Epoxy Coatings Fillers on the Rice Husk Base

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Abstract. The present paper deals with the investigation of properties of epoxy coatings modified by the silicocarbonous fillers on the rice husk base and its ash that represent invaluable renewable agricultural waste material of vegetable origin. Rice husk containing large amount of chemically active amorphous silica, could be seen as efficient filler for linear and cross-linked polymers as it exhibits catalytic effect on the process of epoxy oligomers hardening by amines and leads to reduction of cross-linking degree of epoxy polymers. Polymer compounds become more competitive and the processes of their utilization are accelerated due to biodegradability of fillers. Filling epoxy composites with both naturally occurring and synthetic wollastonite significantly improves their resistance to wear. Synthetic wollastonite as well as naturally occurring one improves hardness, resistance to wear of epoxy polymers and enhances antifriction properties of modified materials.

1. Introduction
Qualified waste processing enables to free up much needed commercial lands previously used as excavation heaps and landfills and also permits to reduce environmental pollution significantly.

That’s why the development of efficient technologies of processing annually renewable agricultural waste of vegetable origin is of utmost importance as such a waste is regarded as an innovative raw material for manufacturing the products of sustainable or green chemistry [1]. Production of fillers on the base of rice husk (RH) could be seen as prospective as rice husk contributes to 20-25% by volume in rough rice processing [2]. Along with that, rice husk is hard to utilize as its incineration leads to toxic gases formation; rice husk is almost non-biodegradable due to the presence of silica in its composition [3]. On the other hand, the presences of this component in rice husk makes this agricultural waste a valuable raw material for production of silicocarbonous fillers for polymer composites [4].

2. Materials and methods
For epoxy coatings production the authors used epoxy diane resin ED-20 (All-Union Standard GOST 10587-84) hardened by aminoalkyl phenol (APh-2) (Technical Conditions TU 2494-052-00205423-2004) during 24 hours at the room temperature. The content of a hardener has been determined by equimolar ratio [epoxy groups]::[amin].
As fillers the authors applied: synthetic wollastonite obtained on the base of rice husk and limestone, at molar ratio of CaCO$_3$ and SiO$_2$ equal to 1.2:1, at the temperature of 1100$^\circ$C during 3 hours [5]; naturally occurring wollastonite of the grade MIVOLL 10-97 (Technical Conditions TU 5777-006-40705684-2003), rice husk (RH) and rice husk ash on its base obtained at 350$^\circ$C (RHA$_1$) and correspondingly 800$^\circ$C (RHA$_2$).

Adsorption of epoxy resin on the surface of researched fillers has been estimated by means of their mixture curing at the ratio of 1:9 at the room temperature for 24 hours, further exposure to acetone solution while maintaining the same conditions for 6 hours and following filtration of the solution and defining the mass of undissolved residuary. Gel-fraction content has been determined with the help of the extraction method in boiling acetone in the Soxhlet apparatus during 6 hours. Application life of filled epoxy compositions has been determined by means of the Vicat apparatus at the room temperature. Hardness tests have been implemented with the help of the portable Barcol hardness meter (All-Union Standard 9013-59, ASTM B648-2000, ASTM D-2583). Oil consumption of fillers was valued in compliance with the All-Union Standard GOST 21119.8-75. Resistance to wear for the coatings has been measured by means of the vertical optimeter IZV-1 at unit area pressure of a counterbody on the tested surface of a specimen $P=1$MPa, slip velocity $V_s=1$m/sec, no lubricant. Frictional coefficient, defining antifriction properties of materials, has been evaluated on the automated computer operated friction apparatus “Tribometer, CSM Instruments” (Switzerland), under the standard testing scheme “ball-disk” (ASTM G99-959, DIN50324 and ISO 20808). The linear rate during the test accounted for 8.94 m/sec, sampling frequency – 10 Hz, temperature – 25$^\circ$C, humidity – 20%.

3. Results and Discussions

Annually in the world millions of tons of rice husk are produced that provides the industry with invaluable, cheap, renewable and biodegradable raw material with chemical composition suitable for manufacturing large amount of chemically active amorphous silica [6].

Rice husk contains about 10-20% mineral components while 80-95% falls to the share of silicon dioxide, 35-43% - cellulose and 20-47% lignin correspondingly. Rice husk ash primarily (92-97%) consists of silicon dioxide [3]. In order to get silicon dioxide from rice husk, it’s necessary to carry out pyrolysis reaction and incineration of carbon residuary at the temperature ranging from 300 to 3000$^\circ$C [7]. Temperature of this process has a significant impact on amorphous state of obtained silicon dioxide and the carbon content in rice husk ash. Rice husk ash has irregular particles shape, large surface area and porous structure that result in efficient interaction with polymer matrix. However, functioning as filler, it also has some drawbacks such as relatively large particles size and increased hydrophilic behavior [9]. Silicon dioxide obtained from rice husk could be seen as an alternative to synthetic silicon dioxide – aerosil [9]. Rice husk and its ash have been investigated as an efficient filler for linear and cross-linked polymers such as polyethylene of low and high-density [10], polypropylene [11], polyvinylchloride [12], polyether, epoxy resins [13, 14], and others. The use of rice processing waste as fillers allows polymer materials to be more competitive and, moreover, accelerates the processes of their utilizing after completion of life durability due to biodegradability of rice husk [15]. At the same time, the properties of polymer materials filled with rice husk ash depend on the particles size and the content of silicon dioxide to an important degree. Thus, the authors of the paper [16] proposed to use rice husk ash with the particles size $\sim$ 45 micrometers and the low content of admixtures as efficient filler (i.e. concentration of silica around 94%).

The obtained results (table 1) prove that filling epoxy compounds with rice husk leads to reduction of cross-linking degree as indicated by lowering gel-fraction content. Similar effect could be observed when applying rice husk ash obtained at the temperature of 350$^\circ$C. At the same time, rice husk ash manufactured at 800$^\circ$C has a little impact on cross-linking degree of polymer material.
Table 1. Sol-gel fraction content in epoxy coatings filled with rice husk and rice husk ash

| Type of filler | Sol-fraction content, %wt | Gel-fraction content, %wt |
|----------------|---------------------------|---------------------------|
| RHA1           | 11.37                     | 88.63                     |
| RHA2           | 9.07                      | 90.93                     |
| RH             | 13.36                     | 86.64                     |
| No filler      | 9.28                      | 90.72                     |

* Filler content 10 % wt for 100% wt of ED-20

When obtaining the researched compositions, interaction of epoxy oligomer and the surface of RH and RHA takes place. When voids’ rating of fillers on the base of rice husk grows, one could observe augmentation of adsorption of epoxy resin on their surface (table 2).

Table 2. Degree of adsorption of ED-20 on the surface of tested specimens

| Type of filler | Degree of adsorption, % |
|----------------|-------------------------|
| RHA1           | 3.28                    |
| RHA2           | 2.36                    |
| Rice husk      | 1.90                    |

In the case of applying RH, increasing the content of silicon dioxide in its composition and reducing the concentration of organic components (at the elevated temperatures of its manufacturing) leads to lowering the degree of adsorption of ED-20 on the filler surface (table 2). These data correlate with the results received for evaluation of oil adsorption of rice husk and its ash (table 3).

Table 3. Oil adsorption of the specimen of rice husk and its ash

| Type of filler | Oil adsorption, % |
|----------------|-------------------|
| RHA1           | 146               |
| RHA2           | 110               |
| Rice husk      | 93                |

Life durability of epoxy compounds also depends on chemical constitution of applied filler. It decreases when both rice husk and its ash are introduced into the composition (table 4). Along with that, this effect is more noticeable when the content of amorphous silicon dioxide in filler compositions is growing as the temperature of manufacturing RHA rises.

Catalytic effect of rice husk and its ash on the process of epoxy oligomers hardening by amines could be explained by the presence of hydroxyl components and metals oxides in the composition of fillers.

Table 4. Life durability of filled epoxy compounds

| Type of filler | Life durability, min |
|----------------|----------------------|
| RHA1           | 25                   |
| RHA2           | 27                   |
| RH             | 31                   |
| No filler      | 35                   |

* Filler content 10 % wt for 100% wt of ED-20

It is worth mentioning that as adsorption of epoxy resin on the filler surface increases, i.e. when a hardener is present in excessive amounts, their life durability is consistently reduced. Applying rice husk ash for synthesis of wollastonite [17] is of great practical importance. Limestone could be regarded as the second high-potential component as an affordable low-cost naturally occurring mineral, available in abundance with the prevalent content of lime carbonate in its composition [17]. Synthetic wollastonite
(CaSiO$_3$) has polymorphic structure. It contains $\alpha$-wollastonite (pseudowollastonite) and $\beta$-wollastonite with identical chemical constitution and similar stoichiometry but different crystalline order.

The maximum content of $\beta$-wollastonite was discovered in the filler specimen synthesized by the authors [5] with the molar ratio CaCO$_3$ and SiO$_2$ equal 1.2:1. This specimen of synthetic wollastonite has the structure closest to naturally occurring filler. Both naturally occurring and synthetic wollastonite on the base of rice husk enhance hardness of epoxy coating, while the former - at the greater extent (figure 1), due to higher content of acicular shape particles.

![Figure 1. Relation between hardness of epoxy compositions and the type of applied filler: 1 – no filler; 2 – MIVOL 10-97; 3- synthetic wollastonite with molar ratio CaCO$_3$ and SiO$_2$ 1.2:1 (\(^*\) Filler content 10% wt for 100% wt of ED-20) ](image)

Filling epoxy composites with both naturally occurring and synthetic wollastonite enhances their resistance to wear significantly and to the same extent (figure 2).

This could be attributed to anisodiamic particles’ shape of these short-fibered fillers that have a reinforcing effect, according to the previously published research [19], and also an impact on materials’ fatigue properties.

Due to its rough surface, wollastonite has improved chemo sorption properties and forms associates with epoxy system particles thus reducing their molecular motion. This improves strength and resistance to wear of epoxy coatings due to the growth of rupture work and inhibiting cracks proliferation at the place of contact with polymer matrix as well as thanks to micro cracking in the area of tip of the crack and change of crack path [20].

![Figure 2. Relation between wear of epoxy compounds and the type of applied filler: 1 – no filler; 2 – MIVOLL 10-97; 3 – synthetic wollastonite with molar ratio CaCO$_3$ and SiO$_2$ 1.2:1 (\(^*\) Filler content 10% wt for 100% wt of ED-20) ](image)
Figure 3 shows dependence of coefficient of static friction on the contacts formation time for compositions filled with wollastonite. The experimental data prove that as synthetic wollastonite as naturally occurring one significantly (almost twofold) reduce the coefficient of static friction for epoxy compositions thus enhancing their antifriction properties. Along with that, naturally occurring wollastonite reduces the coefficient of static friction at slightly more significant extent, if compared with synthetic one. Frictional interaction of polymer compound and metallic counterbody has dual molecular and mechanical character [20]. Deformational losses in a polymer material are mostly conditioned by its viscoelastic characteristics. Appearance of adhesion component of friction is caused by formation of links between macroradicals, according to [20], arising at the destruction of three-dimensional network of polymer matrix and oxide layers of counterbody’s surface as well as interaction of the particles of a layer.

![Figure 3](image)

Figure 3. Dependence of coefficient of static friction on time of contact formation with epoxypolymer: 1 – no filler; 2 – with 10 % wt of MIVOLL 10-97; 3 – with synthetic wollastonite (*Filler content 10 % wt for 100% wt of ED-20*)

Thus, the desired reduction of friction coefficient and enhancement of wear resistance of epoxy composites could be achieved by means of stiffness and hardness growth of polymer matrix, formation of easy slip planes in a transfer film and reduction of particles flow while experiencing friction. This could be conditioned by the introduction of wollastonite.

4. Conclusion
Thus, rice husk and its ash are of great interest for production of epoxy polymers fillers, in particular, those on the base of synthetic wollastonite. Synthetic wollastonite, in the same way as naturally occurring one, improves their hardness, resistance to wear and enhances antifriction characteristics.

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