EXPLOITATION OF HAZELNUT (*CORYLUS AVELLANA*) SHELL WASTE IN THE FORM OF POLYMER–PARTICLE BIOCOMPOSITE*

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Mechanically ground hazelnut (*Corylus avellana*) shells, a food industry by-product of hazelnuts processing, were tested for use as a composite material filler. Mechanical properties and fracture surface of the composite were evaluated using scanning electron microscopy. Polymer composites, i.e. resins filled with microparticles of hazelnut shells, were tested at various concentrations of the filler (5, 10, 20, 30, and 40 wt%). Hazelnut shell microparticles used at low concentration (5 wt%) increased tensile strength. The filler did not considerably influence hardness of the composite. Adhesive bond strength did not significantly change up to 20 wt%. The hazelnut shell microparticles were well wetted with the resin.

hazelnut shell microparticles, composite, *Corylus avellana*, strength, hardness

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INTRODUCTION

Composite materials based on polymers are a significant structural element. Polymeric materials gained their importance due to wide possibilities of mechanical, chemical, and biological modification (Slepicka et al., 2014). These materials are effectively used also in the area of connecting materials, i.e. in the adhesive bonding technology (Kahraman et al., 2008; Grant et al., 2009; Rudawska, 2012; Dadfar, Ghadami, 2013; Muller et al., 2013, 2015). Recent research has focused on the development of biological composites (matrix or reinforcement are of a biological essence). Namely composites with biological reinforcement based on natural fibres have currently been developed (Mizera et al., 2016; Ruggiero et al., 2016).

In some researches on biological materials microscopic analyses should be performed to inspect the structure of the tested materials (Synytsya et al., 2009, 2012). It is necessary to use technologies of the surface treatments, e.g. by means of plasma, in some cases of polymeric and biological materials (Slepicka et al., 2014; Jurik et al., 2017; Mizera et al., 2017; Muller et al., 2017).

A remarkable increase in the development of high environmentally friendly materials has been detected in the field of polymers and polymer composites. The high concern of the society about the environment protection has promoted the development of new 'eco', 'bio' or 'green' materials (Balart et al., 2016).

Designing new materials based on natural renewable resources is essential for both environmental and economic analyses (Valasek, 2015; Mizera et al., 2016). A natural based material can be defined as a product made from renewable agricultural and forestry feedstock, including crops and crop by-products and their residues (Koronis et al., 2013).

With regard to polymer composites, the use of natural reinforcements (fibres, particulates, flours) such

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as vegetable fibres (jute, hemp, flax, sisal, *Posidonia oceanica*, etc.) or lignocellulosic particles (sawdust, peanut shell, almond shell, rice husk, spend coffee ground, etc.) and other cellulose particles, contributes to obtain high environmentally friendly composite materials with new and attracting uses (B a l a r t et al., 2016).

The use of hazelnut kernels in the food production must meet important quality standards, which can be affected by the growing conditions, cultivar, harvest, storage, and roasting process (G i a c o s a et al., 2016). A hazelnut shell is a by-product of the food industry (B a l a r t et al., 2016). It is an industrial waste, so it is cost effective and upgrading, its exploitation is an interesting challenge. This filler can be ground to give a lignocellulosic flour that can provide the polymer composites with a wood-like appearance (B a l a r t et al., 2016). It can be used as the reinforcement/filler with a wide variety of polymeric matrices providing the materials with a wood-like appearance and thus contribute to forestry resources preservation (B a l a r t et al., 2016).

The paper follows up with researches focused on the exploitation of waste from hazelnut processing in the area of composite materials (M a t e j k a et al., 2013; B a l a r t et al., 2016).

The research results of Badano et al. (2010) proved that the use of low-cost materials (fillers) in the area of composite materials represented a relatively simple process. A mixed inorganic–organic structure which represents the synergic effect comes often into being (B a d a n o et al., 2010).

The aim of the research was to evaluate the applicability of hazelnut shell based microparticles as a filler of the structural two-component resin. Tests of the polymer–particle biocomposite based on the waste of hazelnut shells (*Corylus avellana*) were run and evaluated. The tests of tensile strength, hardness, and adhesive bond strength followed up with scanning electron microscopy (SEM). Evaluation were performed with the aim to study the differences in the composite material properties under various concentrations of hazelnut shells microparticles (5 to 40 wt%). The tests were chosen with an emphasis on a potential application area of the 'composite adhesive' based on a putty. The evaluation was performed according to normalized standards.

MATERIAL AND METHODS

Composite materials based on the biological reinforcement were used within the research. The structural two-component epoxy resin Lepox 1200 with the hardener P11 (Sincolor a.s., Zibohlavy, Czech Republic) served as a matrix. Microparticles of hazelnut shells served as the filler. The concentrations of the filler used within the research were 5, 10, 20, 30, and 40 wt%.

Filler preparation

The average mass of the shell (1.23 ± 0.23 g) was determined by a weight analysis (determination based on 100 values) of hazelnuts (hazel, *Corylus avellana*) cultivated in the Central Bohemian Region. The shell represents an essential part of the hazelnut, its mass constitutes ca. 52% of the hazelnut total weight. The shell represents a huge amount of waste in terms of the hazelnuts production (Figs. 1A, B). Exploiting these shells as a filler into the composite materials is one of possibilities of the material utilization. However, their treatment by grinding and fractionalization on sieves is necessary. Hazelnut shell waste was obtained from the food industry and subjected to a grinding process in an industrial grinder V3 (Taurus s.r.o., Chrudim, Czech Republic) to an average particle size of 200–300 μm to give a homogeneous flour (Fig. 1C). The particle

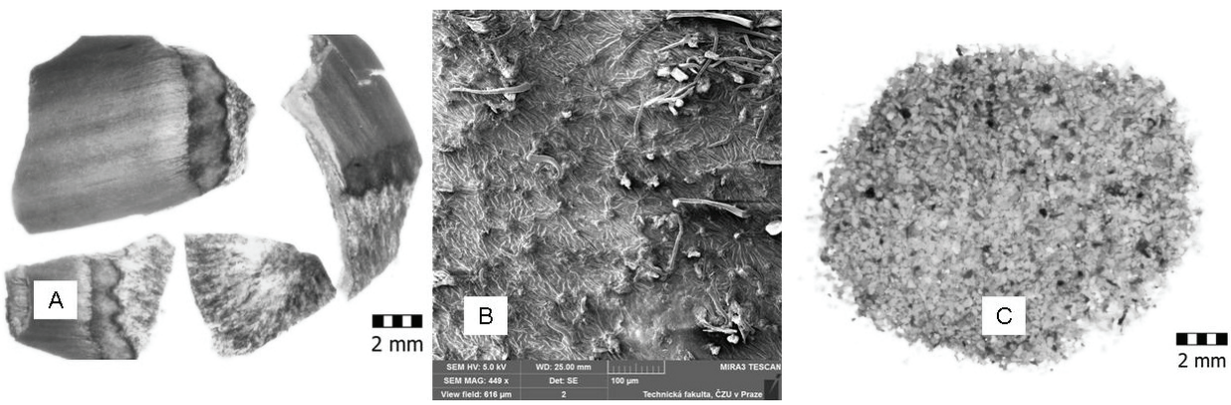

Fig. 1. Filler based on hazelnuts

(A) shell waste from hazelnuts processing, (B) SEM images (secondary electron) of hazelnut shell before grinding, magnification 449 x, (C) filler based on hazelnut shell microparticles

analysis was performed using a Haver EML digital plus analyser (Haver & Boecker, USA). Before application the hazelnut shell microparticles were dried at 105°C for 24 h. The test specimens were cast into the moulds prepared in advance from a two-component silicone rubber and they were hardened according to technological requirements of the resin producer. The composite mixture was applied on the place of the bonding at the overlapped bonds. The filler was mechanically blended with the resin before the casting.

Static tensile test

The test specimens for the tensile properties determination according to the standard CSN EN ISO 527-1 (Plastics – Determination of tensile properties – Part 1: General Principles) were prepared according to the standard CSN EN ISO 3167 (Plastics – Multipurpose test specimens, Czech Standard Institute). Tensile strength was the evaluated parameter. The test specimens were cast into the moulds from Lukapren N1522 (Lučební závody a.s., Kolín, Czech Republic) corresponding in shape and dimensions to the requirements of the standard. The universal tensile strength testing machine LABTest 5.50ST (Labortech s.r.o, Opava, Czech Republic) (sensing unit AST type KAF 50 kN, evaluating software Test&Motion) was used for the tensile strength determination. Loading speed at the destructive testing of the composite material corresponded to10 $mm.min^{-1}$.

Adhesive bond strength

This parameter was analysed to verify the composite mixture behaviour in the interaction with the adhesive bonded material. Laboratory tests were performed using the standardized test specimens made according to the standard CSN EN 1465 (dimensions 100 ± 0.25 × 25 ± 0.25 × 1.5 ± 0.1 mm and lapped length 12.5 ± 0.25 mm) from the structural carbon steel S235J0. The adhesive bonded surface was mechanically treated (grit blasted by Garnet MESH 80 (AWAC, spol. s.r.o, Praha, Czech Republic), fraction size 0.1–0.3 mm) and chemically treated (cleaned in acetone bath). The roughness parameters Ra (arithmetic mean of the absolute departures of the roughness profile from the mean line (in µm), which is universally recognized and most used, an international parameter of roughness) and Rz (average of the maximum peak-to-valley length of five consecutive sampling lengths (in µm)) measured on the surface of grit blasted adherents were: Ra = 1.70 ± 0.15 µm, Rz = 11.02 ± 0.97 µm. The roughness parameters were measured with a portable profilometer Mitutoyo Surftest 301 (Mitutoyo, Michigan, USA). A limit wavelength of the cut-off was set at 0.8 mm. Adhesive bonds were hardened at 22 ± 2°C for 72 ± 5 h.

A universal tensile strength testing machine LABTest 5.50ST (Labortech s.r.o., Opava, Czech Republic) (a sensing unit AST type KAF 50 kN, evaluating software Test&Motion) was used for the adhesive bond strength determination. The loading speed at the destructive testing of the composite adhesive bonds corresponded to 10 $mm.min^{-1}$. The fracture surface of the adhesive bonds was evaluated according to the standard ISO 10365.

Hardness

Hardness of the composite was measured according to the standard CSN EN ISO 2039 by means of a ball on a device Durajet G5 Rockwell Hardness tester (Struers Inc., USA). Loading force of an intender body (a small ball 5 mm in diameter) was 961 N (according to requirements of the standard). The intender body was pushed into the surface of the composite material by this loading force which resulted in a plastic deformation.

Fracture surface analysis

The fracture surfaces and the adhesive bond cut were examined with SEM using a microscope MIRA 3 (TESCAN, Czech Republic) at the accelerating voltage of the pack (HV) 5.0 kV. The samples were dusted with gold using a Q150R ES sputtering and carbon fibre coating system (Quorum Technologies, UK) (sputter current 20 mA, sputter time 60 s, tooling factor 1, gas bleed time 15 s, bleed vacuum 10 Pa, vent time 70 s, operational vacuum 10 Pa).

Statistical analysis

Statistical hypotheses were also tested at the measured datasets (*F*-test by STATISTICA software, Version

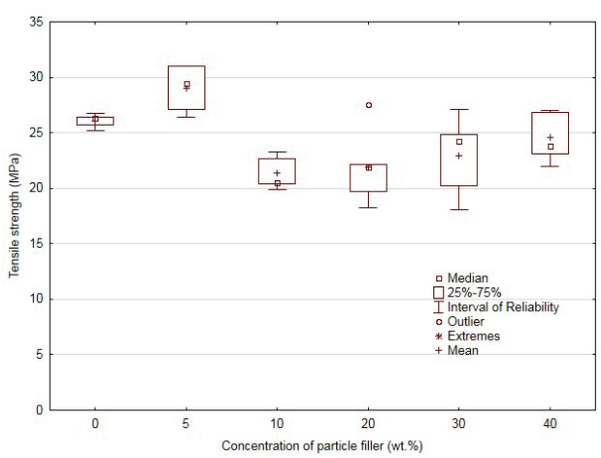

Fig. 2. Influence of concentrations of microparticle filler based on hazelnut shells on tensile strength

12). Validity of the zero hypothesis (H_0) shows there is no statistically significant difference ($P > 0.05$) between the tested datasets. On the contrary, the hypothesis H_1 denies the zero hypothesis and reveals a statistically significant difference between the tested datasets or a dependence among variables ($P < 0.05$).

RESULTS

The results of the hazelnut shell microparticles effect on tensile strength are shown in Fig. 2. Different microparticle concentrations obviously affect tensile strength at the significance level 0.05 ($P = 0.006$), i.e. the hypothesis H_1 is valid.

The experiment results proved a slight increase of tensile strength by the matrix filled with 5 wt% of hazelnut shell microparticles. Strength increased by ca. 11% compared with the matrix. This increase was significant in terms of statistical testing at the significance level 0.05 ($P = 0.0198$). A more significant tensile strength decrease (ca. 6–18 wt%) was registered at the concentration of 10 wt%. The concentrations from 10 to 40 wt% could not be regarded as significant in terms of statistical testing at the significance level 0.05 ($P = 0.3453$).

Fig. 3 shows the effects of the hazelnut shell microparticles filler concentration on hardness. It is obvious from the results that hardness is not affected by different filler concentrations. This conclusion was proved by the statistical evaluation at the significance level 0.05 ($P = 0.0727$), i.e. the hypothesis H_0 is valid. The experiment results proved a slight decrease (2.6–5.5%) in hardness of the composite material when filled with hazelnut shell microparticles.

Fig. 4 presents the results of the hazelnut shell microparticles filler effect on adhesive bonds strength. It is obvious from the results that adhesive bond strength is influenced by different concentrations of the filler ($P = 0.000$). The hypothesis H_0 was not confirmed at the significance level 0.05, the statistical hypothesis H_1 is valid.

The experiment results proved a significant reduction of adhesive bond strength from 30 wt% of the hazelnut shell microparticles filler. The adhesive bond strength decrease was in the interval 25–32%. The effect of the filler concentrations 0–20 wt% on resultant adhesive bond strength cannot be regarded as statistically significant ($P = 0.205$).

The failure type of the adhesive bonds was adhesive, i.e. the adhesive bond failed between the adhesive bonded material and the adhesive. The filler concentration did not change the fracture surface.

DISCUSSION

The research performed by B a l a r t et al. (2016) proved that strength and hardness of composites decreased by adding a filler based on hazelnut shell and a modifier. The filler volume was investigated up to ca. 22 wt%. This research came to analogous conclusions.

The SEM analysis was used to study the fracture surfaces morphology and display the quality of the interaction between the filler and the matrix. The fracture surface of the matrix is visible in Fig. 5A. It is a brittle material. The matrix fracture surface is distinguished for a smooth and homogeneous surface. The fracture propagation signs are visible on the surface. This propagation is stopped by the filler microparticles (Fig. 5C). Fig. 5B shows the used filler microparticles based on hazelnut shells. The microparticles size determined by the image analysis in the program Gwiddion was 231 ± 88 μm. The filler was distinguished for a high microparticles size variability (variation coefficient 38% based on 100 measurements). A reason for such a huge scattering was also the fact that the filler was difficult to separate. The filler was distinguished for

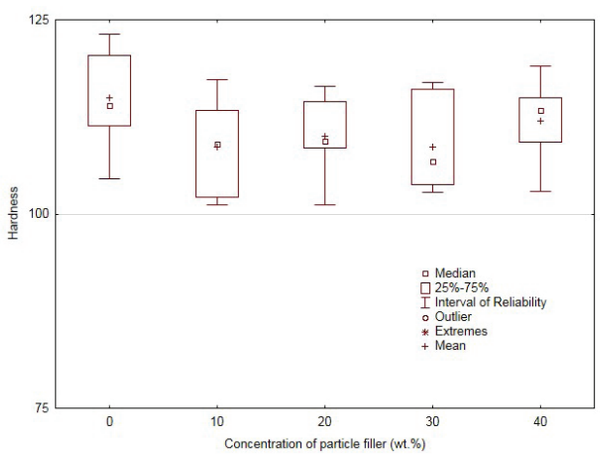

Fig. 3. Influence of filler concentration based on hazelnut shell microparticles on hardness

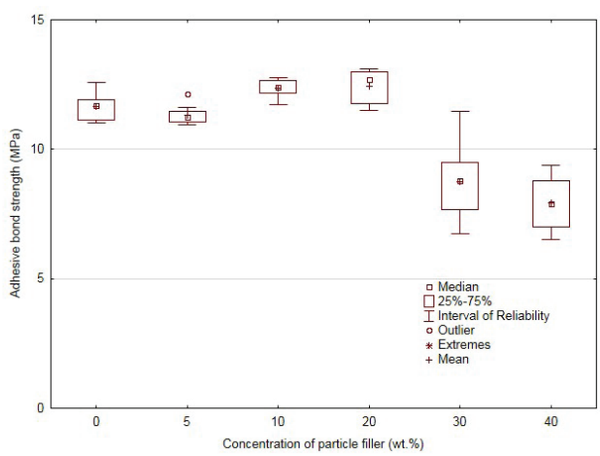

Fig. 4. Influence of filler concentration based on hazelnut shell microparticles on adhesive bond strength

clusters of particles. It was composed of individual wrinkle-shaped segments. Also Matejka et al. (2013) came to similar conclusions stating that the hazelnut powder caused a wrinkled character of the surface. The individual segments ascertained by the image analysis in the program Gwiddion measured 25 ± 7 μm. These segments showed a huge variability (28%), too.

The SEM analysis proved a good adhesion of the matrix and the filler (Fig. 5C, Fig. 6A). It testified about potentially good interactions. Wettability of adhesive bonded surfaces is essential for good adhesive strength (Comyn, 1990; Baker, Chester, 1992; Muller, 2011, 2015; Rudawska, 2012; Muller, Valasek, 2013).

The SEM inspection of the interface between the microparticle filler and the matrix revealed that the surface of the particles is optimally wetted (Fig. 6C). This state was reached without the filler treatment. When using a biological filler, namely fibres, its treatment is recommended (Nechwatal et al., 2003; Herrera-Franco, Valadez-Gonzalez, 2005; Boruvka et al., 2016).

The SEM analysis proved a destruction of the filler at loading (Fig. 6B). This state was distinguished for tearing a greater part of the filler microparticles. Cohesive strength of the particles was in this case higher than adhesive strength of the filler and the matrix, resulting in the destruction at their boundary. Fig. 6C is the opposite case where the filler microparticles were of smaller cohesive strength than the adhesive. The destruction of the filler particles occurred. The maximum transfer of the loading between the matrix and the filler was secured by this. It was obvious from the fracture surface that the upper layer of the filler remained on the surface of the matrix. It is obvious from Fig. 6C that the structure of the filler is composed

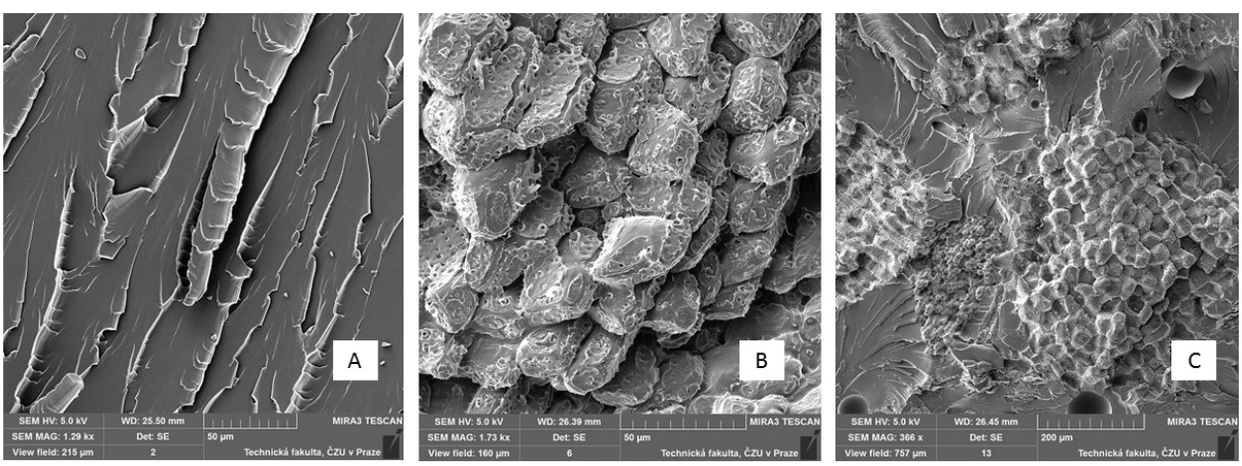

Fig. 5. SEM images (secondary electron)
(A) fracture surface of matrix (resin), magnification 1.29 kx, (B) microparticles of filler based on hazelnut shells, magnification 1.73 kx, (C) polymer particle composite with concentration 40 wt% of hazelnut shell filler, magnification 366 x

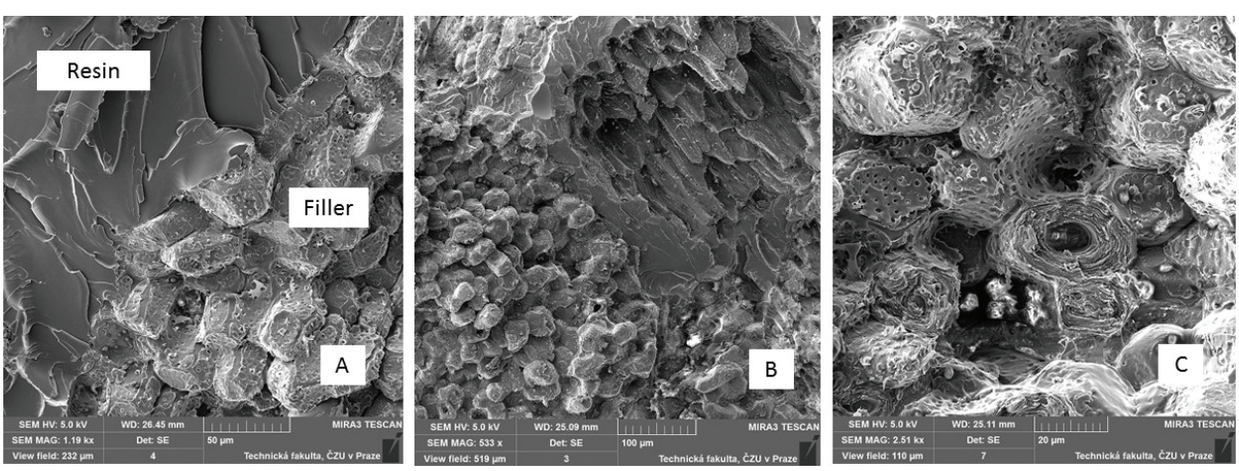

Fig. 6. SEM images (secondary electron)
(A) good wettability of filler with matrix, magnification 1.19 kx, (B) interaction of filler and matrix – filler torn from matrix, magnification 533 x, (C) morphology of filler and destruction of one element, magnification 2.51 kx

of individual layers which are grouped symmetrically around its hollow centre (Fig. 6C). One destroyed segment of the filler microparticles and the structure of the filler are visible in the central part of Fig. 6C. This state leads to the decrease of the loading transfer between the reinforcement (the filler) and the matrix.

CONCLUSION

The paper deals with the utilization of waste from food industry, namely hazelnut shells – a by-product at gaining hazelnut kernels. The experiment results proved the possibility to utilize this waste in the area of polymer–particle composites.

It can be concluded that a low concentration of the filler based on hazelnut shell microparticles (5 wt%) increases tensile strength. Higher concentrations of the filler decrease tensile strength by ca. 18%. Furthermore, an increasing concentration of the filler based on hazelnut shell microparticles did not significantly influence hardness of the tested material. Hazelnut shell microparticles showed to be an effective filler in the area of adhesive bonds. No significant changes of adhesive bond strength appeared compared to the resin until 20 wt%. Last, the SEM analysis proved a good wettability of the filler based on hazelnut shell microparticles. The tests and resulting analyses will serve for optimizing the composite material based on the waste of hazelnut shell (*Corylus avellana*).

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