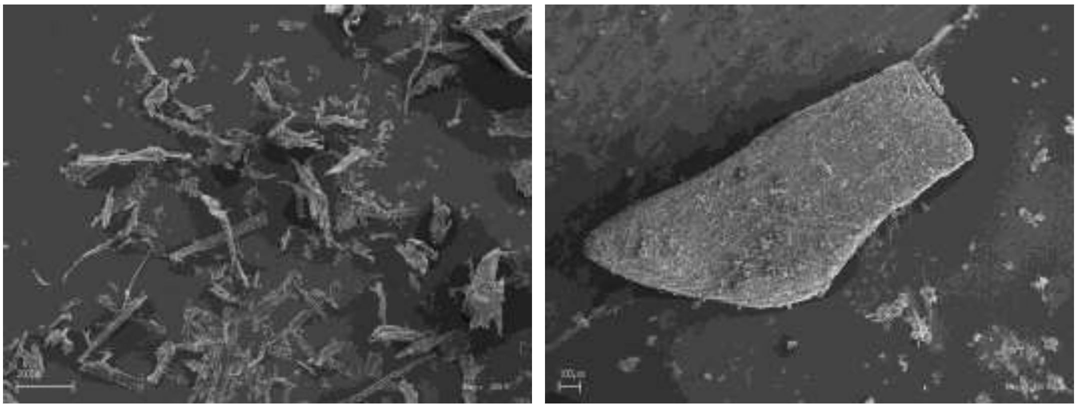
for the samples containing 50% of filler, for the buckwheat husk 2420 MPa (MAPP modified composite), for the wood flour the modulus reached 3050 MPa (unmodified composite).

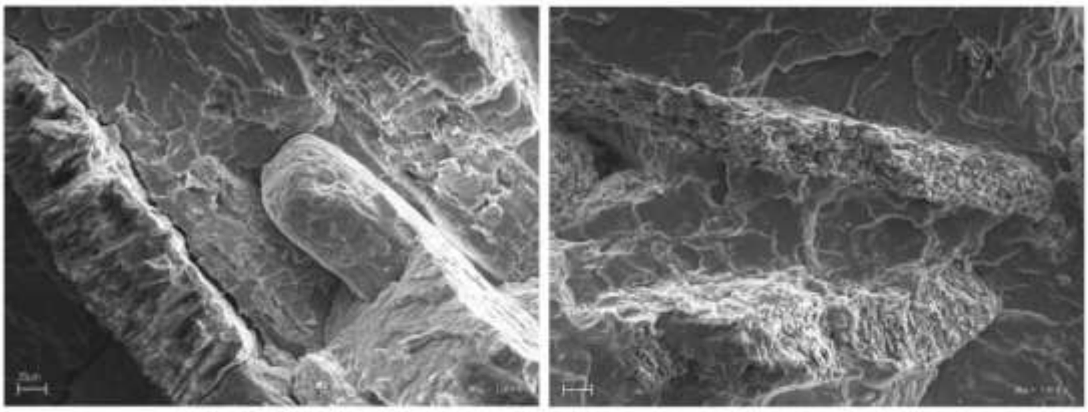
In the case of investigated materials the influence of small particle size for wood flour was the main reason of higher tensile strength and E modulus, but taking into account the increasing impact of MAPP modification on composites, the effectiveness of malec anhydride is higher for buckwheat husk filled materials.

SEM images of pure fillers (Fig. 3) show the big difference in the degree of fragmentation and particle morphology. Despite the use of high speed mill during the preparation the particle size of buckwheat husk varies from 0,5 to 2mm. The subject of further work should be the selection of more effective milling method.



Wood flour (WF) **Buckwheat husk (BH)**

Figure 3. SEM images of pure fillers, wood flour (left) and buckwheat husk (right).



PP+50%BH PP(MAPP)+50%BH

Figure 4. The comparison of injection molded samples, the unmodiefied composite (left) and MAPP modified structure of PP/buckwheat husk composite.

For the samples containing 10% of wood flour and buckwheat husk the impact of maleic anhydride is insignificant, more visible effect of growing wettability was observed for samples filled with 50% of husk (Fig. 4). On the SEM pictures of unmodified sample, the visible gap between husk surface and polymer matrix suggest the poor adhesion level causing the decrease of mechanical properties. The addition of maleic anhydride causes the radical change of the interphase appearance. The surface wettability increase, which leads to increase of the mechanical properties of the treated composite.

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3. Conclusions

Analysis of the results leads to the conclusion that the use of buckwheat as a polymer filler could be the promising application for management of that kind of food industry waste. The use of wood flour as a reference material allows to compare the properties of buckwheat husk composite with the conventionally used wood polymer composites. Results of static tensile tests show an improvement in rigidity of the material for both fillers, including the significant effect of modifications for the samples filled with buckwheat husk. Morphology of composites shown in the SEM images confirmed the influence of maleic anhydride on the wettability of interphase surface. The main conclusion of this work is that buckwheat husk could be used as a filler material for biocomposites. The presented results confirmed the possible use in injection molding technology.

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