DOI 10.31891/2307-5732-2021-303-6-247-250
УДК 544.722.132

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THE USE OF HYDROPHOBIZED PERLITE AS THE BASE LAYER OF SUPERHYDROPHOBIC COATINGS

The development of superhydrophobic materials technology is limited due to low mechanical stability of coatings, complexity of scaling and relatively high cost. One possible way to solve this problem is to use technologies that are used for conventional coatings, such as creating a surface texture by using functionalized fillers. The article considers an example of a method of obtaining such coatings by mechanical grinding of foamed perlite. The geometry of crushed perlite particles, the shape and particle size distribution of their fragments formed during grinding were characterized in the work. An effective surface modifier has been selected to provide superhydrophobic properties and the possibility of forming coatings based on these materials has been established. The structure and water-repellent properties were also characterized. As a result, it is shown that the use of crushed material with hollow particles on the example of expanded perlite after chemical surface treatment is a possible way to obtain coatings with high water-repellent properties. The created systems have a stochastic structure and relatively high values of the wetting angle - up to 140°. The properties of crushed perlite particles were determined - the average particle size is 15 µm, the shape of the fragment and the possibility of modification using siloxane processing agents. In particular, it has been shown that the use of polymethylhydrosiloxane for modification provides its chemical binding on the surface of perlite. The layer of treated particles has a marginal wetting angle of up to 150° and a rolling angle of less than 4°. These particles were successfully bonded with a styrene-acrylic polymer matrix, which led to the formation of coatings with high hydrophobicity at filler levels above 50 wt. %.

Keywords: perlite, superhydrophobic, contact angle, water repellent coatings, organo-mineral composite.

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ВИКОРИСТАННЯ ГІДРОФОБІЗОВАНОГО ПЕРЛІТУ ЯК БАЗОВОГО ШАРУ СУПЕРГІДРОФОБНИХ ПОКРИТТІВ

Розвиток технології супергідрофобних матеріалів обмежено через низьку механічну стійкість покриттів, складність масштабування та відносно високу вартість. Один із можливих шляхів вирішення цієї проблеми – застосування технологій, які використовуються для звичайних покриттів, наприклад створення текстури поверхні за рахунок введення функціоналізованих наповнювачів. У статті було розглянуто приклад способу отримання таких покриттів шляхом механічного подрібнення спіненого перліту. У роботі було охарактеризовано геометрію спучених частинок перліту, форму та гранулометричний склад їх уламків, що утворилися у процесі подрібнення. Підібрано ефективний модифікатор поверхні для забезпечення супергідрофобних властивостей та встановлена можливість формування покриттів на основі цих матеріалів. Також було охарактеризовано структуру та водовідштовхувальні властивості. В результаті показано, що використання подрібненого матеріалу з порожнистими частинками на прикладі спученого перліту після хімічної обробки поверхні є можливим способом отримання покриттів з високими водовідштовхувальними властивостями. Створені системи мають стохастичну структуру та відносно високі значення крайового кута змочування – до 140°. Були визначені властивості подрібнених частинок перліту – середній розмір частинок складає 15 мкм, форма осколка та можливість модифікації за допомогою агентів обробки силоксану. Зокрема, було показано, що використання поліметилгідросилоксану для модифікації забезпечує його хімічне зв'язування на поверхні перліту. Шар оброблених частинок має значення крайового кута змочування до 150° та кута кочення – менше 4°. Ці частинки були успішно пов'язані стирол-акриловою полімерною матрицею, що призвело до утворення покриттів з високою гідрофобністю при рівнях наповнювача вище 50 мас. %.

Ключові слова: перліт, супергідрофобний, кут змочування, водовідштовхуючі покриття, органомінеральний композит.

Formulation of the problem

The technology of superhydrophobic materials is a promising direction, but its development is limited by the insufficient mechanical sustainability of coatings, the complexity of scaling, and the relatively high cost of texturing. One of the possible ways to solve this problem is the use of approaches from the coatings industry: using a mixture of micro- and nano-sized fillers. To obtain suitable textures on their base, preference should be given to such fillers, the shape of the particles of which minimizes the contact of the liquid with the surface. The paper considers an example of a way for producing such particles by mechanical grinding of expanded perlite, which is a solid foam with a low density and a small thickness of interchamber partitions.

Analysis of recent research

Superhydrophobic coatings are water-repellent materials with a specific surface structure, with water contact angle more than 150 degrees, and the roll-off angle less than 10 degrees [1]. Such coatings can be obtained by fabrication of hierarchical textures on micro and nano-level with low intrinsic surface tension. Today, superhydrophobic coatings have a number of problems: difficult scaling, low mechanical sustainability and high cost [2], which makes impossible to use such coatings on large objects. This is partially solved by the application of technologies that are used for conventional coatings, for example, the creation of surface textures through the introduction of functionalized fillers. One of the available options is the use of micro-sized mineral natural fillers [3]. One of perspective candidates is crushed spherical filler due to the geometry of the fragments [4].

To obtain the effect of superhydrophobicity, the surface of the particles of such materials must be treated with low energy compounds.

In [5] the surface of perlite was modified by the applying of polyhexafluorobutyl acrylate in rotating plasma reactor. It was stated that this method does not damage the fine microstructure of perlite. However, this modification is technically difficult and expensive and superhydrophobic properties of the material is not well estimated.

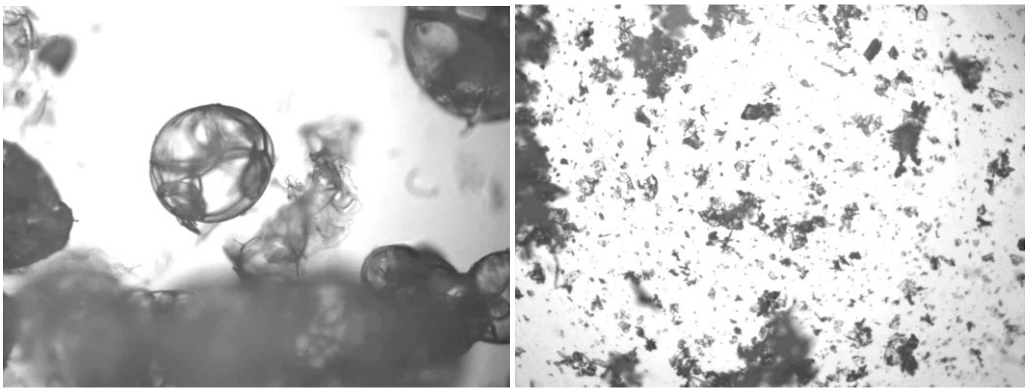
The aim of the paper is to establish the performance of microstructured superhydrophobic base coatings in case of use ground hollow particle materials, particularly, the perlite.

To achieve the above mentioned aim, the following tasks of the work were formulated: to characterize the geometry of expanded perlite particles, the shape and the particle size distribution of their shards, that were formed during the grinding, to select an effective surface modifier to provide its hydrophobic properties, to establish the possibility of superhydrophobic coatings formation on the base of these materials, characterize their structure type and water-repellent properties.

Presentation of the main material

To determine the surface energy in the Owens-Wendt model, mixtures of ethanol and water at different concentrations were used [6]. The contact angles were determined using a digital goniometer. To analyze the morphology of a water drop on the surface, a Delta Optical HCDE-50 digital camera (China) and the corresponding ScopeTek View software (China) were used. The following water repellents were used in the work: DOWSIL HV 495 (Dow inc., USA), DOWSIL 87 (Dow inc., USA), Xiameter MEM-0347G (Dow inc., USA), Xiameter PMX-0156 (Dow inc., USA), Xiameter MHX-1107 (Dow inc., USA).

The geometry of expanded perlite particles was determined by means of optical microscopy (Fig. 1(a)). It may be seen that particles of 30 g/l perlite have a configuration of glassy foam - merged thin wall spheres. The thickness of these walls is in range of 2–5 μm with non-uniform distribution throughout the particle. Material particles are surrounded by a debris, that is predictable if consider a low mechanical robustness of such solid foams. However, the majority of internal voids of spheres remain closed even at the start of mechanical destruction, which provides a stability of material's low density.



a *b*

Fig. 1. Optical microscope photos: of *a*) pristine perlite; *b*) grinded perlite

The material preparation procedure included mechanical grinding of perlite particles in a mortar and sieving the resultant powder through 63 μm opening sieve. The shape of resultant product particles may be seen at Fig. 1 (b). It is mostly flat particles with irregular geometry, sometimes transparent due to their thickness, aggregated with smaller residue particles.

The size of perlite foam shards was determined as a largest possible distance between two points on the particle projection using ScopePhoto instrumentation and may be seen at Fig. 2. An average particle size lays in the range between 10 to 20 μm and the system has comparatively low quantity of elements larger than 40 μm. Together with this – there is a significant volume of tiny particles below 10 μm (and possibly of lower sizes out of the measurement range).

The particle size distribution here is wide and polyfraction, but it may be assumed that it may be sufficient for the micro-structure level forming in case of hierarchical superhydrophobic coatings.

The surface of perlite particles was treated with different hydrophobizing agents of the siloxanes class. The material was merged in the media with predetermined content of the siloxane fluid (or emulsion - in such case the treatment was performed in water) at room temperature for 1 h, filtered and dried at 130 °C, then an excess of hydrophobizer was flushed with media and dried repeatedly.

The effectiveness of the surface modification was determined on a dry layer of powder by placing a water drop with volume 40–60 mkl and estimation of contact and roll off angles. The results of such test (Table 1) showed that almost all hydrophobizers tested provide a value of contact angle of powders above 140°, that may be considered as high for a system with only micro-scale roughness.

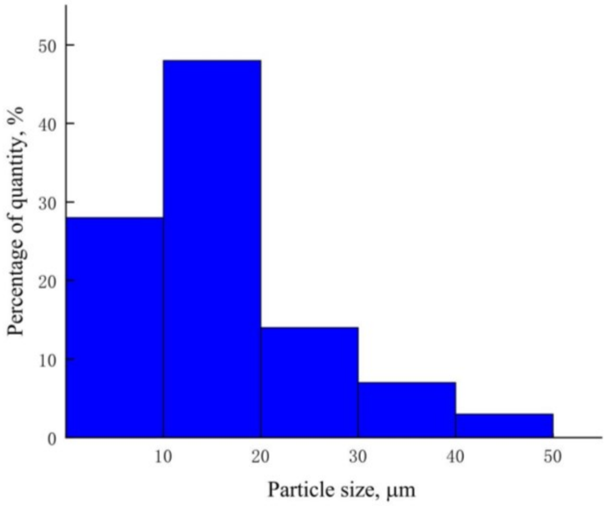


Fig. 2. The particle size distribution of ground perlite

Table 1

Siloxane treatment agents effectiveness

Hydrophobizer	Contact angle, deg.	Roll angle, deg.
DOWSIL HV 495	144.6	17
DOWSIL 87	143.3	19
Xiameter MEM-0347G	145.5	29
Xiameter PMX-0156	150.0	9
Xiameter MHX-1107	145.7	4

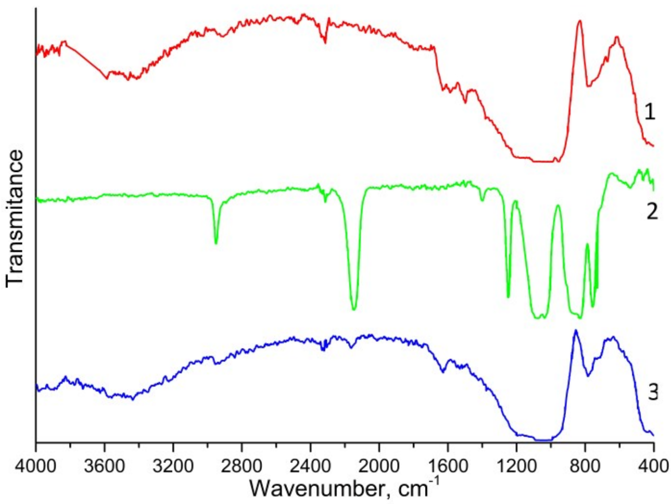


Fig. 3. IR spectra of systems:
1 – Grinded perlite; 2 – Xiameter MHX-1107; 3 – Treated grinded perlite

The roll off angles, however, fall below 10° in case of only two surface modifiers – Xiameter's 0156 and 1107 liquids and, thus, these systems may be considered as superhydrophobic. The latter silane product was selected for the further work.

The interaction between the surface of ground perlite and siloxane treating agent was studied using IR spectroscopy (Specord IR-75, KBr pellet pressing technique for sample preparation). Considering the fact that Xiameter 1107 liquid is a polymethylhydrosiloxane having an active Si-H bonds that able to interact with a silanol and hydroxyl groups on a fresh perlite surface. The spectrum of siloxane fluid (Fig. 3, curve 2) proves the technical data. Absorption bands at 2960 cm^{-1} relate to the stretching vibration of methyl side groups of siloxane, sharp band at 2170 cm^{-1} - to the presence of Si–H functional group [7] the band at 1260 cm^{-1} – $Si\text{-}CH_3$ bending, 1120 cm^{-1} – Si-O-Si bond and 1000 cm^{-1} – Si–O bond [8]. The perlite spectrum (Fig.4, curve 1) indicates the presence of O-H groups of adsorbed water (broad band at 3500 cm^{-1}), wide Si-O band at 1200–1000 cm^{-1}. The spectra of the product of an interaction between the perlite surface and siloxane modifier (Fig 3, curve 3) in weight ratio 100:1,7 contains bands of siloxane at 2960 cm^{-1} and 2170 cm^{-1}. The intensity ratio change of these bands (in comparison to pristine siloxane at Fig. 3, curve 2) indicates the fact of partial consumption of Si–H groups by the perlite surface active centers.

Above mentioned facts and the sustainable water repellency of the modified particles layer let us to conclude that the siloxane undergoes covalent linking to a surface of perlite to some extent. However, it is possible that some fraction of the liquid remains physically bonded on a surface via weak Van-der-Waals interactions.

The modified powder was used to create a coating system on a base of styrene-acrylic polymer (SA). The preparation procedure included the dissolution of SA in the solvent (o-xylene), adding a predetermined quantity of perlite, dip coating of glass slides with this suspension and drying in environmental conditions. An effective content of perlite was determined with the contact angle measurement (Fig. 4).

It may be seen that adding the polymer into the system slightly decreases the value of contact angle in comparison with a pure treated powder. The maximum values of contact angle are reached at filler content above 50 wt. % and are in the range 135–142°. The shape of the curve may be explained by the formation of the matrix-depleted type of a composite at its certain content. After the threshold of 50 wt. % the sustainable surface structure with open pores is formed, that provides the realization of Cassie state of the water droplets during the test.

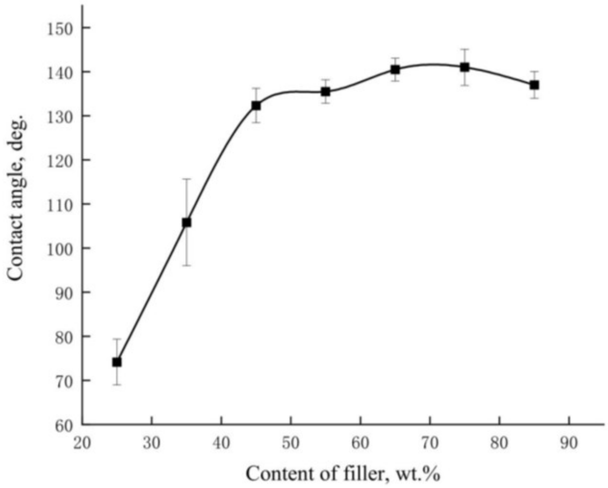


Fig. 4. Contact angle of ground siloxane modified g round perlite – styrene-acrylic polymer coatings

The top-view of a coating is shown at the Fig. 5. It may be distinguished that it is of stochastic type: some fraction of ground perlite shards is directed upwards, particles are aggregated and some major (hundreds of microns) and minor (tens of microns) elements of this structure are present.

In general, the fabricated coating shows a high level of water-repellent ability in comparison to alike systems on a base of treated micro-sized fillers and the shard-like geometry of particles looks like more promising, taking into account the fact that in this case it seems to provide higher texture elements that will increase the sustainability of Cassie state.

Conclusions

It was shown that the use of ground hollow particle material, on the example of expanded perlite, after chemical surface treatment is a possible way to obtain coatings with high water-repellent properties. The systems have a stochastic structure and relatively high contact angle values – up to 140°.

The properties of grinded perlite particles were determined – the average particle size of 15 µm, shard-like shape and the ability to be modified with the siloxane treatment agents. In particular, it was shown that using polymethylhydrogen siloxane provides it's chemical bonding on the perlite surface. Treated particles layer have a contact angle values as high as 150° and rolling angle – below 4°. These particles were successfully bonded by a styrene-acrylic polymer matrix resulting in formation of coatings with high hydrophobicity at filler content levels above 50 wt. %.

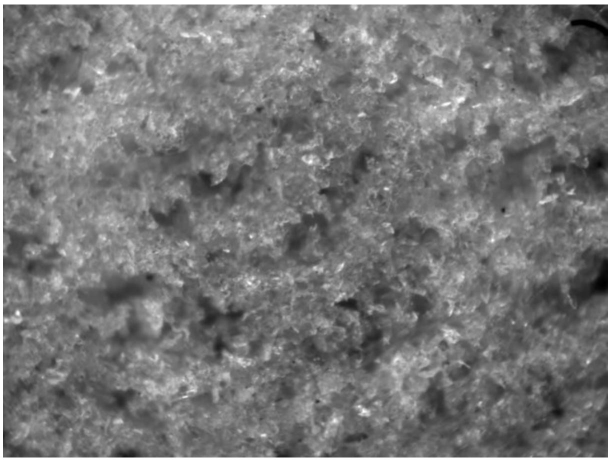


Fig. 5. Photo of coating of modified ground perlite with 1107 and styrene-acrylic resin

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Рецензія/Peer review : 04.12.2021 Надрукована/Printed :30.12.2021