Composite adhesive bonds reinforced with microparticle filler based on egg shell waste

Miroslav Müller 1, Petr Valášek 1
1Czech University of Life Sciences Prague, Faculty of Engineering, Department of Material Science and Manufacturing Technology, Kamýcká 129, Prague, Czech Republic

E-mail: muller@tf.czu.cz

Abstract. A research on composite adhesive bonds reinforced with waste from hen eggs processing, i.e. egg shell waste (ESW) is based on an assumption of the utilization of agricultural/food production waste. The aim of the research is to gain new pieces of knowledge about the material utilization of ESW, i.e. to evaluate possibilities of the use of various concentrations of ESW microparticles smaller than 100 µm based on hen egg shells as the filler in a structural resin used for a creation of adhesive bonds from bearing metal elements. An adhesive bond strength, an elongation at break and a fracture surface were evaluated within the research on adhesive bonds. The experiment results proved the efficiency of ESW filler in the area of composite adhesive bonds. The adhesive bond strength was increased up of more than 17 % by adding 40 wt.% of ESW microparticles.

1. Introduction
The research focusing on the utilization of fillers based on renewable resources is essential. Renewable resources are a suitable material for a substitution of synthetic materials /fillers [1, 2, 3, 4, 5]. The production of waste where also secondary products /waste can be ranked in many cases is a worldwide topic – many secondary materials are burnt or otherwise liquidated without a possibility of alternative handling [1, 3]. The utilization of natural reinforcement leads to a reduction of a mass and a prices of single parts and to an optimization of mechanical properties [1, 2, 3]. A meaningful utilization of secondary materials /waste as the material utilization is an economic and environmental alternative to other handling possibilities or to a liquidation [1, 2, 3, 6, 7, 8]. The research used to be focused on particle and fibre composite materials above all. An area of structural adhesive bonds is one of prospective possibilities of a practical utilization of particle nano and micro filler, fibres in composite materials [9, 10, 11].

The research deals with the utilization of a by-product from the food industry, namely waste coming into being at processing hen eggs. The production of hen eggs on an industrial level leads to an essential amount of shells which are regarded as the waste or they are used as a supplement in the agriculture [12]. Generally it can be said that the egg shells are of no economic value [13]. However, they are rich of minerals. This material can be regarded as a source of the calcium filler [14]. Many studies proved their positive influence as an ingredient in various products [13]. It has been demonstrated that using low-cost materials and a relatively simple process complex supports with a mixed inorganic–organic structure can be synthesized [15].

About several hundred thousand tons of egg shell waste come into being at the industrial processing of eggs. Egg shells represent ca. 11 % of total mass of eggs and they are available as the
waste in huge amounts namely in food industry [13]. Egg shell waste is potentially suitable candidate for an ecological filler material for reinforced biopolymeric composites owing to improving their mechanical properties and a heat stability [13]. E.g. Zieleneiwska et al. dealt with the composite materials based on polyurethane foam with egg shells used as the natural filler [13]. They dealt with a determination of the filler content on a structure of the material and mechanical properties.

The aim of the research is to gain new pieces of knowledge about material utilization of ESW, i.e. to evaluate possibilities of the use of various concentrations of ESW microparticles smaller than 100 \( \mu m \) based on hen egg shells as the filler in the structural resin used for creating adhesive bonds from bearing metal elements. The paper deals with the utilization of a by-product from the food industry, namely waste coming into being at processing hen eggs, i.e. egg shells waste effectively usable as the microparticle filler in the area of composite adhesive bonds. An adhesive bond strength, an elongation at break and a fracture surface were evaluated within the research on adhesive bonds. A scanning electron microscopy (SEM) was used for a description of an interaction of ESW filler and a resin.

2. Materials and Methods

Microparticles in a form of egg shell waste (ESW) were used within the research. ESW was obtained from the food industry and dried for the time 24 h at the temperature 105 ± 5 °C. Subsequently, ESW was grind in an industrial grinder. A fractionalisation was performed on sieves with a mesh size 100 \( \mu m \). The particle analysis was performed at the device Haver EML digital plus. The fraction with the smallest particles, i.e. in the interval 0 to 100 \( \mu m \) was used for the research. The egg shell microparticles were dried before the application to the resin at the temperature 105° C for the time 24 h. Composite adhesive bonds were the subject of performed experiments. The structural carbon steel S235JO was the adhesive bonded material. A layer of the adhesive mixture, i.e. the adhesive was composite, i.e. the continuous phase was in a form of structural two-component epoxy resin CHS EPOXY 324 epoxy 1200 (a matrix / resin – marked as 0 wt.%). Microparticles of ESW were the discontinuous phase (reinforcing particles).

Adhesive bonds were prepared in accordance with the standard ČSN EN 1465, i.e. laboratory tests were performed using the standardized test specimens of dimensions 100 ± 0.25 x 25 ± 0.25 x 1.5 ± 0.1 mm and lapped length of 12.5 ± 0.25 mm. The adhesive bonded surface of the carbon steel was mechanically treated – grit blasted by Garnet MESH 80 and chemically treated – cleaned in the acetone bath. Roughness parameters were measured with a portable profilometer Mitutoyo Surftest 301. A limit wavelength of the cut-off was set as 0.8 mm. The surface roughness at the grit blasted adhesive bonded material, i.e. the structural carbon steel S235JO was Ra = 1.75 ± 0.19 \( \mu m \), Rz 11.42 ± 0.87 \( \mu m \).

The composite adhesive was prepared by adding the filler based on ESW microparticles in 10, 20, 30 and 40 wt.%. The matrix is mid-molecular resin consisted of bisphenol A and epichlorhydrin (an average molecular mass < 700). P11 was the hardener containing amines, polyethylenopoly, triethylentetramine fraction. The composite adhesive was prepared by mixing of the resin and the filler in the form of ESW microparticles for the time 10 min. This step was performed owing to the short time of the adhesive mixture processing and a necessity of a sufficient homogenisation of prepared mixture of the filler and the resin. Subsequently, the hardener P 11 was added. Subsequently, the composite adhesive was deposited on the prepared surface of the structural carbon steel S235JO. Adhesive bonds were hardened for 72 ± 5 h with a temperature 22 ± 2°C. Adhesive bonds were fixed with the weight of 750 g.

Mechanical characteristics of adhesive bonds based on the composite adhesive were performed by means of the universal tensile strength testing machine LABTest 5.50ST (a sensing unit AST type KAF 50 kN, an evaluating software Test&Motion). A loading speed of a deformation corresponded to 5 mm.min\(^{-1}\).

A scanning electron microscopy (SEM) was used for a description of the interaction of ESW filler and the resin. The measurement was performed on the scanning electron microscope TESCAN MIRA 3 GMX. SE and BSE detector were used for the measurement, the accelerating voltage was 5 kV and the working distance was ca. 15 mm. The samples were dusted with gold by means of the equipment
Quorum Q150R ES - Sputtering Deposition Rate using Gold. SEM analysis helps to understand results of mechanical tests. Measured values were processed by means of statistical analysis methods. ANOVA test was used for the statistical comparison of measured data.

3. Results and Discussion

Results of the adhesive bond strength are visible in fig. 1 A. It is obvious from the results that the adhesive bond strength was increased by adding ESW microparticle filler. The adhesive bond strength was gradually increased with increasing wt.% concentration of ESW microparticle filler, namely up of 17.84 % Higher concentration than 40 wt.% was not possible to create. The structural epoxy resin was saturated with the hardener P11. It is possible to say in terms of the statistical testing of the influence of ESW microparticle concentration by means of ANOVA F-test in the significance level 0.05 that the concentrations are statistically non-homogeneous groups (p = 0.0001), i.e. there is the difference in the resultant adhesive bond strength among single tested concentrations. It is obvious from the results that different concentrations influence the adhesive bond strength.

Results of the elongation at break of adhesive bonds are visible in fig. 1 B. It is obvious from the results that the elongation at break of the adhesive bond did not change by adding the ESW microparticle filler. The elongation at break of the adhesive bond was increased with increasing wt.% concentration of ESW, namely up of 13.3 %, it is true, but a dispersion of results was increased from 8.5 % (the resin – 0 wt.% filler) to the interval from 8 to 17 % depending on the concentration of ESW microparticle filler. It is possible to say in terms of the statistical testing of the influence of ESW microparticle filler by means of ANOVA F-test that the concentrations are statistically homogeneous groups (p = 0.0777) in the significance level 0.05, i.e. there is no difference in the resultant elongation at break of adhesive bonds among single tested concentrations. It is obvious from the results that different concentrations do not influence the elongation at break of the adhesive bond.

![Figure 1. Results of experiment: A: Influence of concentrations of ESW microparticle filler on adhesive bond strength, B: Influence of concentrations of ESW microparticle filler on elongation at break of adhesive bond.](image)

A fracture surface of the matrix (the resin – 0 wt.% filler) and the composite bond with 10 wt.% of ESW microfiller was of an adhesive type, i.e. it came to a destruction in the interface of the layer of the adhesive and the adhesive bonded material. The fracture surface changed to the adhesive / cohesive by adding ESW microparticles of the concentration 20 to 40 wt.%. Results of SEM analysis proved the change of the fracture surface (fig. 2). It is evident from fig. 2 B different distribution of ESW microparticles in the constant layer of the adhesive. A detailed view on the interaction between the microparticle filler based on the ESW and the resin is visible from fig. 2. A good wettability is visible from fig. 2 B, C in the layer of the adhesive. SEM analysis proved a good dispersion of the filler in the matrix (fig. 2). Also Krishnan et al. came to similar conclusions [16]. A shape of ESW microparticles is visible from fig. 2. It is evident from fig. 2 that ESW is of very porous structure. A
bad wettability and a non-homogeneity of the natural fillers utilized in the polymeric composites belong among main disadvantages of their use [2, 8]. However, this was not proved.

Figure 2. SEM images of fracture surface of adhesive layer: A: distribution of ESW microparticles – composite layer of adhesive - 30 wt.% ESW (MAG 267 x), B: composite layer of adhesive - 40 wt.% ESW (MAG 4.64 kx), C: composite layer of adhesive - 40 wt.% ESW – detailed view on porous structure of microparticle (MAG 15.8 kx).

Egg shells contain about 95% of calcium carbonate (calcite) and 5% of organic materials such as sulphated polysaccharides, type X collagen and other proteins [13]. Filling of thermoplastics by the calcium carbonate is used in the practice when this filler improves mechanical properties [12]. A positive effect of the filler based on egg shell microparticles in the area of the composite materials is visible from the research results of Zieleniewska et al. Also results of there experiments confirmed this fact [13]. The small particle size aids in a uniform stress transfer between the filler and the matrix, thereby resulting in a composite with superior mechanical performance [17].

4. Summary
The paper described a possible utilization of ESW microparticles, i.e. the secondary raw materials from eggs processing in the food industry, in the area of the composite adhesive bonds. It is desirable to incorporate renewable resources or waste from animal production in the material engineering. The experiment results proved the efficiency of ESW filler in the area of the composite adhesive bonds. Following conclusions can be stated from the results of the experiment using the natural filler based on ESW microparticles:
• The adhesive bond strength is increasing with increasing concentration of ESW microparticles.
• The elongation at break of the adhesive bond does not significantly change with adding ESW microparticles.
• ESW microparticle filler proved good wettability with the matrix, i.e. the resin based on SEM analysis.

5. References
[1] Ruggiero A, Valášek P and Müller M 2016 Compos Part B – Eng. 104 pp 9–16
[2] Mizera Č, Herák D, Hrabě P, Müller M and Kabutey A 2017 Journal of Natural Fibers 14 pp 287–296
[3] Müller M, Valášek P and Ruggiero A 2017 BioResources 12 pp 255–269
[4] Amuthakkannan P, Manikandan V, Winowlin Jappes J T and Uthayakumar M 2013 Materials Physics and Mechanics 16 pp 107–117
[5] Faruk O, Bledzki A K, Fink H P and Sain M 2012 Progress in Polymer Science 37 pp 1552–1596
[6] Valášek P, Ruggiero A and Müller M 2017 Compos Part B: Eng. 122 pp 79–88
[7] Valášek P and Müller M 2015 Tehnicki Vjesnik 22 pp 257–262
[8] Herrera-Franco P J and Valadez-Gonzalez A 2005 Compos: Part B. Eng. 36 pp 597–608
[9] Müller M, Valášek P and Rudawska A 2017 Journal of Adhesion Science and Technology 31 pp 1859–1871
[10] Müller M 2015 Agronomy Research 13 pp 700–708
[11] Müller M, D´Armato R and Rudawska A 2017 16th International Scientific Conference Engineering for Rural Development. Jelgava 24-25.6.2017 Latvia pp 121–127
[12] Petrášek P and Müller M 2017 16th International Scientific Conference Engineering for Rural Development. Jelgava 24-25.6.2017 Latvia pp 175–180
[13] Zieleniewska M, Leszczynski K M, Szczepkowski L, Bryskiewicz A, Krzyzowska M, Bien K and Ryszkowska J 2016 Polymer Degradation and Stability 132 pp 78–86
[14] Oliveira D A, Benelli P and Amante E R 2013 Journal of Cleaner Production 46 pp 42–47
[15] Badanoa J M, Betti C, Rintoulb I, Vich-Berlanga J, Cagnola E, Torres G, Vera C, Yori J and Quiroga M 2010 Applied Catalysis A: General. 390 pp 166–174
[16] Krishnan A, Iyer A and Torkelson JM 2014 Composites Science and Technology 102 pp 152–160
[17] Cheung H Y, Ho M P, Lau K T, Cardona F and Hui D 2009 Composites: Part B. 40 pp 655-663

Acknowledgments
Supported by Internal grant agency of Faculty of Engineering, Czech University of Life Sciences Prague no. 2017:31140/1312/313115.