The impact of production temperature of synthetic wollastonite filled with rice husk on its composition and modifying effect

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Abstract. Due to finite reserves of naturally occurring wollastonite, production of its synthetic analog on the base of available and renewable raw materials is of paramount importance. In this aspect, the by-products of cereal-processing industry, in particular, rice husk, command great attention of manufacturers. The properties of synthetic wollastonite manufactured on the base of rice husk ash and limestone are affected by the proportion of these components at the greater extent, as well as the synthesis temperature and time defining its phase composition. In this regard, the authors of the paper have studied the impact of production temperature on the structure of synthetic wollastonite and its modifying effect in epoxy compositions as against naturally occurring mineral. The obtained synthetic wollastonite, regardless the synthesis temperature, primarily contains β-wollastonite and larnite as an admixture. For the cost-effective purposes, the optimum temperature for manufacturing synthetic wollastonite on the base of rice husk ash is 800°C. Both naturally occurring and synthetic wollastonite on the base of rice husk enhance hardness of epoxy coatings, whereas the former one increase it in a greater degree due to a higher presence of β-wollastonite of needle-like particles in its composition.

1. Introduction
Wollastonite is characterized by the whole spectrum of invaluable properties and has some advantages over other fillers widely applied in polymer industry. These properties comprise the following: lower values of water saturation factor, oil consumption, dielectric constant, viscosity, high abrasion resistance and thermal stability, needle-like particles shape, white colour and relatively low toxicity [1,2]. The microfibers of wollastonite contain calcium metasolicate minerals with an ample range of sources. Wollastonite is a white mineral that occurs in a needlelike form; its aspect ratios range from 3 to 20. The melting point of wollastonite is high, pH equals to 9.9, the specific gravity accounts for 2.9, and it exhibits low moisture absorption. Wollastonite is widely applied as a reinforcing filler and could compete with talc and mica. Applying wollastonite alone for the reinforcement purposes can decrease impact strength, and its abrasivity cause wear on processing equipment.

At the same time, the global volumes of extraction for naturally occurring wollastonite cannot cover the industrial demand. This necessitates the increase in industrial production of synthetic wollastonite on the base of cheap available raw materials [3].
In this aspect, special attention should be given to plant raw materials, in particular, the by-products of rice-processing industry [4]. The advantage of this that non dangerous chemicals or catalysts were used which reduce the pollution due to open burning or rice husk. Furthermore, no purification steps were necessary which helps in reducing the costing, waste dumping problem and shorten the overall process as well as release of toxic gases and hazardous chemicals due to burning rice husk ash.

The properties of synthetic wollastonite on the base of rice husk ash and limestone depend to a greater extent on the proportion of these components as well as temperature and time of synthesis determining its phase composition [5,6].

Due to this, the authors have studied the impact on synthesis temperature on the structure of wollastonite produced on the base rice husk if compared with naturally occurring mineral.

2. Materials and methods
For manufacturing epoxy compositions, there has been used epoxy diane resin ED-20 (All-Union Standard GOST 10587-84) hardened by aminoalkyl phenol APh (Technical specification TU 2492-052-00205423-2004) for 7 days at room temperature. The content of a hardener has been determined by the equimolar ratio [epoxy groups]:[amine].

As fillers, there have been used: synthetic wollastonite obtained from rice husk ash and limestone, at the ratio of CaCO$_3$:SiO$_2$ equal to 1.2:1 [7,8], at the temperature ranging from 800 up to 1100$^\circ$C during three hours; and naturally occurring wollastonite of the grade Miwoll 10-97 (Technical specification TU 5777-006-40705684-2003). The content of wollastonite in the composition has factored in 10 weight parts per 100 weight parts of epoxy oligomer.

The hardness tests have been carried out on the portable Barcol impressor in compliance with the All-Union Standard GOST 9013-50, ASTM B648-2000, ASTM D-2583. X-ray quantitative phase analysis has been done by means of the multifunctional X-ray diffraction meter Rigaku SmartLab at the following parameters: angular spacing from 3$^\circ$ up to 65$^\circ$ with the scanning pitch of 0.02, optical exposure 1 sec at the point. The analysis and interpretation of X-ray diffraction patterns has been implemented by the software PDXL-2 and the database ICDD PDF-2.

3. Results and discussion
Production of synthetic wollastonite is of actual practical importance as the increasing global demand in this effective filler of polymer materials is satisfied only by 40-45% due to use of natural mineral [3].

Rice husk ash (RHA) is considered as a perspective raw material for manufacturing synthetic wollastonite [7] as silicon dioxide being the constituent part of rice husk is amorphous and highly porous material. Thus, these two features precondition an active state of silicon dioxide [8]. It represents an agricultural by-product of rice-processing industry constituting about 20% of the weight of rice. It contains about 50% cellulose, 25–30% lignin, and 15–20% of silica. While burning rice husk, rice husk ash is generated. During the burning process, lignin and cellulose are removed, and only silica ash is left behind. The environment and temperature of burning yields an improved quality of rice husk ash whereas its particle size and specific surface area depend on burning condition. For every 1000 kg of paddy milled rice, about 20% of rice husk, i.e. 200 kg, is produced, and when this husk is burnt in the boilers, about 50 kg of RHA is generated that contributes to 25%. Burnt completely, rice husk ash is grey to white in color, when partially burnt product is blackish. RHA is a very fine pozzolanic material. The combined proportion of silicon dioxide (SiO$_2$), aluminium oxide (Al$_2$O$_3$) and iron oxide (Fe$_2$O$_3$) in the ash should be not be less than 70%, and LOI should not exceed 12% as stipulated in ASTM requirement.

As the second component for wollastonite synthesis, there could be used hydrate of lime produced from limestone. The limestone worldwide deposits are enormous and exceed 120 billion tons. Limestone is used to produce Portland cement, as aggregate in asphalt and concrete, and in an ample array of other products, making it a truly versatile commodity. Limestone are found almost throughout
the world, but only few deposits are easily and clearly identifiable. In many cases, the detailed tests are
required to determine the type of carbonate rock.

The figures 1 and 2 demonstrate X-ray diffraction patterns for the specimens of synthetic wollastonite with the proportion of calcium carbonate and silicon dioxide equal to 1.2:1. The patterns have been obtained at various temperatures during 3 hours of exposure.

Having analyzed the results of X-ray diffraction analysis, the authors identified the phase composition of the synthesized specimens of the filler. The results are presented in the table 1.

The obtained synthetic wollastonite, regardless the synthesis temperature, contains mostly \( \beta \)-wollastonite, with the grid parameters
\[
a = 7.906\text{Å}, \quad b = 7.302\text{Å}, \quad c = 7.048\text{Å}, \quad \alpha = 90.01^\circ, \quad \beta = 95.22^\circ, \quad \gamma = 103.43^\circ.
\]
consists of one layer of lattice cell of triclinic crystal system Spacegroup P-1(2) (database ICDD PDF-2, 01-084-0654).

As an admixture in the composition of synthesized filler, there has been found larnite, the silicate of two calcium molecules \( \text{Ca}_2\text{SiO}_4 \). It is high-temperature monoclinic Lpolymorphous analog of lime-olivine that is stable within the temperature range 520÷670°C. Larnite was found in skarn xenoliths in Kabardino-Balkaria, Lakargi. The structure of the mineral is based on a heteropolyhedral glaserite-like framework of interconnected Ca polyhedral and isolated \( \text{SiO}_4 \) tetrahedra. Larnite is a natural analog of the synthetic \( \beta \)-modification of \( \text{Ca}_2\text{SiO}_4 \). The structure of natural larnite, which is formed in calcic scarns in compliance with the conditions of the larnite-merwinite Korzhinsky facies at a low partial \( \text{CO}_2 \) pressure, still remains unstudied, partially because of its rare mineral manifestations, commonly in the form of fine-grained small precipitates. Larnite crystallizes at thigh temperature and its occurrence is confined to limestone or chalk zone where the contact with semi molten basalts is occurred. The presence of magnesium results in the formation of other high-temperature minerals, e.g. merwinite \( (\text{Ca}_3\text{Mg[SiO}_4])_2 \), bredigite \( (\text{Ca}_7\text{Mg[SiO}_4])_4 \), and alite \( (\text{Ca}_3\text{O[SiO}_4])_2 \).

These phases are structurally very dense and have been postulated as possible components in the Earth's mantle. At minimum, four polymorphs of \( \text{Ca}_2\text{SiO}_4 \) are known, and a few others are generally stabilized by impurities. They often could be found in silicate slags and clinkers.

As opposed to wollastonite with its chain structure, larnite is regarded as nesosilicate. Thus, it cannot ensure the same modifying effect as wollastonite. Due to this, the high content of larnite in the composition of synthetic wollastonite is undesirable.

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**Figure 1.** X-ray diffraction pattern for the specimen of synthetic wollastonite obtained at the temperature of 800°C.
Figure 2. X-ray diffraction pattern for the specimen of synthetic wollastonite obtained at the temperature of 1100°C

The table 1 demonstrates the composition of synthetic wollastonite on the base of RHA taken at various points throughout three hours.

Table 1. Composition of synthetic wollastonite obtained from rice husk ash at various temperatures during 3 hours

| Synthesis temperature, °C | β-wollastonite, % | Larnite, % |
|---------------------------|------------------|------------|
| 800                       | 75               | 25         |
| 850                       | 76               | 24         |
| 900                       | 77               | 23         |
| 950                       | 75               | 25         |
| 1000                      | 56               | 44         |
| 1050                      | 57               | 43         |
| 1100                      | 56               | 44         |

The results of the experimental tests show (table 1) that the greater content of β- wollastonite in the composition of synthesized filler is achieved when the temperature of its synthesis ranges within 800-950°C. These findings correlate with the data obtained in the paper [9].

According to the results of the previous researches [10,11], namely β-wollastonite, with its isodiametric particles shape, is regarded as an effective filler of polymer composite materials [12].

Thus, we can draw a conclusion that the optimum temperature for obtaining synthetic wollastonite on the base of rice husk ash is 800°C in reliance of energy saving aspects. Moreover, the synthetic filler contains β-wollastonite in the proportion close to a natural mineral that could predetermine its high modifying effect in the epoxy compositions hardened by amines.
Figure 3. X-ray diffraction pattern for the specimen of naturally occurring wollastonite of the grade Miwoll 10-97

In the phase composition of the specimen of natural mineral Miwoll 10-97, there could be found quartz (2% wt), clay mineral (chlorite and muscovy glass – 9% wt) as well as calcite (9% wt). The content of wollastonite with needle-like structure accounts for 80% approximately.

This mineral is characterized by modifications with triclinic crystal system, so-called β-wollastonite that is formed at the temperatures up to 1150°C [13].

Both naturally occurring and synthetic wollastonite on the base of rice husk enhance the hardness of epoxy coatings, whereas the former increases the hardness at a greater extent (fig. 4) due to a higher content of β-wollastonite with its needle-like particles shape. The results of the tests are presented in the figure 4 demonstrating the dependency of hardness of epoxy compositions as a factor of the applied filler type.

Figure 4. Dependency of hardness of epoxy compounds on the type of the applied filler: 1 – without filler; 2 – Miwoll 10-97; 3 – synthetic wollastonite with the molar ratio CaCO$_3$ and SiO$_2$ equal to 1.2:1, obtained at the temperature of 800°C.
4. Conclusions
Having based the opinion on the research results, we can draw a conclusion that the optimum temperature of obtaining synthetic wollastonite on the base of rice husk ash is $800^\circ$C. Along with that, the synthesized filler contains $\beta$-wollastonite in the quantity proximal to naturally occurring mineral. This ensures its high modifying effect in the epoxy compounds hardened by amines.

Both naturally occurring and synthetic wollastonite modified by rice husk significantly improve hardness of epoxy coatings, whereas the former one increase it in a greater degree due to a higher presence of $\beta$-wollastonite of needle-like particles in its composition.

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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