

Analysis of Surface Adhesion and Physico-mechanical Properties of Construction Ceramics Hydrophobized by Polymers with the Addition of Nanosilica

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Abstract – The article describes the research on the effectiveness of hydrophobisation of ceramic brick surface by using a formulation based on polymers. Each series of the specimens is subjected to a process of hydrophobization on the surface by immersion for 15 s by using polymer, the structure which was further modified by the addition of nanosilica and sonicated with power of 400W. In order to determine the average absorption of polymer by the samples in the respective series before the hydrophobization, the specimens were dried to a constant weight and weighed. Then, after 14 days of immersion in the formulation, samples were weighed again to determine the percentage change in the weight relatively to the weight of the dried sample. Hydrophobic properties of the nanofilm created on the surface of the brick were determined by measuring the surface free energy γ_s (SFE) with the use of Owens – Wendt method through the designation of contact angles of specimens surface with distilled water (strongly polar liquid) and diiodomethane (apolar liquid), dispersive component γ_{sd} and the polar component γ_{sp} (expressed in mJ/m^2). The effect of polymer use and the method of modifying the structure to the hardness of the samples in relation to the hardness of the standard samples was determined. In order to measure the hardness, the Vickers method was applied with a load of 10 kgf. On the basis of the obtained results, the effect of sonification and nanosilica use on some adhesive and physico – mechanical properties of tested material surface was specified.

Keywords: Polymers, Nanosilica, Surface free energy, Hydrophobization, Sonification.

1. Introduction

Construction materials which include ceramic brick and hollow brick fired out of clay, after installation can be destroyed due to moisture, salinity or stress caused by freezing in the pores and capillaries as shown previously (Tittarelli, 2009). The porous structure of these materials is characterized by a tendency to hold moisture and water in its volume significantly affecting the physico - mechanical properties such as strength, frost resistance, water absorption, durability, thermal insulation, described by Hall, (1984). One way of securing elements made of ceramics from the destructive effects of moisture is hydrophobising (shown by Fowkes, 1969) by using polymers, shown by Barnat – Hunek, (2010). Polymers as solutions, by applying to the surface of ceramics, by the use of different techniques such as painting, spraying under pressure, immersion and saturation, are introduced into the porous structure and to a varying degree fills the voids in the volume of a material. After glazing, polymer on the surface forms a nanofilm which limits the penetration of moisture and water, thereby increasing its strength and other physico-mechanical properties, as shown by Fic (2014).

In this article the impact of fine particle formulation based on alkyl-alkoxy-silanes with the addition of nanosilica to adhesion and physico-mechanical properties of ceramic brick after hydrophobization were evaluated.

Absorption of polymers into the structure of a tested material is dependent on the pore diameter and the particle size of chemical compounds in solution, as shown by Łukasiewicz, (2002). The process of preceding final shaping of nanofilm is very complex due to solution conformation on phase boundary (as previously described by Chlibowski, 1997). In the final phase, the solution becomes glazed and a surface protection of material shall be subjected to the fatigue in the operating conditions. The process of

destruction of material by low cyclic fatigue caused by moisture and temperature gradient starts from the places where there are defects in the material, and in subsequent phases it is followed by their gradual escalation (described by Hall 1984 and Neville, 2012). One of the many methods of measuring the physico-mechanical properties of the material surface is to assess the glazing (Fic, 2014). The degree of plastic deformation of the material can be determined by measuring the hardness, as shown by Dietrich (2009). Hardness measurements can be used to assess physical properties of nanofilm and be helpful in choosing the composition of polymer.

Another important parameter are the adhesion properties of the top layer of nanofilm. As a measure of this size, the surface free energy (SFE) was used, shown by Żenkiewicz, 2007. SFE is one of the thermodynamic functions (shown by Neumann, 1996) describing the equilibrium on the surface of tested material, and is a characteristic property assigned to each physical body (Hutchinson, 2006). The size of surface free energy can be determined by few methods: Fowkes, Owens – Wendt, Wu, Naumann, as shown by Kaczmarzeski (2006). In this article the SFE measurements by method of Owens – Wendt were described by measuring the polar and dispersive component. The individual components depend on interactions at the phase boundary (liquid – solid). Polar component depends on the resulting interaction with nature chemical mainly – polar (shown by Wu, 1973), hydrogen bonds (shown by Oss et. Al., 1986), acceptor - donor, acid – alkaline, inductive. Dispersive component is, however, dependent on the size of the dispersion of the liquid and has a close relationship with the liquid absorption on solid surfaces (shown by Bangham, 1937).

2. Materials and Devices Used in Research

The tests were performed on 5 series in which each series consisted of 6 specimens. Samples were cut from the ceramic brick characterized by the following parameters:

- bulk density – 1,69 kg/m³,
- total porosity – 33,6%,
- water absorption – 12%
- compressive strength – 10 MPa.

The samples were then dried to constant weight, weighed and subjected to hydrophobization with a formulation based on alkyl-alkoxy-silanes and the characteristics:

- viscosity $\eta = 1,479 \cdot 10^{-3}$ Pa·s,
- surface tension $\sigma = 23,11 \cdot 10^{-3}$ N/m,
- ratio of surface tension to viscosity $\eta/\sigma = 15,63$,
- density at 20 °C – $\rho = 0,80$ g/cm³.

Water parameters for comparison, adopted the following values:

- viscosity $\eta = 0,89 \cdot 10^{-3}$ Pa·s,
- surface tension $\sigma = 72 \cdot 10^{-3}$ N/m,
- ratio of surface tension to viscosity $\eta/\sigma = 80,90$,
- density at 20 °C $\rho = 0,99$ g/cm³.

Cutted brick specimens were hydrophobized by their total immersion for 15s in the properly prepared polymers solutions on the basis of fine particle alkyl-alkoxy-silanes.

A series of specimens used in the tests (with the recipe of polymer):

Series 1 – specimens immersed in a solution of polymer for 15s,

Series 2 – specimens immersed in a solution of polymer for 15s which was previously disintegrated by sonification for 15 min,

Series 3 – immersion in a solution of polymer with the addition of the nano- and microsilica in amount of 0,5% by weight of polymer – the mixture was disintegrated by sonification for 15 min,

Series 4 – immersion in a solution of polymer with the addition of the nano- and microsilica in amount of 1,0% by weight of polymer – the mixture was disintegrated by sonification for 15 min,

Series 5 – immersion in a solution of polymer with the addition of the nano- and microsilica in amount of 1,5% by weight of polymer – the mixture was disintegrated by sonification for 15 min.

In addition, the two specimens of series 1 and 2 were re-immersed in a solution of pure polymer whose structure was not disintegrated by sonification (signature 1a and 2a).

Disintegration of the solutions was carried out by using a stationary laboratory sonicator with UP400 pad of power of 400 watts. The device is certified DIN-EN ISO 9001.

All samples were stored for 14 days in laboratory conditions at 20 - 22°C and relative humidity 50 - 55%. After this period, the surface free energy of solution was measured on the specimens of each series by Owens – Wendt method, according to the equations (shown by Titarelli, 2009; Żakiewicz, 2007):

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad [\text{mJ/m}^2] \quad (1)$$

$$(\gamma_s^d)^{0,5} = \frac{\gamma_d \cdot (\cos\theta_d + 1) - \sqrt{\frac{\gamma_d}{\gamma_w}} \cdot \gamma_w (\cos\theta_w + 1)}{2 \left[\sqrt{\gamma_d^d} - \sqrt{\gamma_d^p \cdot \frac{\gamma_w^d}{\gamma_w^p}} \right]} \quad (2)$$

$$(\gamma_s^p)^{0,5} = \frac{\gamma_w \cdot (\cos\theta_w + 1) - 2 \sqrt{\gamma_s^d \cdot \gamma_w^d}}{2 \sqrt{\gamma_w^p}} \quad (3)$$

where:

- γ_s – free surface energy,
- γ_s^d – dispersive component of free surface energy of tested material,
- γ_s^p – polar component of free energy of tested material,
- γ_d – free surface energy of diiodomethane,
- γ_w – free surface energy of water,
- γ_d^d – dispersive component of free surface energy of diiodomethane,
- γ_w^d – dispersive component of free surface energy of water,
- γ_d^p – polar component of free surface energy of diiodomethane,
- γ_w^p – polar component of free surface energy of water,
- θ_d – contact angle with diiodomethane,
- θ_w – contact angle with water,

In the determination of free surface energy, two measuring liquids are used: first liquid- distilled water that is strongly polar liquid as its polar component is 51mJ/m² with a total free surface energy value of 72,8mJ/m²; polar component of diiodomethane of a second liquid is 2,3mJ/m² with total free surface energy of 50,8mJ/m².

Angle measurement θ (described by Neumann et. al., 1999; Yuan et. al 2013) is formed by a drop of liquid with the test surface determined on the basis a computer program „NIS – Elements D” and measuring instrument - the goniometer.

Then the surface microhardness of the samples after hydrophobisation in all series in Vickers Zwick - Roell device was examined with a load range of 200 kgf. The measurements were made and automatically read on the basis of the imprint made after the quadrangular proper pyramid indentation in the surface of the tested material. Microhardness was defined as ratio of the force applied on the sample surface to the surface of imprint. For each sample, the hardness measurement in amount of 25 was performed, taking as base load of 10kgf.

3. Analysis of the Results

The measurement of surface free energy and its components – polar and dispersive and contact angle with the surface of tested material, allowed to determine the actual hydrophobic properties obtained by the use of polymer modified by additives and sonification.

The measurement results of the free energy components (dispersive and polar) are shown in Table 1, but their graphic chart in Figure 1.

Table 1. Surface free energy γ_s and its components – polar surface energy γ_s^p and dispersive free energy γ_s^d

Series designation	γ_s [mJ/m ²]	γ_s^d [mJ/m ²]	γ_s^p [mJ/m ²]
series 1	43,63	38,37	5,26
series 1a	18,02	17,00	1,02
series 2	11,42	10,41	1,01
series 2a	10,38	9,74	0,64
series 3	10,44	9,78	0,66
series 4	8,25	7,68	0,57
series 5	11,40	10,28	1,12

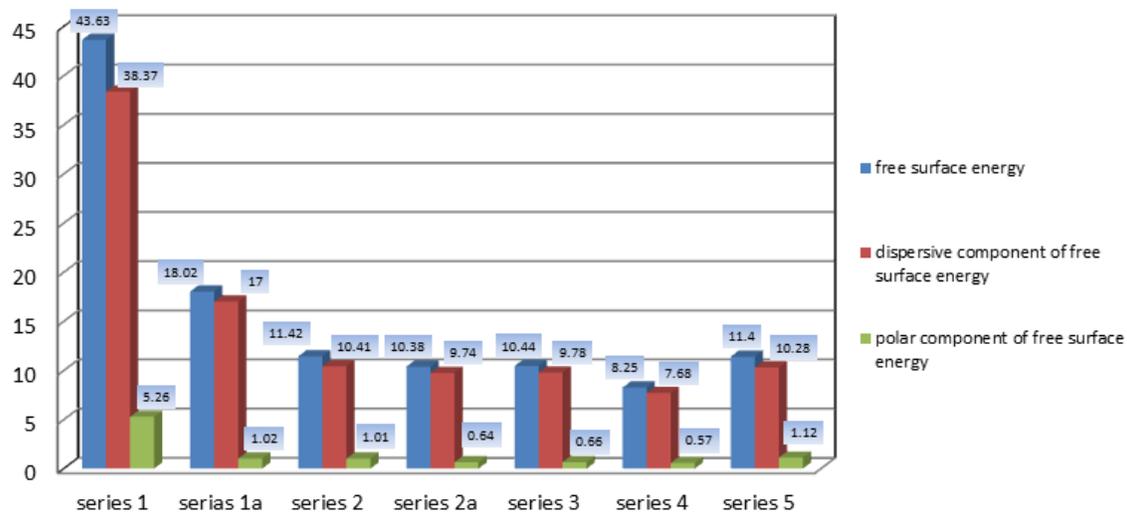


Fig. 1. Free surface energy and its components.

Figure 2 shows the shape of a drop of distilled water and diiodomethane at the surface of the specimen of series 1, together with an indication of the contact angle.

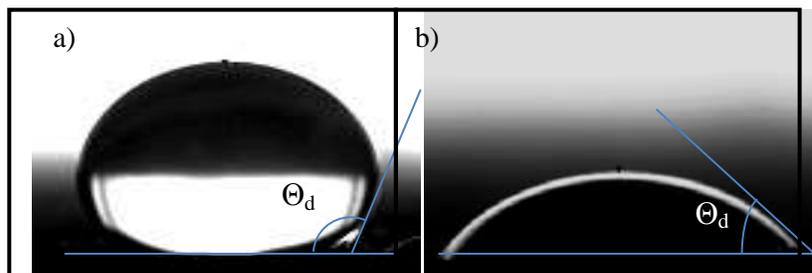


Fig. 2. Drops on the surface – a) water , b) diiodomethane; θ_d – contact angle.

From the obtained results, it can be concluded that the surface free energy decreases in the case of disintegration of the polymer structure by sonification (table 1). Series of samples immersed in a solution of an ordinary polymer have a higher surface energy by 3,8 times - higher are both the dispersive (3,7 times) and the polar components (5,2 times) in comparison to the samples immersed in the sonificated preparation. It should also be noted that re-immersing the specimens of series 1 in the hydrophobising

formulation causes a reduction of surface free energy and thereby increases the hydrophobic properties of the surface of the bricks. A significant impact on the size of the SFE has the use of sonification - as a result of the disintegration and destruction of the original structure of polymer. Ultrasound energy absorbed by the polymer particles causes a number of phenomena: spot heating, the movement (vibration of molecules), and partial melting of the polymer which facilitates mixing of the mass. This phenomenon is closely related to the adhesion and the formation of mechanical microjoints consisting of polymer particles injection (under external pressure) in the pores of the more permanent material - in this case the test brick. Another factor significantly contributing to the reduction of SFE is the use of nanosilica as a component of polymer – in this particular case the sonification makes nanosilica enter the structure of polymer. This is demonstrated by the images made with the scanning electron microscope SEM and analysis of the surface of the test samples as shown in Fig. 3.

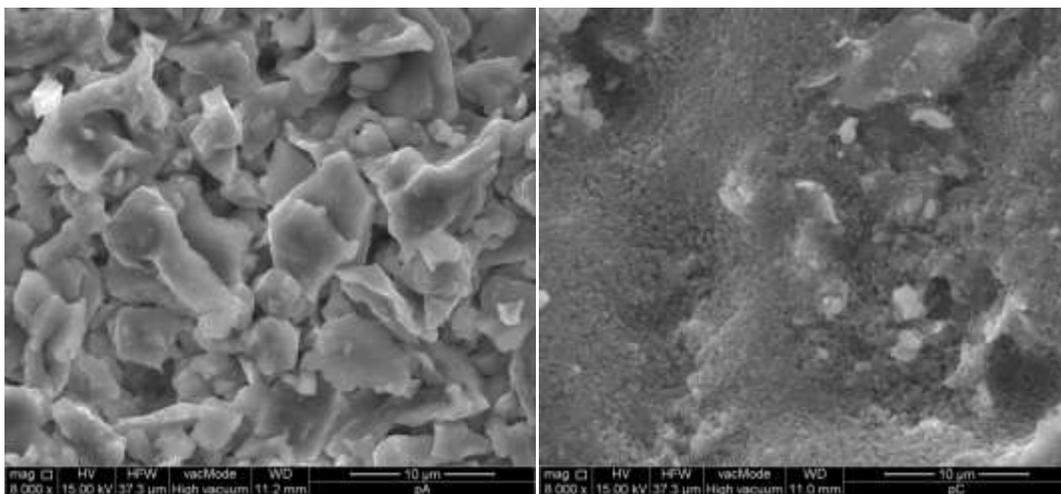


Fig. 3. SEM microscope image of the specimens surface: a) series 1, b) series 5.

The SEM study, shown in Figure 3 shows the image of the characteristic shape of the specimen surface immersed in a solution of polymer (Fig. 3a) and immersed in a solution of polymer subjected to sonification and with 1,5% addition of nanosilica (Fig. 3b). Images show a clear difference in shaped grains of crystallized polymer. The structure and grain size of the sample series 5 is clearly ordered, homogeneous with grains of equal shape in comparison to the sample series 1. On this basis it can be concluded about the positive impact of addition of nanosilica and sonification on the formation of nanofilm at the surface of brick sample. The result is a low value of the polar component of the surface energy (with a relatively small value of the dispersion component). The relationship between the SFE components values can also be seen on the example of contact angles determined for two liquids – for samples of series 1 value θ_d ranges between 40° and 65° , value θ_w - about 130° , while for specimens of series 4 θ_d clearly rises to $102 - 110^\circ$. For this reason, the resulting coating is more effective, because it prevents the absorption of both: polar character liquid (water) and organic solvents (apolar). It is worth noting, however, that there is no strict relationship between the amount of nanosilica and surface energy values – the lowest value of SFE, and so, consequently the best hydrophobic properties achieve the samples of series 4, with a nanosilica content equal to 1%.

Subsequently, the percentage of absorption of the hydrophobic preparation was checked and determined as average gain of specimens mass of each series expressed as percentage. The registered absorption measurements are presented in Table 2. The obtained results (Table 2) show that the samples from series 1 reached the highest absorption – 0,51%. The value of absorption for series 2 was lower (0,42%). The samples immersed in polymer with the addition of nanosilica were characterized even lower absorption – the lowest absorption reached the samples from series 3 (0,26%). It is worth mentioning that gain of specimens mass after re-immersing for series 1 is larger than for a series 2a.

The next step was to determine the surface hardness of the samples measured after a period of 14 days assuming the load value equal to 10 kgf.

The results of measurements of the surface hardness (after statistical verification) are shown in Table 2, and their graphic illustration is shown in Figure 4.

Table 2. The results of the polymer absorption and surface hardness.

Series of samples	Average absorption [%]	Average hardness HV10	Percentage change of HV [%]
Ceramic brick	-	7,767	0
Series 1	0,51	9,896	27,41
Series 1a	0,63	10,823	39,34
Series 2	0,42	11,296	45,43
Series 2a	0,45	13,03	67,76
Series 3	0,26	12,658	62,98
Series 4	0,29	12,876	65,78
Series 5	0,32	13,325	71,56

The evaluation of the surface hardness of the tested samples was made assuming as the pattern the element from ceramic brick which was not subjected after the drying process to hydrophobisation. Surface hardness measurements on samples in which the solution was treated by ultrasounds, and with additions of nanosilica showed significant changes in physico – mechanical properties. By pressing the pyramid in the surface, the plastic deformation in the material was reached in the area of imprint.

Among the tested samples, the lowest plastic deformation was registered on the surfaces of series 5 specimens (with the addition of 1,5% of nanosilica). Comparing the samples which were once coated by the preparation (series 1) to samples series 5, the difference in the surface hardness was 44,15%. The data obtained from the measurements reflect the plastic changes of tested material and they are generally limited to the surface of tested samples.

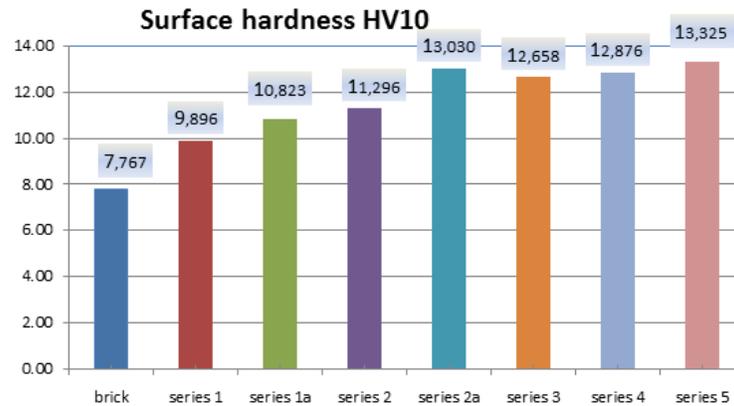


Fig. 4. Results of surface hardness testing.

It is important in the case of hydrophobization since under operating conditions and under the influence of temperature and humidity gradient, the plastic deformation associated with the local deformations, the movement of dislocations as well as the segregation of the elements can lead to extrusion and intrusion at the phase and grain boundary.

4. Summary and Conclusions

On the basis of obtained results, it is concluded that the disintegration of the polymer structure by using sonification is an effective method leading to the increase of the hydrophobic properties of material surface which was hydrophobised. A number of processes in solution of sonicated polymer caused a marked reduction in the surface free energy values, particularly the polar component that is greatly influenced by the properties of the tested hydrophobic surfaces. It should also be noted that the addition of nanosilica (with simultaneous ultrasonic agitation) not only caused a significant increase in contact angles for both highly polar liquid (distilled water) and the apolar liquid (diiodomethane), but also increased the surface hardness of the test samples. It should be emphasized that the brick as a heterogeneous, porous material, requires a carefully prepared samples to be tested because the heterogeneity of material causes noise in measured values, which may result in necessary remeasurement. The tests and their analysis may be helpful in practical use as a guideline which improves the security of porous building materials against moisture and water. The applicability of the modified in this way polymer in practice results in greater resistance to mechanical damage and, consequently, the loss of hydrophobic nanofilm.

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