Mechanical Properties of Polymeric Composite Based on Pine Seeds Production Residues

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An aim of the research is mechanical properties evaluation of the polymeric particulate composite based on the pine seeds production residues, i.e. the pinecones. Current trends in composite materials field are a substitution of synthetic fillers by biological fillers. An adhesive modification by biological fillers can improve its mechanical properties and reduce cost, which reduces total costs for composite system production. The polymeric adhesive was modified by the filler with concentration 30 wt. % and tested on mechanical properties i.e. the tensile strength, the elongation at break, the hardness and the impact strength. Results of the statistical analysis proved significant difference between measured values *(p <0.05)*. The mechanical properties were influenced by homogeneity of the composite system i.e. by adding the biological filler. The tensile strength of the composite was increased up to 10.95 % and the hardness was increased up to 44.94 %. For better understanding of the mechanical properties the electron microscopy (SEM analyses) was used.

Keywords: tensile strength, elongation at break, hardness, impact strength, SEM

1 Introduction

Primary sources saving has been currently main subject in the material engineering field. These primary sources are gradually replaced by secondary sources i.e. based on a biological material [1, 2]. A composite system is a promising area for using these materials [3, 4, 5, 6].

Particles or fibres can be used as fillers in the composite systems. Modification of an adhesive by fillers based on biological materials can improve the mechanical properties and reduce the cost of the adhesive. The most important factors that influence the mechanical properties of a particulate composite include size and concetration of particles [7, 8, 9, 10].

The growing use of forest resources has been adversely affected by the growing population. One of these items are the pinecones that are collected and dried for release of the seeds and burnt in the end. For this reason, the pinecone can act an important role in the polymericic composite production with the filler based on biologic materials [11]. The pinecones contain lignin, cellulose and hemicellulose, which give hydrophilic character of the pinecones [12] and can inhibit weak cohesion between the polymeric matrix and the filler.

Some researches dealt with the mechanical properties of the polymeric composite based on the pine seeds production residues, i.e. the pinecones. Arrakhiz et al., Baştürk et al. and Pérez-Fonseca et al. have found that they improved the mechanical properties by adding the filler from the pinecones in particles form [13, 14, 15].

An aim of the research is the evaluation of the mechanical properties i.e. tensile strength, elongation at break, hardness and impact strength of the polymeric particulate composite based on the pine seeds production residues. This aim corresponding with application of the composite materials used as a look surface in the furniture industry.

2 Material and Methods

The matrix was the low-viscosity epoxy resin LH 288 with viscosity 500-900 mPa.s/25 °C and hardener H 282 with viscosity 4-15 mPa.s/25 °C from the company Havel Composites CZ s.r.o. Preparation of the filler was following: Residues from pine seeds production, i.e. pinecones, were dried in a chamber dryer with an air circulation at the temperature 105 ± 5 °C for the time 24 h. The mass loss was stopped after this drying and it was possible to proceed to multi-stage crushing and fractionalisation on sieves. The filler was the pinecones production residues in the microparticle form of the size 44.89 ± 23.94 μm and the microfibre form with the diameter 28.74 ± 13.75 μm and the length 710.49 ± 154.00 μm. The dimensions of used filler were measured by Gwyddion programme from images gained by SEM analysis. ze snímků získaných SEM analýzou.

The SEM images (Fig. 1) present the fillers in the microfibre form (Fig. 1A) and microparticle form (Fig. 1B). From the Fig. 1C the surface texture of the microfibre filler is evident. The filler added in the matrix contained microparticles and microfibres.

The composite plate was made by the vacuum infusion method (Fig. 2). The vacuum pump was with flow 16 m3.h-1 and maximum vacuum 2 mbar. Subsequently a preparation of moulds for the composite plate production and vacuum sealing of the plate space was performed. The composite plate production at vacuum with dimensions 300 x 400 x 4 mm. Adding the filler with concentration 30 wt.%. The testing samples production was performed by cutting of the composite plate by the abrasive water jet method (AWJ) on the machine AWAC CT 0806. The testing samples for tensile test were made according ČSN EN ISO 3167 (Fig. 2). The conditions for hardness measurements and tensile test were following: the temperature 21 ± 2 °C and 60% relative humidity

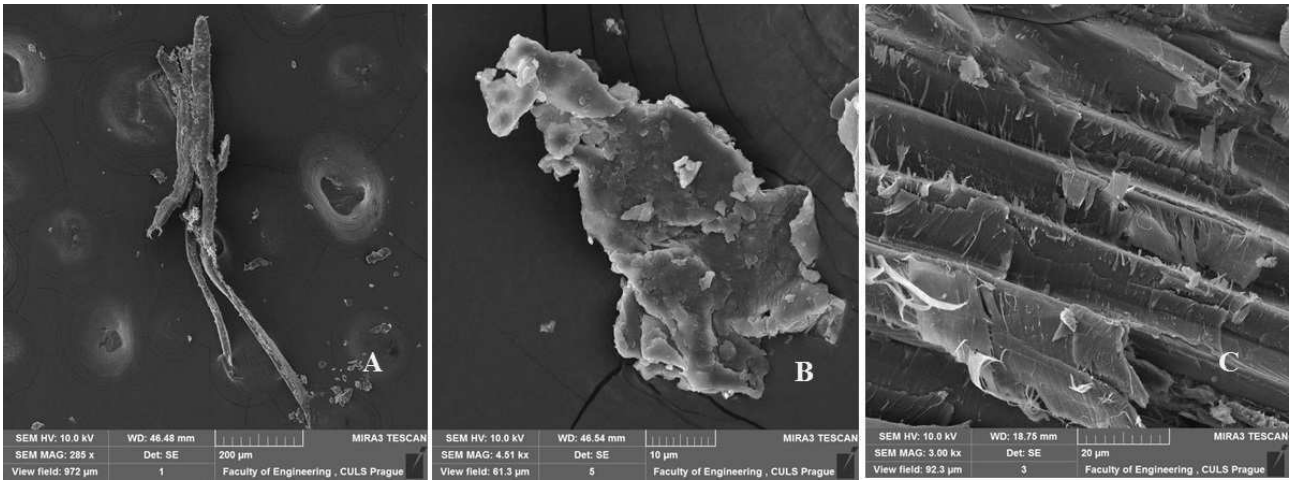

Fig. 1 *SEM images of filler for composite: A: filler in microfibre form (MAG 285 x, SE), B: filler in microparticle form (MAG 4.51 kx, SE), C: detail surface of microfibre filler (MAG 3.00 kx, SE)*

Devices used for the mechanical properties testing:

- The tensile test – the universal testing machine LABTest 5.50ST with measuring unit AST KAF 50 kN and software Test & Motion for the test evaluation; the loading speed was set to 3 $mm.min^{-1}$.
- The hardness test – testing of the polymeric materials according to ČSN EN ISO 2039-1 "Plastic – determination of hardness – Part 1: Ball indentation method". Ball for test with diameter 5 mm, force load 358 N, loading time 30 s.
- The test of impact strength – Dynstat according to ČSN 64 0611.

Evaluation of the results:

- Evaluation of the measured values with the programme STATISTICA by ANOVA F-test, i.e. hypothesis H_0 presents the statistical nonsignificant difference between the measured values *($p>0.05$)* and hypothesis H_1 presents a rejection of the hypothesis H_0, i.e. statistically significant difference between measured values *($p<0.05$)*.
- The technology of electron microscopy (SEM) was used for fracture surface evaluation by electron microscope MIRA 3 TESCAN; tested samples were powdered by gold by device Quorum Q150R ES.

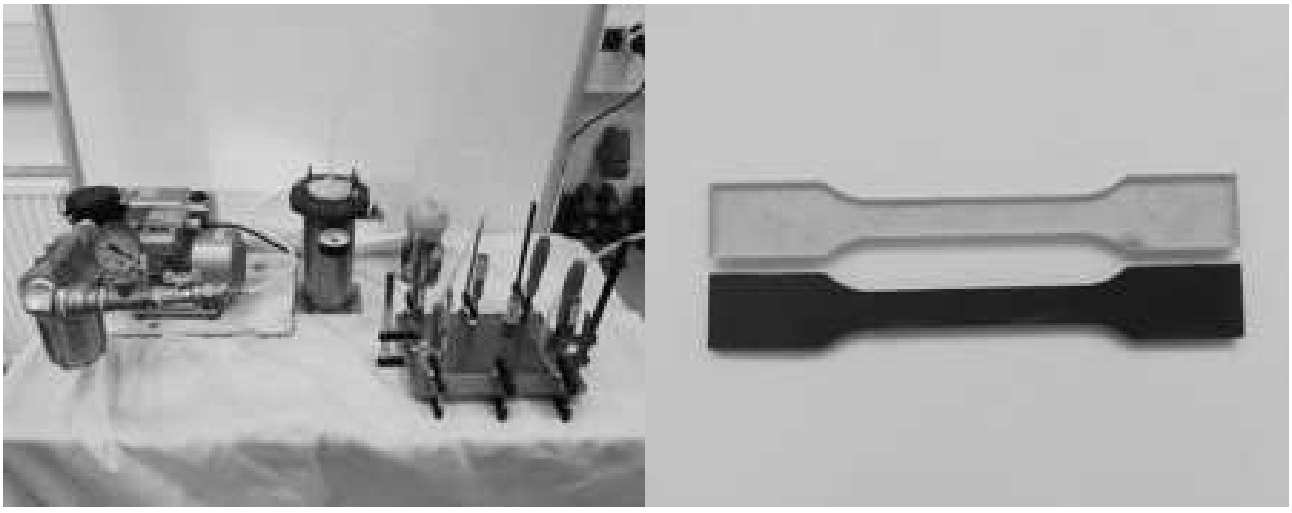

Fig. 2 *Composite plate production system based on vacuum infusion (left); testing samples for tensile test (right)*

3 Results and Discussion

Average tensile strength was 30.66 ± 1.60 MPa with filler concentration 0 wt. % and 34.02 ± 3.26 MPa with filler concentration 30 wt.%. The tensile strength was increased up to 10.95 %. However, adding of the filler manifested itself in the positive way on the increase of the tensile strength but at the expense of an increase of results dispersion which is visible in Fig. 3. It is the biological filler at which it is not possible to ensure the homogeneity.

Fig. 3 presents statistical nonhomogeneous group, i.e. it exists statistically significant difference between measured values *($p<0.0125$)*.

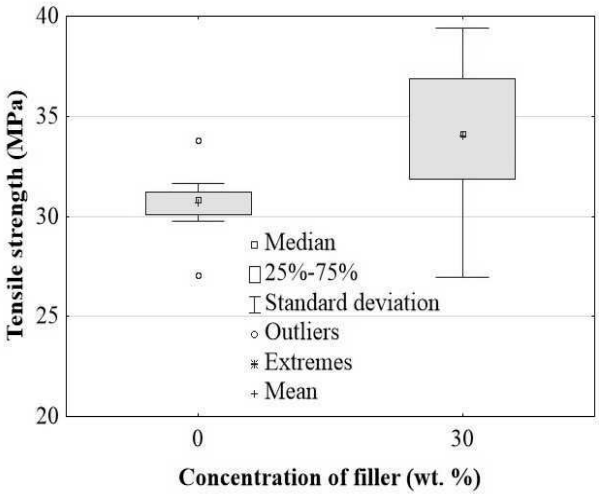

Fig. 3 *Dependence of tensile strength on filler concentration*

Average elongation at break was 2.46 ± 0.27 % with filler concentration 0 wt. % (matrix) and 1.51 ± 0.45 % with filler concentration 30 wt.%. The elongation at break was decreased up to 48.46 %. The reason for the decrease of the elongation at break was nonhomogeneous composite system that was caused by biological filler, i.e. the composite turned to more fragile by adding the filler.

Fig. 4 presents statistical nonhomogeneous group, i.e. it exists statistically significant difference between measured values *(p <0.00004)*.

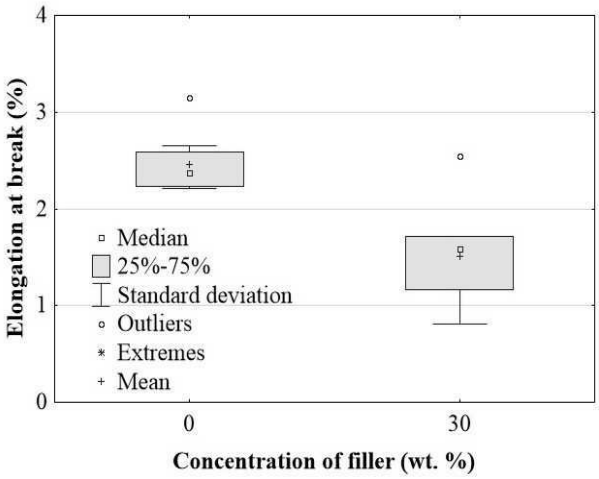

Fig. 4 *Dependence of elongation at break on filler concentration*

Average hardness was 207.86 ± 0.96 HB 5/358 with filler concentration 0 wt. % (matrix) and 231.30 ± 3.52 HB 5/358 with filler concentration 30 wt. %. The hardness was increased up to 11.28 %. The significant increase of the hardness is very important for a potential application area of a furniture industry with an emphasis on an outer surface, i.e. functional. This surface will absorb external influences.

Fig. 5 presents statistical nonhomogeneous group, i.e. it exists statistically significant difference between measured values *(p <0.00000)*.

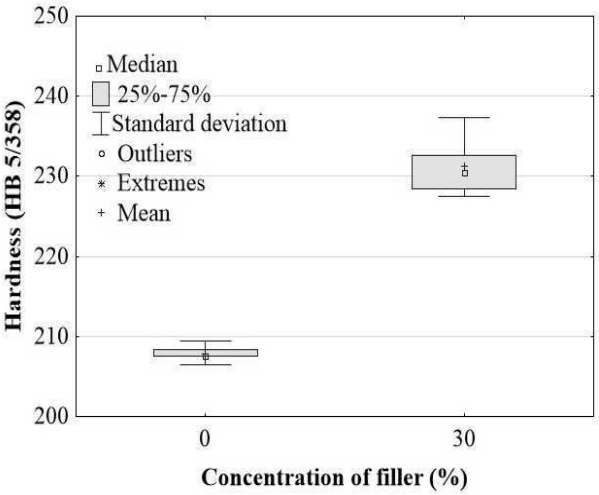

Fig. 5 *Dependence of hardness on filler concentration*

The average impact strength was 2.89 ± 0.31 kJ.m^{-2} with filler concentration 0 wt. % (matrix) and 2.21 ± 0.29 kJ.m^{-2} with filler concentration 30 wt. %. The impact strength was decreased up to 25 %. The reason for the impact strength decreasing was decreasing of the elongation at break (Fig. 4), i.e. the composite turned to more fragile by adding the filler. Another reason is a fact that the filler causes the material non-homogeneity.

Fig. 6 presents statistical nonhomogeneous group, i.e. it exists statistically significant difference between measured values (p <0.0001).

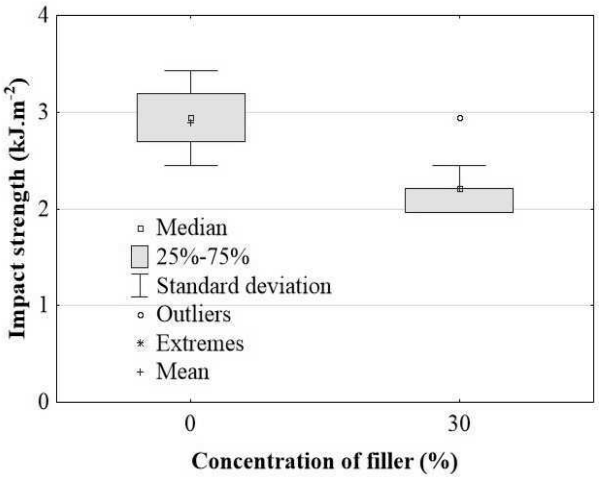

Fig. 6 *Dependence of impact strength on filler concentration*

From the results it is evident that the filler influenced mechanical properties of the matrix, i.e. resulting mechanical properties of composite. Authors Baştürk et al. have found that filler from pinecones with concertation 30 wt.% negatively affected tensile strength 21.83 ± 5.2 MPa compared with tensile strength 25.24 ± 3.39 MPa of adhesive with no filler. The tensile strength was decreased [15].

In the Fig. 7 the fracture surface of the composite material after static tensile test is evident. The Fig. 7A shows fracture surface of the matrix, i.e. thermoset epoxide. It is

evident from the fracture surface (Fig. 7A) that the matrix was a fragile material. Fig. 7B and fig. 7C present fracture surfaces of the composite material. From the SEM images good interaction between the filler and the matrix is obvious that influences the strength of composite material. From Fig. 7B the filler destruction is evident. The adhesion force between the matrix and the filler was stronger than cohesion strength of the adhesive. This conclusion is important for a possibility of practical usage of the filler type.

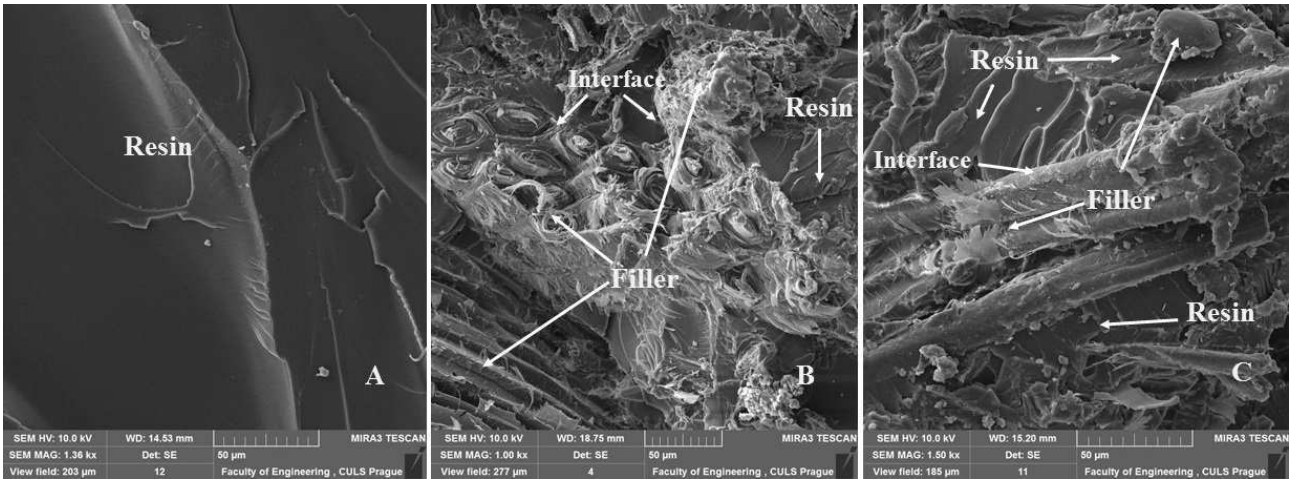

***Fig. 7** SEM images of fracture surface at static tensile test: A: matrix Havel Composites LH 288 + hardener Havel Composites H 282 (MAG 1.36 kx, SE), B: composite material – cohesive failure of filler (MAG 1.00 kx, SE), C: composite material (MAG 1.50 kx, SE)*

Author Petrasek and Muller 2017 have found that adding of biological filler in eggs shell form led to the filler destruction, i.e. adhesion forces between the matrix and the filler were stronger than cohesion strength of the matrix [16].

4 Conclusions

This paper follows the research on utilization of biological residues (waste) in the area of the polymeric composite materials. Namely the results of hardness, tensile strength and good interfacial interactions of the filler and the matrix proved an applicability of tested filler based on pine seeds production residues. The results of the mechanical properties proved increasing of the tensile strength up of ca. 11 % and of the hardness of ca. 11 % with filler concentration 30 wt.%. Conversely the elongation at break was decreased up of ca. 48 % by the non-homogeneity of the composite system. There is also the decrease of the impact strength up of 25 % versus the adhesive with no filler. The statistical test proved that the mechanical properties i.e. the tensile strength, the elongation at break, the hardness and the impact strength, were the nonhomogeneous group and there were statistically significant differences between the measured values ($p < 0.05$). SEM analysis proved good interaction between the matrix and the filler that increased the strength of the composite system. The results of the research contributed to a utilization possibility of composite systems in a practice in the area of design surface layers, e.g. used in the furniture industry.

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