The impact of crystallite size of naturally occurring and synthetic wollastonite on its modifying effect in epoxy coatings

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Abstract. The efficiency of application and finiteness of raw material supply base of naturally occurring wollastonite leads to the fact that the synthesis of this filler on the base of available renewable raw material, for example, rice husk, is of actual importance. Depending on the ratio of calcium carbonate : silicon oxide (received from rice husk), synthetic wollastonite could have different phase constitution. It consists mainly of pseudowollastonite and wollastonite. Other silicates of lime, for example, larnite, could be also present in its composition. The maximum content of wollastonite was registered in the sample with the ratio CaCO₃:SiO₂=1.2:1 and it is significantly lower than of naturally occurring mineral Miwoll 10-97. Naturally occurring wollastonite demonstrates the highest modifying effect, from the perspective of wear reduction and harshness enhancement of epoxy coatings. Synthetic wollastonite obtained at the ratio CaCO₃:SiO₂=1.2:1 is slightly less efficient. Along with that, there could be observed the regularity that the larger the crystallite size of wollastonite, the higher its abrasion resistance and harshness of filled epoxy coatings. When the content of silicon oxide in the composition of synthetic wollastonite grows, the size of its crystals has a tendency to decrease. Given this, the synthesis of wollastonite should be directed towards the enlargement of its crystals size, i.e. it is recommended to increase the content of calcium carbonate in its composition and to lower fusion temperature in order to reduce pseudowollastonite formation.

1. Introduction
Wollastonite as a naturally occurring calcium metasilicate [1] could be seen as the most promising filler of polymer composites; the efficiency of its use is preconditioned, first of all, by needlelike structure of its crystals when the grains of aniso-diametric shape are formed at their disruption [2].

It is well known [3] that fillers with the great discrepancies in the linear dimensions of particles are oriented in polymer compositions performing reinforcing functions; this causes high modifying effect of naturally occurring wollastonite in epoxy materials [4].
Due to finiteness of raw material supply base of this mineral, the synthesis of synthetic wollastonite on the base of available resources, in particular of plant origin by-products, e.g. rice husk, is of utmost practical interest [5].

Along with that, identifying wollastonite structure could be seen as one of the important factors determining the efficiency of its application as a filler.

2. Materials and methods.

As fillers of epoxy materials on the base of diane resin ED-20 (All-Union Standard GOST 10587-84) cured by aminophenol APH-2 (technical regulations TU 2494-052-00205423-2004), the authors have used the specimens of synthetic wollastonite obtained at the temperature 1100°C during 3 hours on the base of natural silicon dioxide from the rice husk ash and limestone, when the molar ratio of CaCO₃ and SiO₂ were taken as 1.2: 1, 1: 1 and 1: 1.2 correspondingly [6]. For comparison, naturally occurring wollastonite Miwoll 10-97 (technical regulations TU 577-006-40705684-2003) was used.

Abrasion resistance of specimens has been tested of the vertical optimeter ISV-1 at unit area pressure of counter body on the specimen’s tested surface P=1MPa, sliding velocity \(V_{sl} = 1 \text{ m/sec}\) without lubrication.

Hardness was determined by the Barcol method in modification TPBa (All-Union standard GOST 9013-59).

X-ray diffraction phase analysis was done by means of X-ray diffraction meter Rigaku SmartLab, in the range from 3 to 65° 2θ, with the interval of 0.02 and optical exposure 1 sec in a point. X-ray diffraction patterns were analyzed and interpreted by the software PDXL-2 and the database ICDD PDF-2.

The data regarding the size of coherent scattering regions (CSR) have been obtained on the base of full-profile description of experimental X-ray diffraction pattern by the Pauli method [7] and the sequent analysis with the use of common formulas [8]. The computation of microstructural parameters was done by the Halder-Wagner approach [9].

3. The results and discussion

The results of X-ray diffraction phase analysis have shown that phase composition of synthetic wollastonite with the ratio \(\text{CaCO}_3:\text{SiO}_2=1.2:1\) is determined mainly by the presence of pseudowollastonite with the content reaching 60 % wt. The presence of wollastonite in this specimen accounted for approximately 20 % wt. Along with that, in its composition there could found other calcium silicates, for example, larnite (Ca₂SiO₅) with its content 20 % wt. (figure 1).
Figure 1. X-ray diffraction pattern of the synthetic wollastonite specimen obtained at the ratio of CaCO$_3$ and SiO$_2$ equal to 1:2:1.

The specimen of synthetic wollastonite with the ratio CaCO$_3$ : SiO$_2$ = 1:1 proved to be pseudowollastonite almost completely (92 % wt.) with the presence of larnite (7 % wt.) and wollastonite (1 % wt.) (figure 2). The traces of crystalline silica could also be found in the specimens.

Phase composition of the specimen with the ratio CaCO$_3$ : SiO$_2$ = 1:1.2 is also mainly presented by pseudowollastonite (85 % wt.) and wollastonite (15 % wt.) (figure 3).

When obtaining synthetic wollastonite, formation of larnite and pseudowollastonite could be explained by the fact that the optimal temperature and duration of synthesis of this filler had not been chosen [10].

Actually, pseudowollastonite, being a high temperature dimorph of wollastonite, is of mainly manmade origin and is formed at the temperatures exceeding 1150°C. It has monoclinic crystal system and contains isolated rings in its structure (Si$_3$O$_9$)$^-$ [10].
Figure 2. X-ray diffraction pattern of the specimen of synthetic wollastonite obtained at the ratio CaCO₃ and SiO₂ 1:1.

Table 1. Crystallite phase size for the specimens of naturally occurring and synthetic wollastonite

| Ratio CaCO₃ and SiO₂ in the composition of synthetic wollastonite | Crystal size, nm/ content % wt. |
|---------------------------------------------------------------|---------------------------------|
|                                                               | Wollastonite | Pseudowollastonite |
| 1.2:1                                                         | 4340/20      | 1150/60            |
| 1:1                                                           | 810/1        | 970/92             |
| 1:1.2                                                         | 2820/15      | 1190/85            |
| Miwoll 10-97                                                  | 5850/80      | -                  |
Figure 3. X-ray diffraction pattern of the synthetic wollastonite specimen obtained at the ration CaCO$_3$ and SiO$_2$ 1:1.2.
In the phase composition of naturally occurring mineral Miwoll 10-97, there could be found both silica (2 % wt.) and clay minerals (chlorite and potash mica – 9 % wt.) as well as calcite (9 % wt.). The content of wollastonite with needlelike structure factors in approximately 80%. This mineral is characterized by modification with triclinic crystal system, so-called $\beta$-wollastonite, formed in the temperature interval not exceeding 1150 °C.

All the phases in the investigated specimens are thoroughly crystallized as the climaxes of X-ray diffraction patterns are clearly exhibited. This allowed carrying out the full-profile analysis of all the specimens and identifying the crystallites’ size through computation of the coherent-scattering region (table 1).

Naturally occurring wollastonite has the maximum modifying effect, from the point of reduction of wear resistance and enhancement of hardness of epoxy coatings; among the researched synthetic fillers it is the one obtained at the ratio $\text{CaCO}_3:\text{SiO}_2=1.2:1$ (table 2).

**Table 2.** Wear resistance and hardness of filled epoxy materials.

| Type of the filler     | Wear resistance, $x10^{-6}$ m | Hardness, HV |
|------------------------|-------------------------------|--------------|
| Non-filled polymer     | 19                            | 31           |
| Miwoll10-97            | 11                            | 42           |
| Synthetic wollastonite with the molar ratio CaCO$_3$ and SiO$_2$: equal to 1.2: 1 | 12 | 38 |
|---------------------------------------------------------------------------|----|----|
| Synthetic wollastonite with the molar ratio CaCO$_3$ and SiO$_2$: equal to 1: 1 | 14 | 35 |
| Synthetic wollastonite with the molar ratio CaCO$_3$ and SiO$_2$: equal to 1: 1.2 | 13 | 37 |
Thus, the interrelation between the crystallite size of wollastonite and efficiency of its modifying action in epoxy compositions are clearly observed. The larger the value of this characteristic parameter of filler’s structure, the higher wear resistance and hardness of epoxy materials filled with wollastonite.

4. Conclusions
The obtained experimental data confirm that the content of wollastonite in the composition of synthetic calcium methylsilicate and the crystals size of this filler depend on the ratio of silica dioxide and calcium.
carbonate. The size of the crystal is reduced with the growth of silica oxide content in the composition of synthetic wollastonite.

It was demonstrated that epoxy materials filled with wollastonite with the maximum crystal size have the maximum wear resistance and hardness.

Based on the above stated, it is worth directly synthesizing wollastonite with the maximum crystal size, i.e. trying to increase its content in the calcium carbonate composition and to lower the synthesis temperature to 1100°C in order to avoid formation of pseudowollastonite.

At the same time, with the decrease of the pseudowollastonite content in the composition of synthetic calcium methylsilsiclate, the properties of filled materials improve and substantially do not depend on the size of its crystallites. Thus, pseudowollastonite cannot be considered as perspective filler for obtaining wear resistant epoxy coatings.

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