Journal of the University of Chemical Technology and Metallurgy, 44, 3, 2009, 257-261

SILICA PRODUCTS FROM RICE HULLS

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Received 30 January 2009
Accepted 05 June 2009

ABSTRACT

Rice hulls are a waste product and their annual worldwide output is approximately 75 million tons. The purpose of this investigation is to find the solution for rice hulls utilisation, optimum for our country. The chemical analysis made shows a high content of amorphous SiO_2 *– 17.9 %. The optimum scheme for rice hull processing has been developed, which includes the recovery of thermal energy during their incineration and the production of silica products from the ashes.*

Keywords: rice hulls, silica products from ash.

INTRODUCTION

Rice hulls are a by-product of the rice industry, with their amount reaching 75 million tons worldwide [1]. In terms of properties they have a unique nature [2], low bulk density (below 150 kg/m^3), low water and moisture permeability, low value of equilibrium moisture content (below 10 % at an air relative humidity (RH) of 65 %), low value of the coefficient of temperature conductivity (below 0.036 W.m^{-1}.k^{-1}), high resistance to the action of harmful fungi, good anticorrosion properties to steel, aluminium and copper. The chemical composition of the ash in mass % is: Si – 94; SiO_2 – 4.4; Al_2O_3 – 0.61; K_2O – 1.06; Na_2O – 0.77; MnO – 0.59; CaO - 0.33; MgO – 1.21; Fe_2O – 0.03 [3].

Due to their characteristic properties and chemical composition the rice hulls have found application in construction, energy production, production of various chemical derivatives, etc. Most authors [4-8] and patents [9-13] relate their efficient use as a raw material source for production of amorphous silicon. The amorphous silicon finds wide application in various chemical idustries, such as ceramics, glass-making [14] , steel production, pharmaceuticals, rubber, plastics, refractory materials, cement, paints, soaps, polymer composites, refining of vegetable oils, etc. The processing of crystalline silicon from sand to an amorphous is a complex process that requires high temperature (1400-1500°C).

The aim of the investigation performed is to find the solution for rice hulls utilisation, optimal for our country, and to develop options for their processing.

EXPERIMENTAL

The physical characteristic of rice hulls was determined on samples (about 2 kg) taken from the regular production in the factory in Tsalapitsa.The following indices were determined: appearance, average linear dimensions, fractional composition, bulk density, percentage of water content and equilibrium moisture content. The tests were performed with standard methods used in production of wood particleboards. The result are obtainted in Table 1.

Rice hulls have very low bulk density (118 kg/m^3). This characteristic index is favourable for their use as an insulation material. At the same time, however, the

Table 1. Physical characteristics of rice hulls.

Average linear dimensions, mm	Fractional composition, %	Bulk density, kg/m^3	Equilibrium moisture content at 65% RH and T-20°C, %666
Length – 7.2 Width – 3.3 Thickness – 0.6	Above 2 mm – 2.5 1.0-2.5 mm – 77 0.6–1.0 mm – 15.5 below 0.6 mm – 2.5	118	10.89

Table 2. Chemical analysis of rice hulls.

Substances soluble in cold benzene 24h, %	Cellulose after Küschner-Hoffer, %	Lignin after modified Komarov method, %	Ash according to BDS ISO 2144, %
1.3	38.0	21.8	18.9

Table 3. Chemical analysis of rice hull ash.

Oxides content, % of oven-dry inorganic ash									
SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	ZnO	Mn	PbO
93.54	1.11	0.84	0.79	0.15	3.12	0.05	0.15	0.30	0.05

low bulk density of rice hulls makes them untransportable.

Rice hulls are a hygroscopic material, i. e. they change their equilibrium moisture content depending on temperature and relative air humidity. Under weather conditions typical for Bulgaria (average temperature 20°C and relative air humidity 65 %), the equilibrium moisture content of the rice hulls examined is 10.89 %. The value of this index is lower than that of wood (12 %) at the same parameters of the air environment. Rice hulls are a flammable material that burns with flame. For use as a fuel it is necessary to supply air to the incineration appliances. Their calorific value of 15.3 MJ/kg [1] is close to that of wood and other lignocellulosic materials.

The chemical analysis of the rice hulls (Table 2) shows that the values obtained do not differ substantially from those for wood and other plant materials ,used for production of pulp and panels.

The explanation for the observed unique properties of rice hulls should be sought in their considerable silicon content. For the specific rice hulls studied the analysis showed 18.9 % ash, which fully coincides with the literature data. The results obtained from the elemental chemical composition, recalculated for the inorganic part of the ash, are presented in Table 3. It is indicative that the amorphous SiO_2 is 93.54 %, potassium oxides are 3.12 %, iron oxides – 1.11 %, and the remaining oxides are in minimal amounts.

Therefore, in the rice hull ash from the factory of the Agra Grand company, only iron is present in a more tangible amount. When interpreting the results obtained, one should have in mind that depending on the incineration conditions the ash may contain different amounts of carbon residue than the unincinerated inorganic part of the rice hulls.

RESULTS AND DISCUSSION

Low-toxicity urea-formaldehyde resin (UF) with a hardener for cold bonding (20°C) – 10 % oxalic acid solution, epoxy resin, cement M450 with an additive for the solution of calcium chloride ($CaCl_2$) were used

Table 4. Physico-mechanical properties of panels made from rice hulls with different bonding substances, obtained under laboratory conditions.

Bonding substances	Density, kg/m^3	Bending strength, N/mm^2	Water absorption, %	Swelling in thickness, %
Epoxy resin – 20%	260 - 290	1.9 - 2.4	32 - 38	7 - 10
UF – 15%	270 - 330	1.8 - 2.3	51 - 63	23 - 31
Cement – (1:3:2)	480 - 580	1.1 - 2.7	65 - 78	3 - 5

in the investigation. The percentage ratio of the epoxy resin to the rice hulls (with a moisture content of 11 %) during the individual experiments was 10, 15 and 20 %. The percentage ratio of the UF to the rice hulls was 12 and 15 %. Two mixtures of rice hulls + cement + water mass were prepared : 1) 1:2:1.5 and 2) 1:3:2.

Data for the physico-mechanical properties of the panels made from rice hulls, obtained under laboratory conditions,and glued with different compositions of bonding substances, are given in Table 4.

The results obtained show that the panels made of rice hulls meet the requirements for insulation materials for the density index. For their hygroscopic properties, best results are obtained when using epoxy resin as a bonding substance (water absorption below 38 % and swelling in thickness below 10 %). The strength indices of the panels are relatively low, but for application as an insulation material they are completely satisfactory. The recommended quantitative composition of the mineral insulation panels is: hulls : cement : water = 1: 2,5: 1,8. An economic compromise solution for the amounts of the polymer bonding substances is: 15 % for the epoxy resin and 12 % for the urea-formaldehyde resin.

At the present stage, it is not rational to organise production of construction insulation panels from rice hulls for following reasons: complexity of plant and expensive equipment that is not economically justified in the case of the small capacity – below 15,000 m^3/year, availability of more competitive similar products (fibreboard, wood-fibre concrete, etc.), the desired consumer demand is not provided.

Series of laboratory experiments were conducted to obtain potassium solutions of silicon – potassium water glass. The investigations were performed in autoclaves rotating in a bath with polyglycol for 2 hours at 140°C with variation of the molal ratio SiO_2 : KOH from 1:1 to 2:1. Water glass with various viscosities was obtained, with amount of undissolved substances below 5 %.

Laboratory experiments were also conducted to obtain potassium water glass when heating on water bath at atmospheric pressure and molal ratio of 1:1. In this case, the established insoluble part of the ash was below 10 %.

The investigations performed show the possibility of producing alkaline silicon solutions from the rice hull ash. The products obtained are technical water glass. They are coloured dark brown because of the content mainly of iron compounds. To clean the ash from heavy metals, it is necessary to perform preliminary acid treatment.

Comparison of mechanical properties of vulcanisates based on butadiene-styrene rubber (Bulex-1500) filled with ingredients containing mainly silica (product of Bayer) and two products obtained from rice hulls was made. The one is almost pure silicon dioxide, and the second one also contains carbon with a definite grain size distribution.

The main elastomer mixture contains: butadiene-styrene rubber (Bulex-1500) 100 mole fractions (m.f.), zinc oxide – 5 m.f., stearic acid – 1.5 m.f., N-cyclohexyl-2-benzothiazolyl sulphenamide – 0.5 m.f., diphenylguanidine – 0.5 m.f., sulphur – 2 m.f. Upon preparation of the master batch, mixture No. 1 – silica (Bayer) 50 m.f. per 100 m.f. of elastomer; mixture No. 2 – silica obtained from rice hulls of the methods developed in the this work 50 m.f. per 100 m.f. of elastomer; mixture No. 3 – silica and carbon (incomplete combustion) to the amount of 50 m.f. per 100 m.f. of elastomer; mixtures Nos. 4 and 5 in the same mass ratios like mixtures No 2 and 3, respectively, after additional grinding, were added to the main mixture in an open two-shaft mixer. Rheograms of the elastomer mixtures obtained were taken on a Monsanto rheograph to

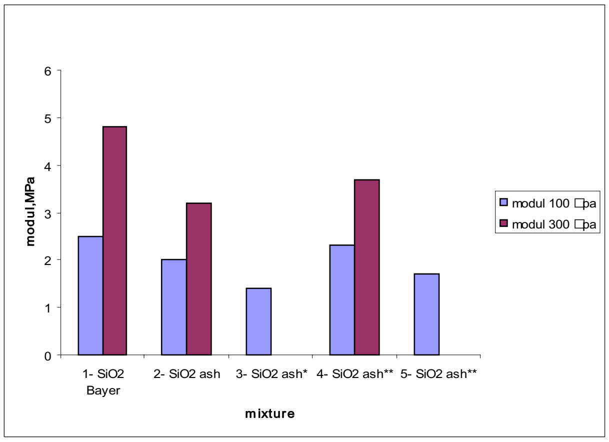

Fig. 1. Effect of SiO_2 content on the modull of flexibility *(incomplete combustion), **(ground), ***(incomplete combustion and ground).

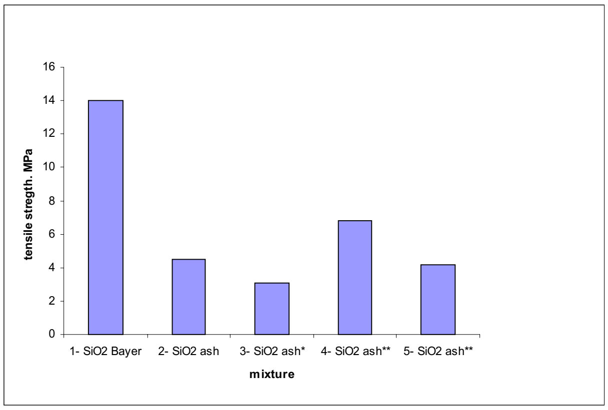

Fig. 2. Tensile strength, MPa *(incomplete combustion), **(ground), ***(incomplete combustion and ground)

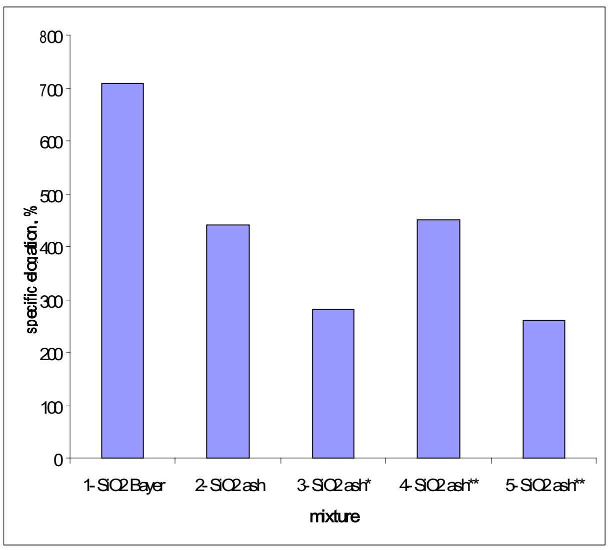

Fig. 3. Specific elogation % *(incomplete combustion), **(ground), ***(incomplete combustion and ground).

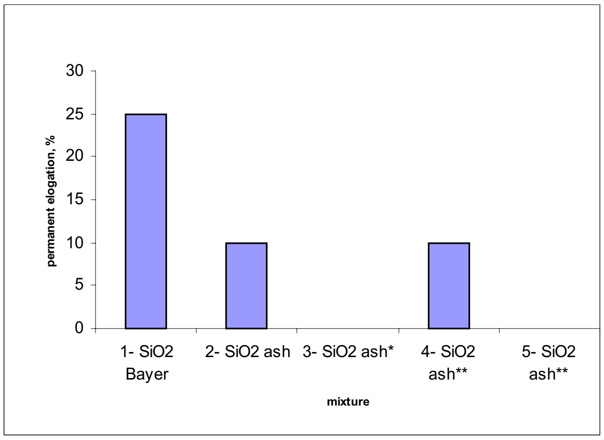

Fig. 4. Permanent elongation, % *(incomplete combustion), **(ground), ***(incomplete combustion and ground).

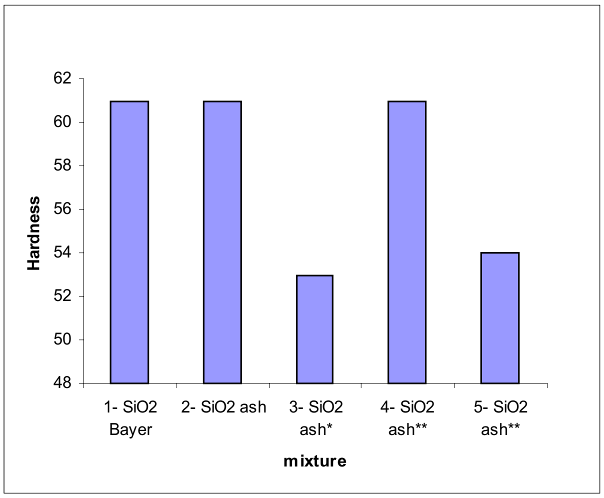

Fig. 5. Hardness, S *(incomplete combustion), ** (ground), *** (incomplete combustion and ground).

determine the time of vulcanisation at a temperature of 160°C. The vulcanisation of the test specimens was performed on a Metal List hydraulic press. The sheets are 2 mm thick. Test shovels were cut from the sheets obtained and the main mechanical indices of the vulcanisates – stress at 100 %, 300 % elongation, critical strength, specific and permanent elongation, Shore hardness, were determined with a dynamometer.

The experimental results obtained (Figs. 1-5) show that the process of with rice hull ash (compositions 2, 3, 4, 5) does not differ substantially from that in which standard silica is used. The reception and dispersion of the products is easy and does not load the mixing equipment, which is established by the instruments for measuring the effective power during processing.

The products obtained (2, 3, 4, 5) do not change the nature of the vulcanisation curve, obtained with Monsanto rheograph. The same rheograms confirm the possibility of using of the fillers obtained into industrial compositions. It should be noted that in the product with carbon, vulcanisates with uneven surface and eventually bubbles in the mass of the samples, are obtained. The tensile strength increases with the increase of the fineness of the silica products. The hardness measured byr the Shore method changes from 53 to 61 degree for the vulcanisates tested. The specific elongation is lowest for mixtures No 3 and 5 and highest for mixture No 1.

CONCLUSIONS

Rice hulls as a residual product in processing of unshelled rice may be utilised quickly and with small investment for production of ash with high content of amorphous silicon (above 90 %) and at the same time the thermal energy from their incineration may be used.

The rice hull ash is a marketing product with application in various spheres of the industry – production of water glass; strengthening filler in rubber; additive to cement and concrete to accelerate the hardening and increase their hydrophobic properties; in production of ceramics; etc..

It is found that the rice hulls ashes can replace successfully the standard SiO_2 in the vulcanization of the Styrene-Butadiene Rubber.

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