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The Effectiveness of Hydrophobisation of Building Ceramics by Sonificated Polymers

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Abstract- The article describes the studies of efficacy of ceramic brick surface hydrophobisation by preparations based on alkyl-alkoxy-silanes (nanopolymer) and silicones (micropolymer). The different series of specimens were subjected to a process of surface hydrophobisation by immersion for 15 s using the hydrophobizing formulations, whose structure was further sonificated by power of 400 W. In order to determine the average absorption of nanopolymer by specimens in respective series, before the hydrophobisation samples were dried to a constant weight and weighed. Then, after 14 days of their immersion in the formulation, specimens were weighed again in order to determine the percent change in the sample weight to the weight of the dried sample. The impact of ultrasonic energy on the viscosity of the polymer (measured by Ostwald viscometer) and on the surface tension (measured by stalagmometer) was determined. The hydrophobic properties of the resulting nanofilm created on the surface of the ceramic brick were determined on the basis of the measurement of surface free energy γ_s (SFE) by using Owens – Wendt method measuring the sample surface contact angles with distilled water (highly polar liquid) and diiodomethane (a polar liquid) to determine the dispersive γ_{sd} and polar γ_{sp} components (expressed in mJ/m^2). Based on the results, the effect of sonification on some adhesive and physico – mechanical properties of the tested material surface was determined.

***Keywords*:** polymers, surface free energy, viscosity, surface tension, hydrophobisation, sonification

1. Introduction

Construction materials which include ceramic elements fired from clay, such as ceramic brick and hollows, can be destroyed due to destructive activities of moisture, salinity or stresses caused by freezing water in the pores and capillaries as previously shown (Tittarelli, 2009). The porous structure of these materials is characterized by a tendency to keep the moisture in its volume, which significantly affects the physico – mechanical properties such as strength, frost resistance, water absorption, thermal insulation described by Hall, (1984). One of the most common ways of securing the elements made of construction ceramics from the destructive effects of moisture is hydrophobising (shown by Fowkes, 1969) by solutions based on nano- and micropolymers shown by Barnat – Hunek, (2010). Polymers as solutions, applied to the ceramic surface by different techniques such as painting, spraying under pressure, immersion and saturation, are introduced into the porous structure and to varying degrees fill the voids in the volume of the material. After glazing the polymer forms a nanofilm on the surface of the material limiting the penetration of moisture and water and thereby increasing its strength and other physico – mechanical parameters as shown by Fic (2014). The structure of the nanofilm depends on the primary structure of the used polymer and has a close relationship to the size and arrangement of chemical particles.

This article investigated the impact of fine particle formulations based on alkyl-alkoxy-silanes (series 1) and silicones (series 2), whose structure was originally disintegrated by sonification, on the adhesive and physico – mechanical properties of ceramic brick after hydrophobisation. The effect of sonification on the surface free energy value, viscosity and surface tension of the two polymer solutions was compared.

The pore diameter of the porous material, particle size and the rheological properties of polymer affect its absorption at the sample surface as shown by Łukasiewicz, (2002). The final configuration of the nanofilm on the surface of the material is a complex process influenced by the conformation of the solution molecules at the boundary of liquid and solid phases, as previously described by Chlibowski, (1997). In the final stage, the polymer solution becomes glazed as the material is subjected to fatigue under operating conditions. The destruction of the material due to moisture and temperature gradient starts from the sites where there are defects in the material and in subsequent stages gradual escalation of degradation occurs (described by Hall, 1984 and Neville, 2012). One of several methods to determine the physico – mechanical properties of the material surface is to assess the glazing process (Fic, 2014).

Among the rheological properties of polymers determining their ability to penetrate into the porous structure of the material, the most important parameters are the viscosity and the surface tension. Viscosity is a property resulting from the shear stresses in the fluid causing its flow and characterized by the internal friction of the fluid caused by the relative movement of the particles, shown by Schramm (1998). Viscosity depends on many factors: physico – chemical properties of the liquid, temperature, shear rate, time and pressure. Surface tension is a property characterizing intermolecular interactions resulting from the existence of chemical bonds and cohesive forces in relation to the interface of two phases, for example: liquid – solid.

The most important parameters which determine the effectiveness of the hydrophobisation are the adhesive properties of the coating which, depending on the used polymer solution, may vary. As a determination of magnitude, the measurement of surface free energy (SFE) was used, shown by Żenkiewicz, 2007. SFE is one of the thermodynamic functions (shown by Neumann, 1996) describing the state of equilibrium on the surface of the tested material and is a characteristic value proper to every physical body (Hutchinson, 2006). The magnitude of surface free energy can be determined by methods: Fowkes, Owens – Wendt, Wu, Naumanna, as shown by Kuczmaszewski (2006). In this article, SFE was studied by the Owens – Wendt method by measuring the polar and dispersive components. The individual components depend on interactions at the liquid – solid phase boundary. The polar component depends on resulting interactions whose nature is mainly chemical - polar (shown by Wu, 1973), hydrogen bonds (shown by Oss et. al., 1986), acceptor – donor, acid – alkaline or induction. The dispersive component is, however, value dependent on the size of the dispersion of the liquid and has a close relationship with the adsorption of liquids on solid surfaces (shown by Bangham, 1937).

2. Materials and devices used in research

The tests were performed on 4 series in which each series consisted of 5 specimens. Samples were cut from the ceramic brick characterized by the following parameters:

- Bulk density – 1,69 kg/m^3,
- Total porosity – 33,6 %,
- Water absorption – 12 %
- Compressive strength – 10 mpa.

The samples were then dried to constant weight, weighed and subjected to hydrophobisation using the two formulations with the following characteristics:

FORMULATION 1 - polymer based on alkyl-alkoxy-silanes:

- viscosity $\eta = 1{,}08 \cdot 10^{-3}$ Pa·s,

- surface tension σ = $23{,}51 \cdot 10^{-3}$ N/m,
  - ratio of surface tension to viscosity σ/η = 21,59,
  - density at 20 °C – ρ = 0,81 g/cm^3.

FORMULATION 2 – polymer based on silicones, diluted with water in ratio 1:8 (polymer/water):

- viscosity η = $0{,}981 \cdot 10^{-3}$ Pa·s,
- surface tension σ = $77{,}24 \cdot 10^{-3}$ N/m,
- ratio of surface tension to viscosity σ/η = 78,735,
- density at 20 °C – ρ = 1,026 g/cm^3.

Water parameters for comparison, adopted the following values:

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

Cut brick specimens were hydrophobized by their total immersion for 15 s in the properly prepared two polymer solutions of fine particle alkyl-alkoxy-silanes and silicones.

A series of specimens was used in the tests related to the polymer:

Series 1 – specimens immersed for 15 s in a solution of nanopolymer based on alkyl-alkoxy-silanes,

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

Series 3 – immersion for 15 s in an aqueous solution of micropolymer based on silicones,

Series 4 – immersion in a solution of micropolymer which was previously disintegrated by sonification for 15 min.

Disintegration of the solutions was carried out using a stationary laboratory sonificator 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):

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad [\mathrm{mJ/m^2}] \tag{1}$$

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

$$(\gamma_s^p)^{0.5} = \frac{\gamma_w \cdot (\cos\theta_w + 1) - 2\sqrt{\gamma_s^d \cdot \gamma_w^d}}{2\sqrt{\gamma_w^p}} \tag{3}$$

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: firstly, liquid distilled water being a strongly polar liquid with polar component equal to 51 mJ/m^2 and a total free surface energy value of 72, 8 mJ/m^2; secondly, the liquid polar component of diiodomethane equal to 2, 3 mJ/m^2 with total free surface energy of 50, 8 mJ/m^2.

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

To determine the rheological properties of polymer solutions the viscosity measurements were performed with an Ostwald viscometer over a measurement range of 0, 5 – 2, 0 mPa·s and surface tension was measured using a capillary stalagmometer.

In the final stage of the study, an analysis of the structure of the surface film based on photos taken with a scanning electron microscope (SEM) was also carried out.

3. Analysis of the obtained results

The first stage of the study was to measure the viscosity and the surface tension of the polymer solutions in order to determine the effect of sonification on their rheological properties. Results of this study are presented in Table 1.

Table 1. Viscosity and surface tension of polymer solutions

Series	Density [g/cm^3]	Viscosity η [mPa·s]	Surface tension σ [N/m]	Quotient σ/η
1	0,81	1,09	0,0235	21,59
2	0,79	1,07	0,0231	21,48
3	1,03	0,98	0,0771	77,24
4	1,00	0,91	0,0622	62,35

The conducted studies of the rheological properties of the solutions show that the sonification caused a decrease in the values of viscosity and surface tension of both nanopolymer solutions based on siloxanes as well as silicone based micropolymer. This is most evident in the case of the surface tension of the formulation based on an aqueous polymer solution. The change in values is closely linked with a decrease in the density of the solutions which affects their absorption on the surface of the porous structure of the ceramic brick. Lower viscosity and surface tension make the penetration of polymer into the pores of the ceramic material and the formation of tight coating easier. It is important that the ultrasonic energy reduces the magnitudes of the above mentioned parameters without changing the chemical composition of the polymer. These values can be adjusted by selecting the appropriate power, frequency, amplitude and sonification acting on the solution.

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

The measurement results of the free energy components (dispersive and polar) are shown in Table 2 and their graphic chart in Figure 1.

Table 2. Surface free energy γ_s and its components – polar surface energy γ_{sp} and dispersive free energy γ_{sd}

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 2	11,42	10,41	1,01
Series 3	12,88	12,44	0,46
Series 4	12,40	12,18	0,22

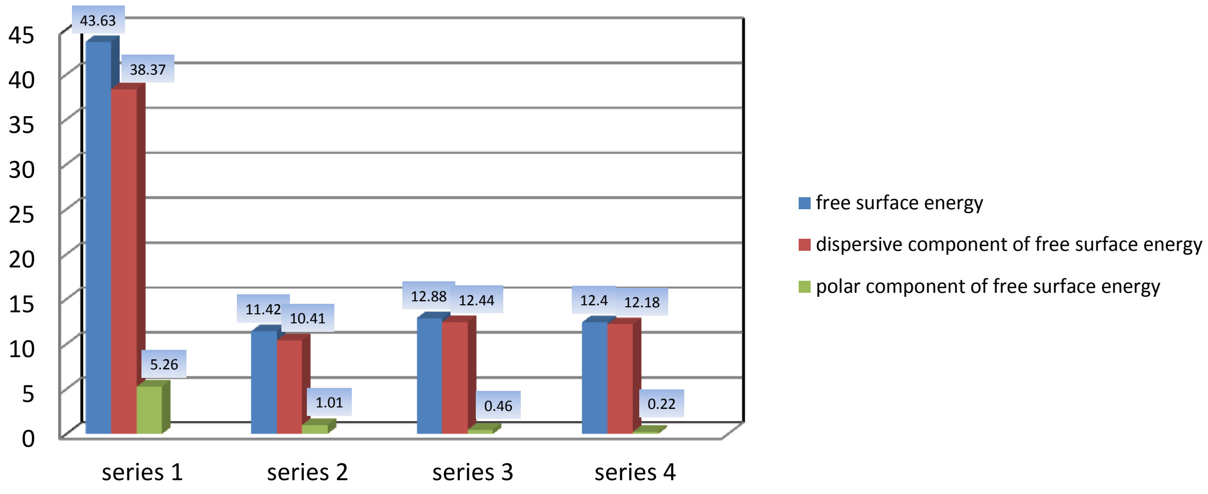


Fig. 1. Free surface energy and its components

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.

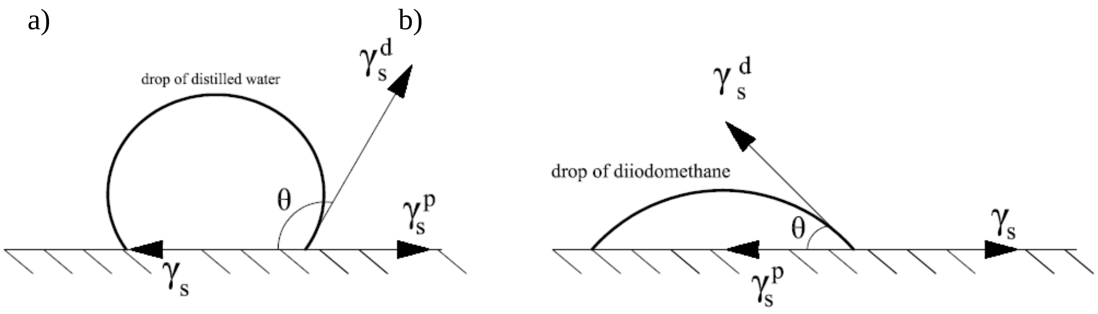
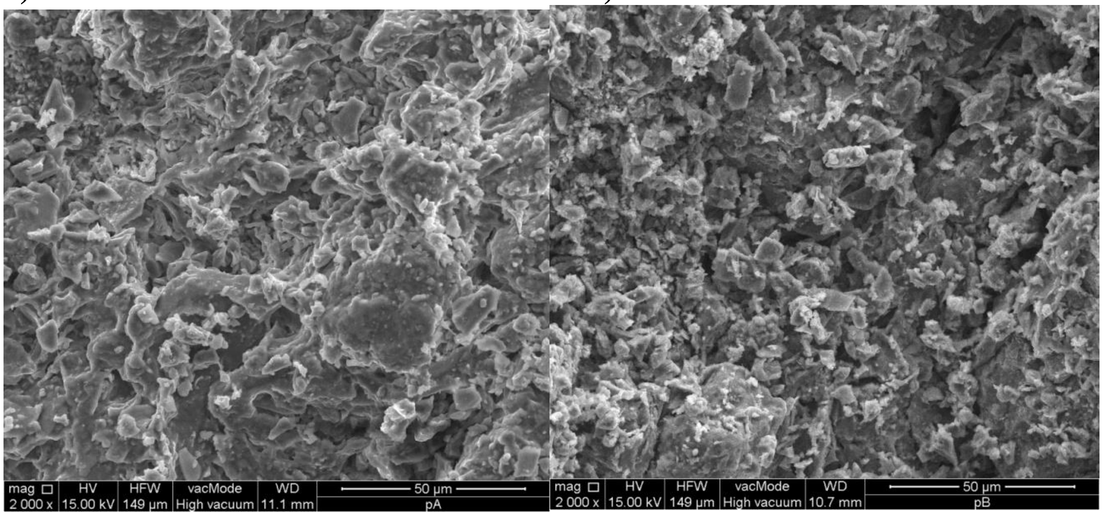


Fig. 2. Drops on the surface – a) water, b) diiodomethane; θ – contact angle

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). The 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. In the case of a preparation based on aqueous solution of micropolymer, the differences were not so significant – the total surface free energy of the samples of series 3 is 1, 04 times greater than energy value of the specimens of series 4; in the case of the dispersive component, the values for series 3 are 1, 02 times higher, the polar component 2, 1 times higher. However, the small values of

SFE of series 3 and 4 in relation to specimens of series 1 should be noted. The polar component value is especially very small for the samples of series 4 – it is 4, 6 times less than the value of this component for series 2. The relationship between the values of the individual components of the SFE can also be seen in the contact angles determined for the two liquids – for samples of series 1 the average value of θ_d was 50°, θ_w value approximately 130°; for samples of series 2 the value of θ_d clearly rose to 95° with the θ_w equal to 139,5°; for samples of series 3 the value of θ_d was 92,5°, θ_w was 125°; and for series 4 the value of θ_d reached 91°, θ_w was 128,5°. For this reason, the resulting coating is more effective because it prevents the absorption of polar liquid (water) and organic solvents (a polar). A significant impact on SFE size results from the use of sonification as a result of the disintegration and destruction of the original structure of polymer and its secondary reorganization on the sample surface. 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 micro-joints resulting from the injection of polymer particles under external pressure into the pores of the more permanent material in this case, the test brick. On analyzing pictures of the surfaces of tested samples using a scanning electron microscope SEM, the characteristic structure of a film formed on the surface of bricks can be observed. For specimens of series 1 and 2 the structure is more ordered than the samples of series 3 and 4. This is closely related to the nanostructure of alkyl-alkoxy-silanes polymer. The impact of sonification is visible in the formation of film on the brick surface, it is clearer and uniform. The image of specimens of the surfaces of each series is shown in Fig. 3.


a) b)

The SEM research, shown in Fig. 3. shows the image of the characteristic shape of the specimen surface immersed in solutions of polymer: Fig. 3a – the surface of the sample immersed in nanopolymer; Fig. 3b – the surface of the sample immersed in nanopolymer disintegrated by sonification; Fig. 3c – the surface of the sample immersed in the aqueous solution of micropolymer; Fig. 3d – the surface of the sample immersed in the aqueous solution of micropolymer disintegrated by sonification. The SEM photos show the difference between the structure of nanopolymer and micropolymer surfaces. The pictures show the lumpy structure of the resulting layers. Depending on the type of polymer, the crystal size of polymers varies – the greatest degree of fragmentation is shown for specimens of series 2 for which the primary structure of nanopolymer was disintegrated by sonification while the largest lumps are visible on the image of specimens of the series 3 surface. Lump size depends not only on the ultrasound action but also on the chemical structure of the polymers themselves – in the case of samples series 1 and 2 the bases for polymer are siloxanes particles, which penetrate more easily into the structure of ceramic brick. In the series 3 and 4 the bases for polymer are macromolecular silicones that form a uniform coating on the surface of the sample but penetrate into the ceramic material capillaries to a lesser extent.

The effect of sonification and the particle size resulting from the type of polymer used for absorption on the brick surface can also be seen by analyzing the chemical composition of the resulting film on the surface of the sample. The average percentage content of Si (silica is an essential component of siloxanes and silicones and consequently formed the film) on the specimen surface of series 1 was 29, 18% while for samples of series 2 the value equaled to 26, 56%. A similar situation occurs in the case of an aqueous solution of micropolymer – for samples of series 3 the average content of Si was 62, 3%, with 61, 3% in the case of samples of series 4. The relatively small difference has to do with the size of the polymer particles whose basic components are silicones. Siloxanes, as compounds having lower durability and chemical resistance than silicones, are faster and more easily fractured under the influence of ultrasonic energy than the particles of silicones. Therefore, the content of SiO_2 on the surface of samples series 3 and 4 is greater than for series 1 and 2, because the portion of nanopolymer was absorbed on the inner surfaces of the pores and capillaries of the brick, which in turn resulted in a decrease in the surface free energy. It should be noted that the application of ultrasonic achieves similar hydrophobic properties on the brick surface regardless of the type of polymer.

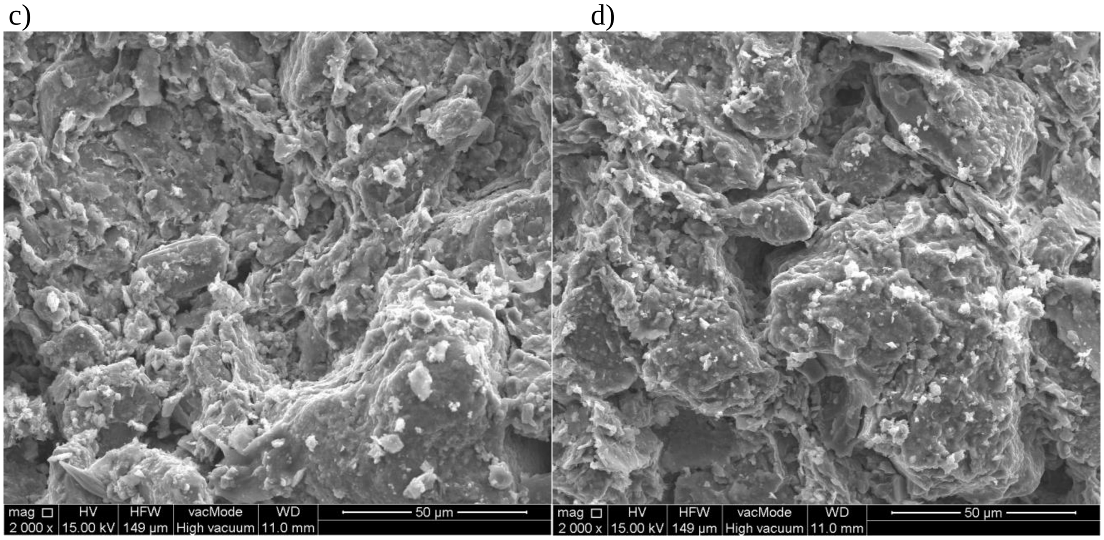


Fig. 3. SEM microscope image of specimens of the surfaces of: a) series 1, b) series 2, c) series 3, d) series 4

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 an increase in the hydrophobic properties of material surfaces which were hydrophobised. A number of processes in solutions of sonicated polymer caused a marked reduction in the surface free energy values, particularly the polar component that is greatly reflected in the properties of the tested hydrophobic surfaces. Sonification resulted in a change in the density of each polymer consequently lowering their viscosity and surface tension. The decrease in the SFE values is affected by the type of polymer used, its chemical structure resulting from particle size and disintegration caused by sonification. It should be emphasized that the brick as a heterogeneous, porous material, requires carefully prepared samples to be tested because the heterogeneity of material causes noise in measured values, which may result in a necessary re-measurement. The tests and their analysis may be helpful in practical use as a guideline to improve the security of porous building materials against moisture and water. The applicability of this modified polymer in practice results in greater resistance to water and increases the durability of the built-in ceramic materials especially in historic buildings.

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