NATURAL ORGANIC-INORGANIC MATERIAL UTILIZED AS A FILLER IN POLYMER SYSTEMS

Dora KROISOVÁ, Kinga ADACH, Mateusz FIJALKOWSKI

Technical University of Liberec, Studentska 2, Liberec, Czech Republic dora.kroisova@tul.cz

Abstract

The aim of this work is to evaluate an influence of organic-inorganic natural filler on the selected parameters of epoxy resin composite systems. The natural filler investigated has a character of agricultural waste and is characterized by a high silicon dioxide content. Silicon is absorbed by a plant in the form of a silicic acid colloidal solution and as a consequence of biological processes silica particles of nanometre or submicron dimensions are created in the plant. These particles form a compact barrier in grain husks and protect grains from different environmental influences. The filler of 1 to 100 µm particle size was prepared by grinding and it was subsequently added to the commercially produced epoxy resins in order to evaluate the influence of the filler on the selected mechanical parameters. An impact of the filler in composite systems was evaluated in the range from 0.1 phr to 50 phr. It was found that adhesion between filler particles and the polymer matrices is good and so was the homogeneity of samples studied by scanning electron microscopy and EDX analysis. The cured and filled epoxy systems were evaluated in order to find out the influence of the filler on the tribological behaviour. The wear rate (the weight loss of the sample) after a total sliding distance of 20,000 cycles was measured, as well as the influence of the filler on micro hardness and the Young's modulus. The wear rate reduction depends on the amount of the filler and can reach 70 %.

Key words: composite system; epoxy resin; particle filler; tribological behaviour; wear rate reduction.

1. INTRODUCTION

Polymers have long been modified by fibre or particle fillers with an aim to improve their mechanical and physical properties or reduce the product price. Today, glass or carbon reinforcing fibres are used on a regular basis and natural fibres are also applied as reinforcing materials. However, plant-based fillers, with their characteristic compositions and high content of silicon dioxide, have attracted little attention so far. Certain plants are reinforced with silicone, that is, with hydrated amorphous silicon dioxide. The content of amorphous silicon dioxide varies depending on the kind of plant and also the part of a plant's body. This reinforcement in the form nano- to micrometer-sized particles is present in various amounts in cell walls where it adds to plants' basic protection. The particles also form more or less compact structures or layers which protect plants through increasing their hardness and strength. This physical and mechanical protection is related to the necessary resistance of plants to attacks by other organisms, whether microorganisms or herbivores. Silicon enters the plant body with the soil solution. This solution is supplied with various elements through the process of weathering, dissolving, ion exchange, the presence of gases and water in soil and their mutual interactions. Silicon is easily absorbed by plants in the form of a silicic acid colloidal solution and as a consequence all plants grown in soil contain some amount of it. The content of silicon in plants varies between 0.1 % and 10 % or more. Plants with a high silicic acid absorption capacity include the field horsetail (*Equisetum arvense*), the rough horsetail (*Equisetum hyemale*, syn.: *Hippochaete hyemalis*), barley *(Hordeum vulgare L.)* and rice (*Oryza sativa)* [1, 2]. Agricultural waste-type natural fillers with the necessary content of silicon dioxide such as rice husks have a high potential of becoming fillers to be used to improve required parameters. Filling with small amounts of appropriately ground rice husks can ensure a reduction in the coefficient of friction while simultaneously increasing wear resistance. As a result, rice husks become fillers which can compete in terms of their price and ecology with fillers typically used today [3].

2. EXPERIMENTAL

2.1 Materials

The organic-inorganic filler used were ground rice husks *(Oryza sativa)* with a characteristically high content of silicon dioxide compared to the other kinds of natural fillers commercially used so far. The size of particles resulting from the grinding process varied between 1 and 100 µm. The rice husks were imported from the Khánh Hóa region in Vietnam where the rice had been grown. Epoxy resin ChS Epoxy 520 (a low molecular weight epoxy resin prepared by a reaction between bisphenol A and epichlorhydrin without modifying components) hardened with hardening agent P11 (diethylenetriamine) with a 100:11 weight ratio as declared by its producer, DCH - Sincolor, a.s., was used as a polymer matrix for the experiments described below. This resin is used in various fields of industry for waterproofing, mounting, casting and gluing, and it is also suitable for production of cements, adhesives and coatings [4].

2.2 Methods

The input material – rice husks – was characterized in terms of describing its surface and localizing silicon using a Carl Zeiss Ultra Plus scanning electron microscope, which was also used to evaluate the size of particles and the formation of their clusters and assess adhesion between filler particles and the epoxy matrix. Before microscope analysis a film of gold 3 nanometres thick was vacuum-deposited on the surface of specimens. The same instrument was also used to determine the chemical composition of rice husks and the homogeneity of filler distribution within the polymer through EDX analysis. Filler particles were obtained by grinding rice husks without prior treatment in a CryoMill Retsch nano mill using steel balls of various sizes at standard temperatures and frequencies of around 30 Hz. The filler thus obtained was mixed into an epoxy resin without further treatment and subsequently homogenized for 5 minutes at 40-60 rpm. After adding hardener P11, the mixture was homogenized for 2-3 minutes at 40-60 rpm. The mixture was then left to harden for 48 hours at standard laboratory temperature and a relative humidity of between 50 and 60 %. The tests were conducted on fully hardened specimens after 10 days. The coefficient of friction was evaluated in a CSM ball-on-disc tribometer, with a 100Cr6 steel ball, at a load of 15 N with 20.000 friction cycles at a linear speed of 0.1 m/s under standard laboratory conditions. The wear rate of specimens was determined via a tribological measuring method as a specimen's weight loss after 20.000 cycles. Micro hardness and the Young's modulus were measured using a CMS hardness tester at a test load of 5 N using a diamond indenter under standard laboratory conditions.

3. RESULTS AND DISCUSSION

The microscopic and chemical analysis of rice husks established that silicon dioxide is present particularly below the husk's surface, with its highest concentrations found in superficial projections. The nature of the surface and its chemical composition, that is, the presence of silicon dioxide, are clearly seen Figures 1 and 2.

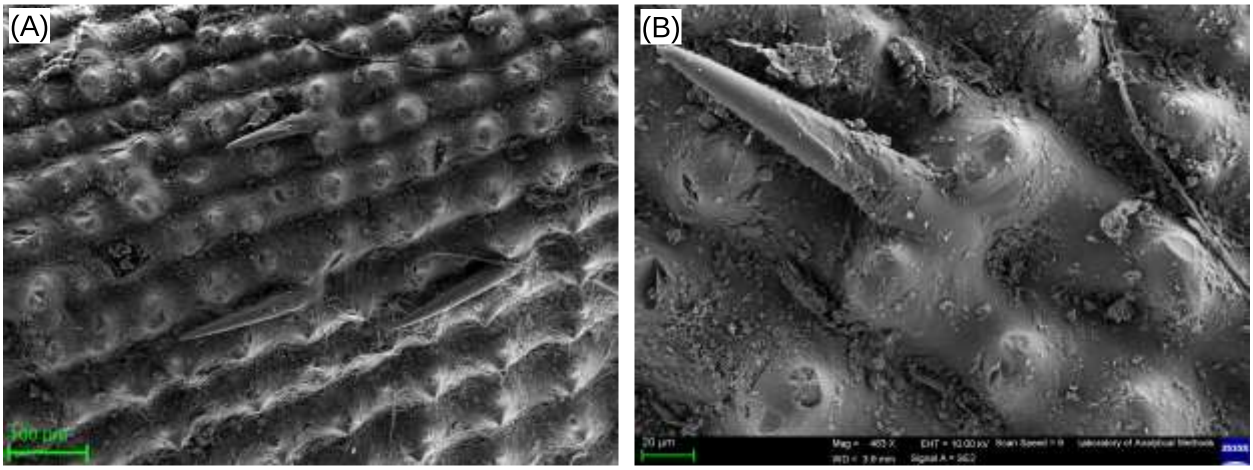

Fig. 1 SEM image of the rice husk surface: (A) low magnification, (B) high magnification

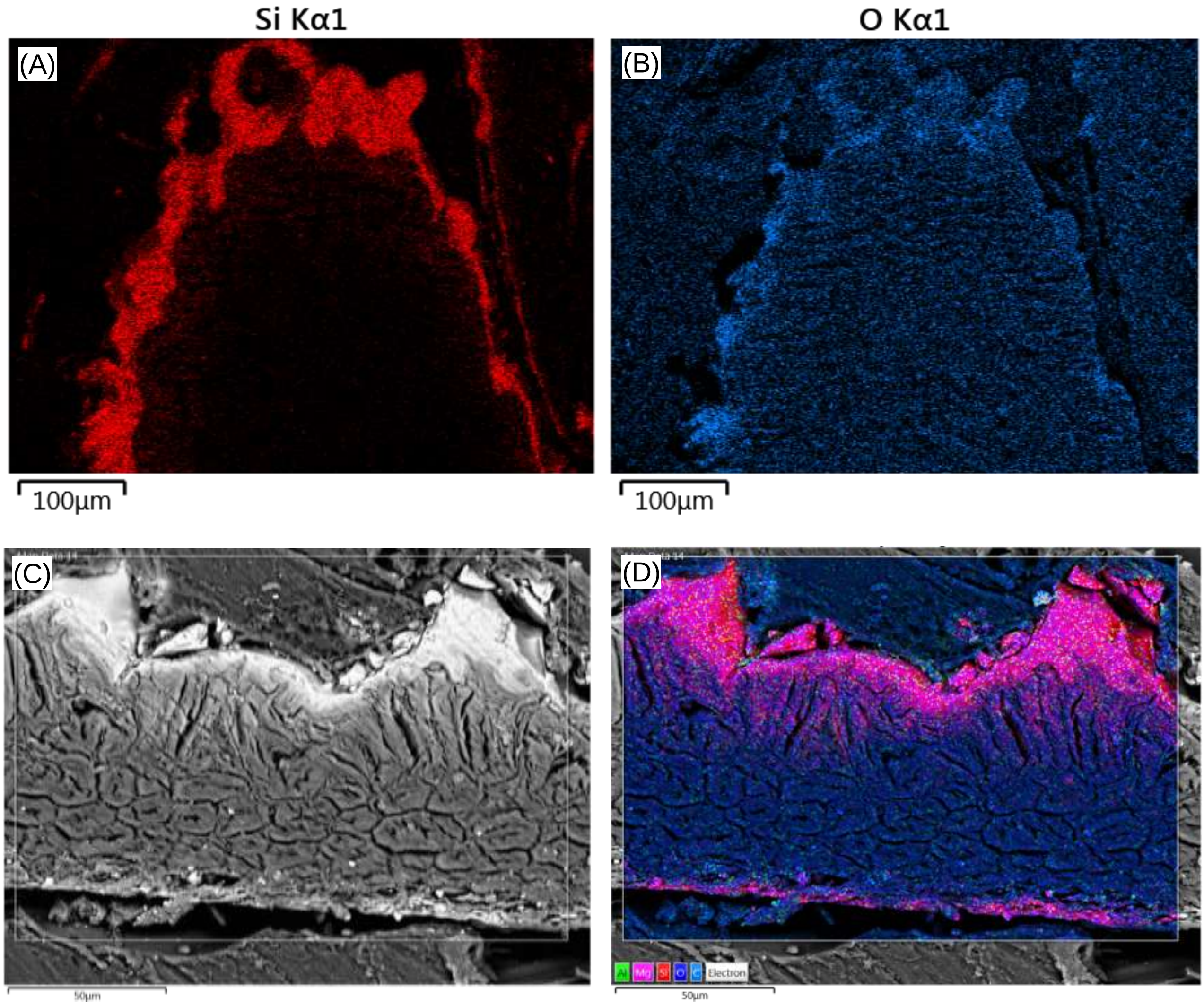

Fig. 2 EDX analysis showing the distribution of elements typically found on the surface of rice husks: **(A)** silicon, **(B)** oxygen, **(C), (D)** silicon dioxide in superficial projections

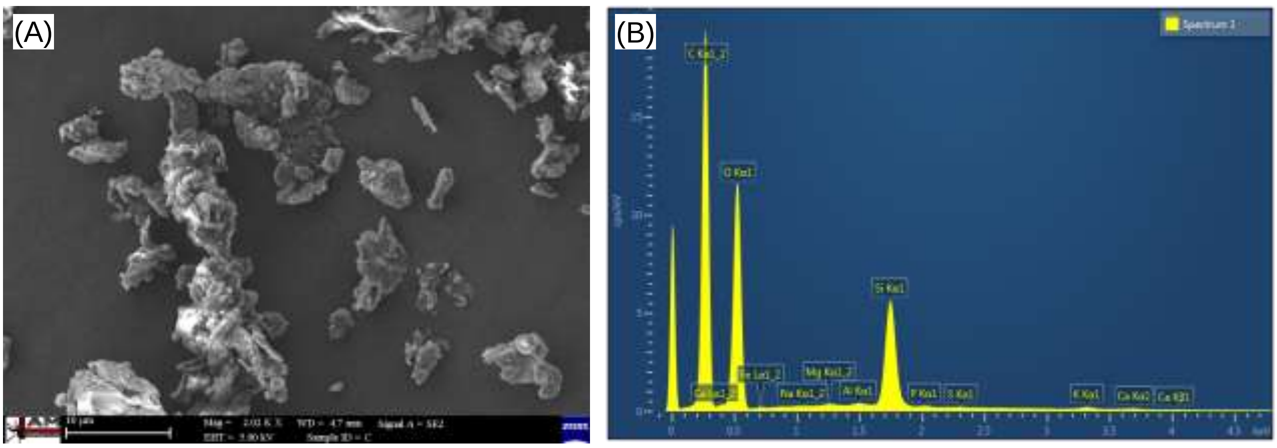

Fig. 3 Ground material characteristics: **(A)** SEM of filler particles – rice husks, **(B)** EDX analysis of filler particles obtained by grinding from input material

It is apparent from this analysis that for the filler to be used with maximum efficiency, that is, utilizing silicon dioxide particles, it is necessary to grind the input material to obtain particles as fine as possible. After grinding in a nano mill, the particle size varies between 1 and 100 micrometers – see Figure 3. The particles easily agglomerate and the number of particles with sizes of around 100 micrometers is small. The EDX analysis of ground particles clearly shows that as well as the organic phase (cellulose, hemicelluloses and lignin) filler particles contain other inorganic elements (Table 1 and Figure 3), with silicon and potassium, that is, silicon dioxide, having the highest content [5].

Table 1 Chemical composition of ground particles in mass and atomic percents determined using EDX analysis

Element	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe
wt.%	52.10	34.20	0.01	0.12	0.19	11.72	0.20	0.08	0.65	0.42	0.31
at. %	62.44	30.77	0.01	0.07	0.10	6.01	0.09	0.04	0.24	0.15	0.08

Filler particles adhere well to the epoxy resin. Images from the scanning electron microscope clearly show that there are no gaps between particles and the polymer which would suggest insufficient filler-binder bonding. Natural organic filler particles are substantially difficult to detect in the organic material. – see Figure 4. The nature of the ground and polished specimen surface makes it hard to distinguish between particles and the matrix.

The homogeneity of organic particles contained in the organic material was evaluated using the EDX analysis of a specimen's ground section. Elements – silicon and potassium – with the highest content in ground husk particles were identified – see Table 1, Figure 4. EDX analyses showed that the homogeneity of organic-inorganic filler distribution is maintained in both micro and macro volume, which means that no undesired filler sedimentation occurs during the hardening process – Figure 4.

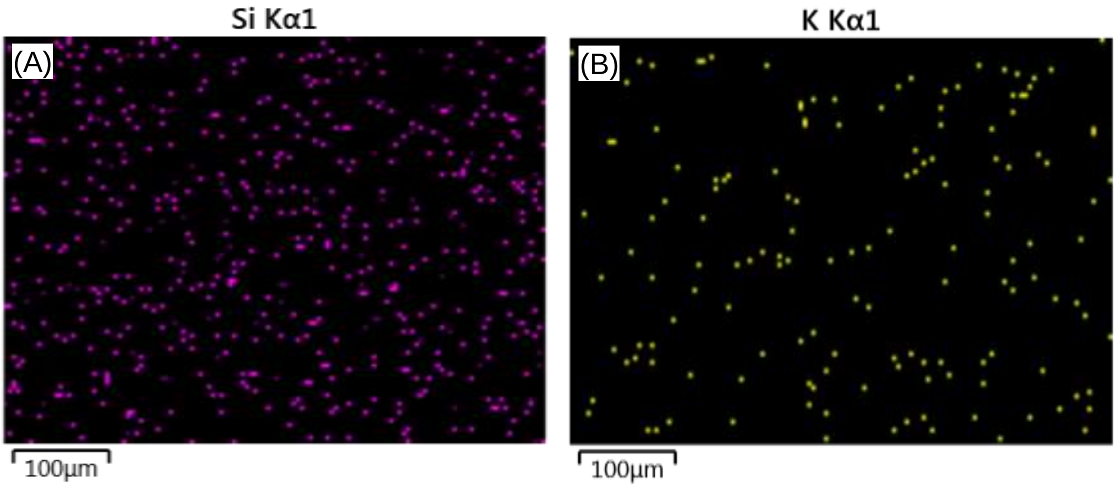

Fig. 4 EDX analysis of a ChS Epoxy 520 epoxy resin system – filler at 0.5 phr performed for: **(A)** silicon, **(B)** potassium

The coefficient of friction was determined under the above conditions. A small amount of this organic-inorganic filler type and particle size was found to reduce the coefficient of friction compared to the original unfilled resin. Filling with fillers at 0.1 phr reduces the coefficient of friction from the initial 0.410 ± 0.014 in an unfilled epoxy resin to 0.390 ± 0.010; filling at 1 phr reduces it from 0.410 ± 0.014 to 0.360 ± 0.008. This is shown in Figure 5 (A).

Due to the presence of filler the wear rate of the compact hardened material made from the resin and filler described above is reduced. This wear rate is expressed as a specimen's weight loss in milligrams. The weight loss is reduced from 9.70 ± 0.35 mg in an unfilled epoxy resin to 4.00 ± 0.30 mg in a resin filled with a ground filler at 0.1 phr. The weight loss in a resin filled at 1 phr is reduced from 9.70 ± 0.35 mg to 2.30 ± 0.15 mg. This is shown in Figure 5 (B).

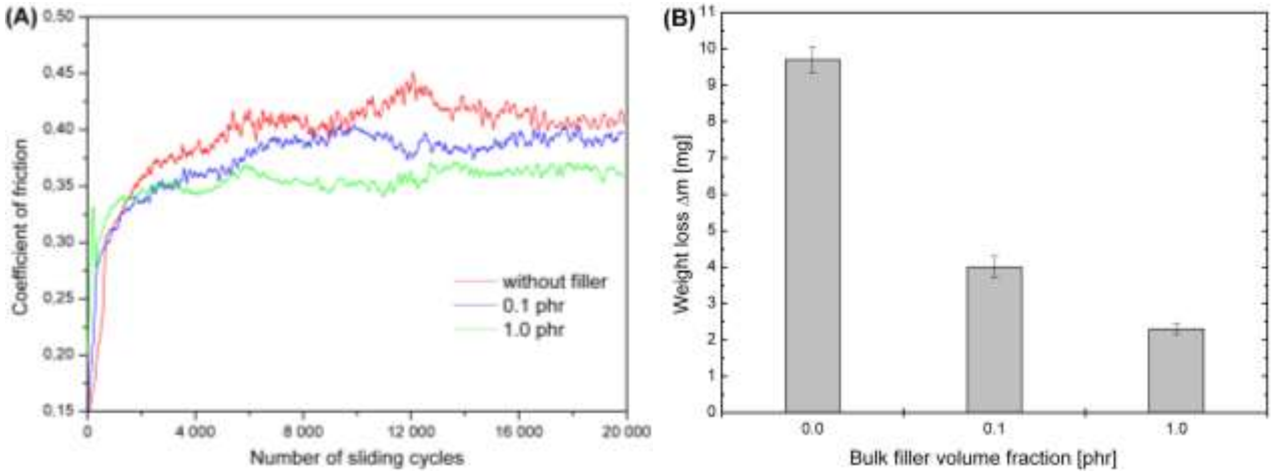

Fig. 5 Tribological behaviour of epoxy resin composite systems: **(A)** Relationship between the coefficient of friction and filler volume; **(B)** Influence of the filler volume on the reduced wear rate in a hardened specimen from epoxy resin

The explanation of the above values is in keeping with studies whose results are summarised and discussed in a comprehensive publication on polymer tribology [6]. Inorganic particle fillers are characterized in terms of their size, chemical composition and hardness. It is generally true that solid and hard particle fillers increase the Young's modulus and may reduce the coefficient of friction and wear rate at suitable filling amounts. Micrometre-sized fillers reduce the coefficient of friction and increase wear resistance at 25-35 % of filling volume while fillers in nanometre sizes can be used at 1-3 % of filling volume. Studies published to date have found positive influences of Al_2O_3, SiO_2, SiC and Si_3N_4 nano particles. The filler described and used, obtained from rice husks with a high inorganic phase content and small-size particles, appears to act in a polymer system in two ways. The inorganic phase – silicon dioxide – acts as a hard particle, contributing to a reduction in the coefficient of friction and simultaneously increasing wear resistance. The organic phase – cellulose, hemicelluloses and lignin – firmly bonds with the silicon dioxide, but is soft in comparison and does not increase the Young's modulus or the hardness of the system. The explanation of the behaviour of this less traditional filler is in keeping with an understanding of what kinds of influences hard particles have on polymers. Hard particles transfer part of the load, thus protecting soft polymers from wear and tear. The effects of the volume and size of filler and filler adhesion to the polymer matrix are apparent.

Neither hardened mixture described displays any significant material hardness change; the hardness of an unfilled epoxy resin is 22 HV while the hardness of a compact hardened material at filling volumes described above is between 21 and 22 HV. The modulus of elasticity is reduced in the hardened mixture described; the modulus of elasticity of an unfilled epoxy resin is 3.4 GPa while the modulus of elasticity of a compact hardened material at filling volumes described varies between 2.5 and 3 GPa. This is shown in Figure 6.

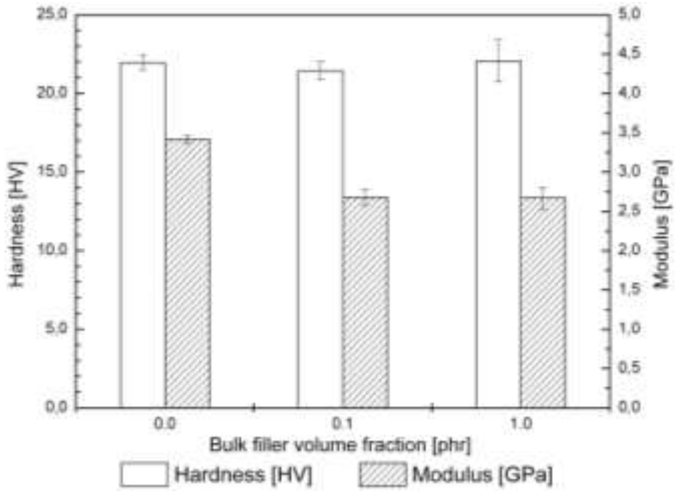

Fig. 6 Relationship between hardness / the Young's modulus and the volume of filler in the matrix

4. CONCLUSION

The tests established that an organic-inorganic filler containing ground rice husks with 12 percent by mass of silicon and the particle size between 1 and 100 micrometres influences the original epoxy matrix by reducing its coefficient of friction by about 10 % at a low filling volume of 0.1 – 1.0 phr. Low filling volumes of 0.1 – 1.0 phr increase the wear resistance of a filled epoxy resin by 55 – 75 %. Compared to an unfilled epoxy resin, the hardness of the filled kind of resin remains almost unchanged; this is positive in terms of mechanical parameters initially suggested by the producer. The modulus of elasticity of a filled epoxy resin is reduced and the material's toughness increases. In contrast, a higher filling coefficient increases friction and decreases wear resistance.

The results are protected by patent and utility model applications [7, 8].

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