UTILIZATION OF SECONDARY RAW BIOMATERIALS IN FORM OF MICROPARTICLES IN INTERACTION WITH REACTIVE RESIN

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Abstract. Understanding of basic characteristics and principles of polymer materials and composites is a significant factor for understanding of possibilities of filling reactive resins. The described characteristics belong to one of the most important parameters, which have an impact on possibilities of application of resin filled with organic and anorganic microparticles in practice. The experimental programme itself and its conclusions describe newly emerging materials, which are based on mutual interaction of secondary raw materials in form of microparticles (organic microparticles) and reactive resins (epoxy resin and polyurethane resin). The epoxy resin was represented by two-component epoxy resin – Epoxy 1200/324, the polyurethane resin was represented by resin Sika Force 7723. As a filler biomicroparticles from *Jatropha Curcas* L. seed cakes were used. The test samples were created by 5-35 vol. % of the microparticle filler in the epoxy and polyurethane resins. The mixture of the resin and the filler was prepared by mechanical mixing. The filled system combines properties of the epoxy resin and of the biomicroparticles filler. Particularly the description of cohesive and adhesive characteristics of these systems is one of the very important factors. The paper describes mechanical properties of these filled systems such as: hardness, tensile strength, lap-shear strength.

Key words: adhesion, biocomposite, cohesion, *Jatropha Curcas* L., material utilization.

Introduction

Reaction resins (e.g., an epoxy or polyurethane resin) evince beside adhesion to anorganic particles also good adhesion to organic materials. The material which uses the interaction of anorganic and organic phases can be described as biocomposites. Biocomposites are materials composed of component phases based on organic materials or they are combining organic materials (phases) with anorganic phases [1]. Biocomposites are among the materials that are progressively developed, but the biological nature of the material encounters limitations. Bio-fillers are used in interaction with resins in order to optimize certain characteristics or to minimize the price. Funabashi et al. [2] used polyurethane for filing the particle filler in form of powder from bamboo, wood powder, coffee grounds and powdered cellulose. Saturation of polyurethane of these fillers was in the range 10 to 90 wt. % while the size of the particles was in the interval from 12 µm (cellulose) to 1726 µm (coffee grounds). Inclusion of bamboo powder, for example, led to an increasing strength of resin. The research also proved a clear influence of the shape of the filler particles on the resulting mechanical characteristics. Dwivedi and Chand [3] describe the possibility of using wood flour made of teak wood the size of which was smaller than 355 µm. Shivamurthy et al. [4] utilized seed cake of pressed seeds of the plant *Jatropha Curcas* L. as a filler of resins. He added this secondary raw material (seed cake) to epoxy resin in the form of particles with a size of 36.6 µm.

Attention is recently paid to seeds of *Jatropha Curcas* L. plants at both, academic institutions and in practice. Production of oil from *Jatropha Curcas* L. seeds is a renewable form of profit of this commodity. The terms of pressing seeds and optimization of the pressing process are described by many authors; see, for example, the work of Ruzbarsky et al. [5-6] and Herak et al. [7]. In their works the authors indicate that in the coming years we can expect an increase of the production of oil from the seeds of this plant, mainly due to the declining supply of fossil fuels and particularly with regard to the environmental aspect, which should be one of the basic indicators. As it is reported in literature, production of oil from the plant *Jatropha Curcas* L. becomes profitable, but there is a condition, which requires also the use of other parts of the plant and seeds - the secondary raw materials produced during pressing seeds [8].

Description of options for emerging secondary raw material management allows describing comprehensively the problems of pressing oil from the seeds of *Jatropha Curcas* L. This experiment is focused on the possibilities of using secondary raw materials emerging from the seeds of *Jatropha Curcas* L. (seed cake) during oil extraction in the form of microparticles which are suitable to perform reaction resins. The results can be also used as an information source for hybrid systems – such

experiments of Gogoi et al. [9], which confirmed the possibility of creating hybrid composites with organic and anorganic fillers.

Materials and methods

Particle preparation

Pressing of the seeds (*Jatropha Curcas* L.) itself was carried out by the device Labor Tech MP Test 5.050 5 kN, the rate of deformation corresponds to 10 mm·min^{-1}, and thus the cake (seed cake) arises, which was further milled into microparticles, which were then used for filling of resins. Seed cake fulfils according to the Waste Catalogue of the Czech Republic the definition of waste 02 01 03 – Waste of plant tissues. Seed cakes (secondary raw material) from which the prepared microparticles were dried in a dryer at 105 ºC (drying time: 20 h) were then grounded by a knife mill with 20 000 rpm·min^{-1}. Dimensional analysis for determination of the particle size distribution was subsequently performed on a stereoscopic microscope.

Test sample preparation

The matrix was represented by two-component epoxy resin Eco Epoxy 1200/324 (EP) and by two-component polyurethane resin Sika Force 7723 (PU). The comparison between the epoxy resin and polyurethane resin was selected quite deliberately – both resins are used as polymeric matrices, e.g., in the automotive and in other industries. The test samples were created by 5-35 vol. % of the filler (seed cake particles) in the matrix (epoxy and polyurethane resins). The mixture of the resins and the filler was prepared by mechanical mixing.

Hardness

The hardness of the test specimens was measured by the method Shore D – CSN EN ISO 868 (on specimens of sizes 35 x 25 x 9 mm).

Lap-shear tensile strength

The evaluation was performed according to the standard CSN EN 1465 (Determination of tensile lap-shear strength of rigid-to rigid bonded assemblies). For the lap-shear strength description in the lap assemblies were made. The tests were performed using the steel S235J0 specimens of dimensions 100 x 25 x 1.5 mm. The surfaces of steel sheets were applied, which were at first blasted using the synthetic corundum fraction F80 under the angle of 90º. In this way the average surface roughness of $R_a = 1.53 \pm 0.36$ µm was reached. Then the surface was cleaned and degreased using perchlorethylene and prepared to application. The surface preparation is important and should guarantee good strength on the boundary adherent [10; 11].

Tensile strength

The test specimens had the basic shape and size defined by CSN EN ISO 3167 (Plastics – Multipurpose test specimen). Moulds for casting the test specimens had been made of Lukopren N with the use of the prepared steel models. According to the standard CSN EN ISO 527-1 (Determination of tensile properties) the destructive tests were performed.

A statistical comparison of the chosen mechanical properties of composites with different filler concentration on the basis of seed cake particles made by means of ANOVA and T-test is stated. A zero hypothesis H_0 ($p > 0.05$) specifies that there is no statistically significant difference among the tested sets from the mean value point of view.

Results and discussion

The real density (calculated from the volume and weight) of dried seed cake was 0.81 ± 0.11 g·cm^{-3}. Seed cakes were dried in an oven - moisture reached 9.2 %. The average size of particles corresponded to 578 ± 259 µm.

In terms of Shore D hardness it is not possible to talk about constant hardness (see results of ANOVA, Fig. 1) throughout the considered interval (0-35 %) from the statistical point of view (0 % means resin without filler – unfilled resin). The biological nature of the microparticles has an influence on measuring of hardness, and also the fact that these microparticles are formed by microparticles from individual parts of the seed (i.e., seed shells and kernel seeds).

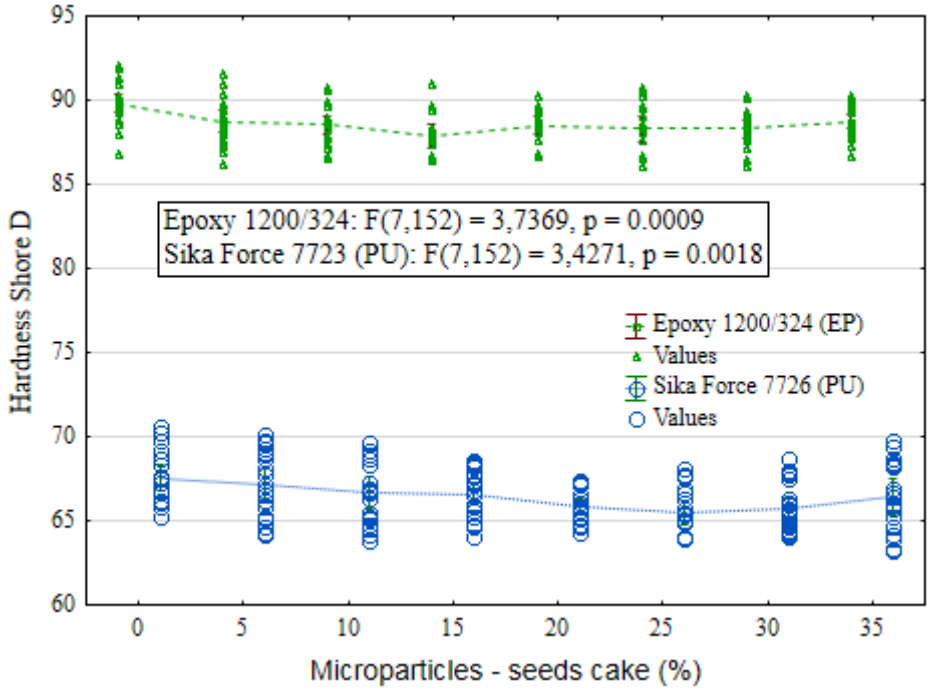

Fig. 1. **Hardness Shore D of composite systems**

The presence of microparticles from seed cake from whole seeds of *Jatropha Curcas* L. led to a decrease in shear strength in the resin. The shear strength of resin Epoxy 1200/324 decreased by 5.26 MPa to 6.22 ± 0.55 MPa and the strength of polyurethane resins Sika Force 7723 decreased by 4.12 MPa to 5.03 ± 0.54 MPa (see Fig. 2).

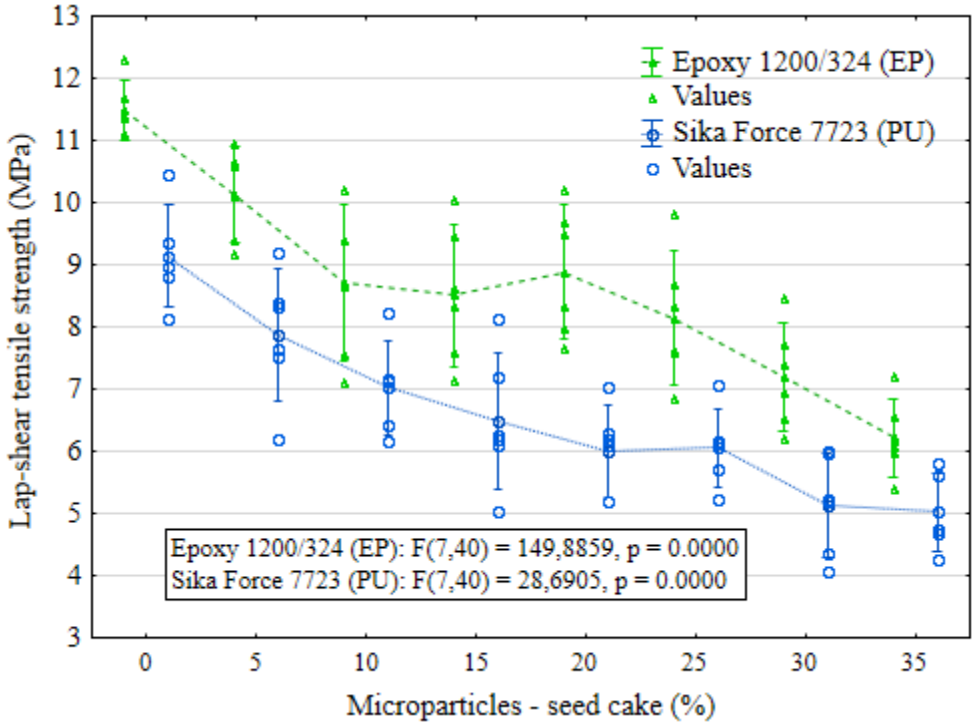

Fig. 2. **Lap-shear tensile strength of composite systems**

Inclusion of microparticles of resin Epoxy 1200/324 led to sharp decrease of lap-shear strength in the interval 0 to 10 %, and then the inclusion led to a consequent stabilization of decrease in the interval 10 to 25 % (compared to the concentrations each $p > 0.40$). The statistical comparisons are shown in Table 1.

Table 1

Statistical comparison – Lap-shear strength

T-test H_0: $\mu_1=\mu_2$ (p>0.05)		Epoxy 1200/324 (EP)							
		0	**5**	**10**	**15**	**20**	**25**	**30**	**35**
Sika Force 7723 (PU)	**0**	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	0.04	-	0.03	0.01	0.04	0.00	0.00	0.00
	10	0.00	0.13	-	0.77	0.80	0.40	0.03	0.00
	15	0.00	0.04	0.33	-	0.57	0.56	0.04	0.00
	20	0.00	0.00	0.03	0.37	-	0.25	0.01	0.00
	25	0.00	0.00	0.03	0.41	0.87	-	0.11	0.00
	30	0.00	0.00	0.00	0.03	0.08	0.05	-	0.04
	35	0.00	0.00	0.00	0.01	0.03	0.01	0.78	-

Adhesive failure occurred in connection of adherent materials in resin Epoxy 1200/324, cohesive failure was observed in polyurethane resin. Just as there was a decrease of values in shear strength, the tensile strength decreased in proportion to the higher concentration of microparticles in the resin (cohesive strength was decreasing). For comparison to unfilled resin, the tensile strength decreased from 27.58 MPa to 17.88 ± 1.28 MPa for resin Epoxy 1200/324, and the strength decreased by 2.73 MPa to 3.10 ± 0.36 MPa for resin Sika Force 7723 see Fig. 3. The statistical comparisons are shown in Table 2.

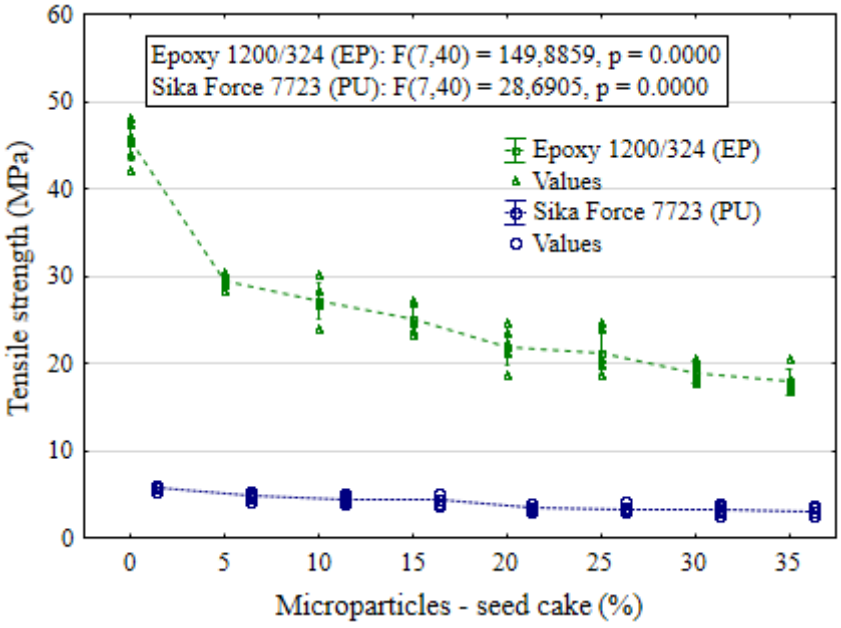

Fig. 3. **Tensile strength of composite systems**

Microparticles prepared from seed cake of *Jatropha Curcas* L. formed the appropriate interface with epoxy and polyurethane resins. Interaction of these fillers with reactive resins is possible – interaction of epoxy resin with organic and anorganic fillers described in many papers [12-15] was confirmed.

This opens a way to material recovery of this secondary commodity, which can extend the area where it is possible to use it. Other alternative methods of use are feeding or energetic recovery [5-6]. Filled resins described in this work may find application in areas where high mechanical properties are not required. Inclusion of these particles reduces the cost of resin. It is necessary to respect the mechanical properties of the complex in the process of their application.

Table 2

Statistical comparison – Tensile strength

T-test H_0: $\mu_1=\mu_2$ (p>0.05)		Epoxy 1200/324 (EP)							
		0	**5**	**10**	**15**	**20**	**25**	**30**	**35**
Sika Force 7723 (PU)	**0**	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	0.00	-	0.04	0.00	0.00	0.00	0.00	0.00
	10	0.00	0.34	-	0.07	0.00	0.00	0.00	0.00
	15	0.00	0.14	0.55	-	0.01	0.01	0.00	0.00
	20	0.00	0.00	0.00	0.01	-	0.61	0.01	0.00
	25	0.00	0.00	0.00	0.00	0.63	-	0.06	0.01
	30	0.00	0.00	0.00	0.01	0.61	0.93	-	0.18
	35	0.00	0.00	0.00	0.00	0.24	0.50	0.61	-

Conclusions

Inclusion of microparticles based on secondary raw materials from seed cake of *Jatropha Curcas* L. influenced the used resins in the interval of concentration 5 to 35 % as follows:

1. Shear strength was decreasing by up to 46.7 % (Epoxy 1200/324) by up to 46.2 % (Sika Force 7723).
2. Tensile strength was decreasing by up to 36.22 % (Sika Force 7723) and by up to 62.4 % (Epoxy 1200/324).
3. The price was decreasing by up to 27 % (Epoxy 1200/324) and by up to 23 % (Sika Force 7723).

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References

1. Fowler P.A., Hughes, J.M., Elias R.M. Biocomposites: Technology, environmental credentials and market forces. Journal of the Science of Food and Agriculture, Vol. 86, No. 12, 2006, pp. 1781-1789.
2. Funabashi, M., Hirose, S., et al.: Effect of filler shape on mechanical properties of rigid polyurethane composites containing plant particles. Macromolecular Symposia, Vol. 197, 2003, pp. 231-241.
3. Dwivedi U.K., Chand N. Influence of wood flour loading on tribological behavior of epoxy composites. Polymer Composites, Vol.29, No. 11, 2008, pp. 1189-1192.
4. Shivamurthy B., Murthy K., et al. Mechanical properties and sliding wear behavior of Jatropha seed cake waste/epoxy composites. Journal of Material Cycles and Waste Management, 2014, pp. 1-13.
5. Ruzbarsky J., Muller M., Hrabe, P. Analysis of physical and mechanical properties and of gross calorific value of Jatropha curcas seeds and waste from pressing process. Agronomy Research, Vol. 12, 2014, pp. 603-610.
6. Ruzbarsky J., Muller M., et al. Jatropha curcas-analysis of gross calorific value. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis, Vol. 62, No. 6, 2014, pp. 1381-1384.
7. Herak D., Blahovec J., Kabutey A. Analysis of the axial pressing of bulk Jatropha curcas L. seeds using reciprocal slope transformation. Biosystems Engineering, vol. 121, 2014, pp. 67-76.
8. Guedes R.E., Cruz F.D.A., et al. Detoxification of Jatropha curcas seed cake using chemical treatment: Analysis with a central composite rotatable design. Industrial Crops and Products, Vol. 52, 2014, pp. 537-543.
9. Gogoi P., Boruah M., et al. Jatropha curcas oil based alkyd/epoxy resin/expanded graphite (EG) reinforced bio-composite: Evaluation of the thermal, mechanical and flame retardancy properties. Progress in Organic Coatings, Vol. 77, 2014, pp. 87-93.

10. Affatato S., Ruggiero A., et al. On the roughness measurement of the knee femoral components. In: BIOMODLORE 2013 Palanga (LT) 20-22 Sept. 2013 Vilnius Vilnius Gediminas Technical University Press Technica (Sauletekio al.11, LT-10223, Vilnius, Lithuania.), 2013, pp. 16-18.
11. Novak, M. Surface duality hardened steels after grinding. Manufacturing technology, Vol. 11, 2011, pp. 55-59.
12. Valasek P., Muller M. Polyurethane resins filled with inorganic waste particles, Manufacturing Technology, Vol. 13, No. 2, 2013, pp. 241-247.
13. Valasek P., Muller M. Polymeric particle composites with filler saturated matrix Manufacturing Technology Volume 12, Issue 13, 2012, pp. 272-276.
14. Valasek P., Zarnovsky J., Muller M. Thermoset composite on basis of recycled rubber. Advanced Materials Research, Vol. 801, 2013, pp. 67-73.
15. Muller M. Polymeric composites based on Al_2O_3 reinforcing particles. In Engineering for Rural Development 26.05.2011, Jelgava. Jelgava: Latvia University of Agriculture, 2011, pp. 423-427.