TRIBOLOGICAL ANALYSIS OF GEOPOLYMERS COATED WITH MODIFIED EPOXY COATINGS AND AFTER PLASMA TREATMENT

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Abstract

This paper investigates the properties of epoxy based coatings modified with antimicrobial metal nano- and microparticles. Surface modifications have been applied to geopolymer materials in order to improve their properties. Samples of modified epoxy coating with 1% of copper or silver nano- or microparticles were prepared, applied on geopolymer samples and their tribological properties were investigated by linear reciprocating tribological test and drop test to measure change in wear resistance and hydrophobicity. Properties of coatings on geopolymer samples treated with cold, atmospheric plasma were also investigated to determine its effect on adhesion between epoxides and geopolymer, as well as other properties of the coating, as plasma may be used to increase adhesion of various coatings, thin layers and other surface modifications.

Keywords: Geopolymer, epoxy coating, wear resistance, microparticles, nanoparticles, hydrophobicity, metal

1. INTRODUCTION

Geopolymers, as named by Joseph Davidovits in 1970s, are ceramic-like inorganic materials formed by polycondensation of various aluminosilicate precursor materials [1], including metakaolin [2] or fly ash [3], in strongly alkaline environment, usually produced by water solution of hydroxides and/or silicates of alkali metals. They are a potential alternative to OPC (Ordinary Portland cement) based materials for use as a construction materials [4], as when compared to OPC based materials, geopolymers have higher compressive strength [5], resistance against high temperatures [2] etc. Like OPC based materials, geopolymer properties may also be enhanced by the use of various aggregates or additives (similar to concrete), including sand, silica fumes (amorphous silicon oxide nanoparticles) and various types of fibers [6]. They may also be used for multitude of other special applications, such as passive fire protection [2] or insulation [7], especially in foamed form with low heat conduction, or fixation of various waste materials, some of which may even improve geopolymer properties and serve as substitute for aggregates or additives. These materials may include various slags or other industrial by-products, such as coke dust waste [8] or byproducts of aluminium industry [9].

Both geopolymers [10] and OPC based materials [11] are susceptible to microbially induced degradation, especially in humid environment, as their surface may be colonized by alkali-resistant bacteria, usually sulphur-oxidizing bacteria. These bacteria produce acidic compounds, which lower pH of geopolymer surface and allow its colonization by other microorganisms, which may lead to chemical and/or mechanical degradation of geopolymer. Various methods of surface protection are used or investigated, including epoxide coatings [12]. Metal nanoparticle additives were also investigated as a potential antimicrobial aditive to epoxy coatings [12]. Various hydrophobic or epoxy-based coatings are already commercially available for the surface protection of concrete.

In this study, nano- and micro-particles made of silver and copper were used to modify a commercially available epoxy coating called Izolak. The research is focused on evaluating the effect of surface modification on the hydrophobicity and wear resistance of the surface. Furthermore, the effect of pre-treatment of the geopolymer surface with atmospheric plasma before the application of the epoxy coating and the Repesil Aqua hydrophobic coating was investigated. This analysis is meant to determine whether metal microparticles may serve as a potential antimicrobial reagent in epoxy coatings without compromising their protective properties. Plasma treatment is investigated as a potential simple and relatively cheap way to further improve the properties of coated geopolymer, especially the adhesion between epoxy coating and geopolymer surface, as well as the properties of the surface layer of geopolymer itself, as epoxy coatings may also be used to penetrate porous surfaces.

2. MATERIALS AND METHODS

2.1. Geopolymer samples preparation

The geopolymer samples were prepared using locally sourced Baucis L_K metakaolin base and potassium based activator, both manufactured by Czech company ČLUZ, a.s [13]. In addition to geopolymer base and activator, the geopolymer samples were also made with quartz sand, silica fumes and carbon fibers, some of the most commonly used additives to geopolymer composites. After hardening, the samples were cut to roughly 3×1×1 cm. The composition of geopolymer samples is shown in **Table 1**.

Table 1 Geopolymer samples composition (materials are listed in weight proportion to the geopolymer base)

Material	Weight proportion
Geopolymer base	100
Activator	90
Sand	100
Silica fumes	8
Carbon fibers	1

2.2. Microparticles, nanoparticles and modified coating

Copper microparticles were made by Fischema and sized below 45 µm in diameter. Silver nanoparticles were made by PkChemie and likewise sized below 45 µm in diameter. Silver nanoparticles were made by Sigma-Aldrich, sized below 100 nm in diameter and with PVP (Polyvinylpyrrolidone) as dispersant. Copper nanoparticles were made by Carl Roth company (ROTI®nanoMETIC), sized below 100 nm in diameter and with oleic acid as dispersant. For each modified coating, 1 % by weight of each type of micro- or nanoparticles was used (only one type was used for each modified coating).

Two coatings were used for testing - Izolak, an epoxy resin protective/penetration coating made by Stachema, and Repesil Aqua, a siloxane hydrophobization/primer coating. Izolak was also used as a base for modified coating with micro- or nanoparticles, this was done by adding micro- or nanoparticles in the form of powder directly into the mix of epoxy coating and hardener (standard Izolak package contains both components) and mixing for at least 2 minutes with a magnetic stirrer. After the mixing process, the modified coating was applied on geopolymer samples by a brush, after which the coating was left to harden for at least a day before further testing. The unmodified epoxy coating and Repesil aqua were likewise applied with a brush and left to harden for at least a day.

2.3. Plasma pretreatment

To test the effect of plasma pretreatment on hydrophobic and tribological properties of geopolymer coatings, some geopolymer samples were treated by atmospheric plasma generator Piezobrush 2. This device uses piezoelectric direct discharge to create low-temperature (less than 50°C) atmospheric plasma. Samples of geopolymer were treated by this plasma for a minute before application of coatings (both Izolak and Repesil AQUA, without modification by microparticles or nanoparticles. Plasma pretreatment is generally used to activate a surface and improve adhesion or bonding of various surface treatments.

2.4. Hydrophobicity and tribological tests

Drop method was used to measure the hydrophobicity of samples by measuring contact angle of 4 µl demineralized water drop on Surface energy evaluation system device. In total, each sample was measured six times with the interval of one minute, including the initial contact angle, to determine whether the drop of water will soak into the surface or at least wet its surface. Minor changes in contact angle may be attributed to water evaporating from the drop. Control measurements were taken to confirm the reliability of the results.

The wear resistance of the surfaces was tested by a linear reciprocal test, using a tribometer TRB^3 from Anton Paar company. For the purpose of this test, ceramic Si_3N_4 sphere (counterpart during the tribological experiment) with 6mm diameter was used with 10 N load and 833 cycles on 12 mm long track of samples, linear speed 2.6 cm/s. The measurement result is the average value of the coefficient of friction and the standard deviation. The amount of wear on each surface was then determined by S Neox 3D Sensofar confocal microscope analysis, to compare the wear resistance of samples with various modified coatings and after plasma pretreatment.

3. RESULTS AND DISCUSSION

3.1. Effect of microparticles and nanoparticles on Izolak

The addition of 1% nanoparticles had no effect on the wettability of the Izolak epoxy coating for both copper and silver particles. Their effect on coefficient of friction was also low. The average coefficient of friction was slightly increased in comparison to the coefficient of friction of pure Izolak. As seen in **Figure 1**, nanoparticles caused the coefficient of friction to increase faster from its initial value to the stable value of around 0.6 to 0.65 (the coefficient of friction of unmodified geopolymer). These changes indicate a slight reduction in wear resistance of the protective coating, at least until the Izolak-geopolymer interface is reached, as Izolak also penetrates the upper layers of geopolymer and reinforces them as well. Confocal microscope analysis has shown no noticeable effect on depth and appearance of the groove in Izolak surface created by tribological test. However, the 1% nanoparticle content was mainly used for the purpose of comparing its effect to the effect of 1% microparticle content, and is unsuitable for most applications, especially due to the high price of nanoparticles. Generally, much lower nanoparticle contents are required to achieve antimicrobial effect.

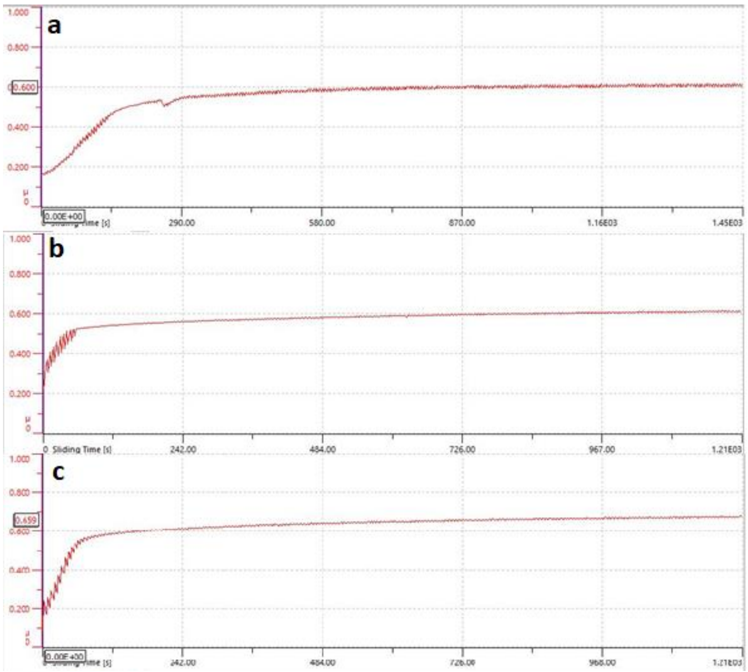

Figure 1 Coefficient of friction measurements for (a) unmodified epoxy coating Izolak, (b) epoxy coating Izolak modified with silver nanoparticles and (c) epoxy coating Izolak modified with copper nanoparticles

1 % content of microparticles has slightly lowered the hydrophobicity of Izolak. For both types of microparticles, the initial contact angle of water drop was lower in comparison to unmodified Izolak and the contact angle also decreased more quickly. Metal microparticles therefore increase the wettability of epoxy coating Izolak, although water still did not soak to the geopolymer surface. The effect is more significant for silver microparticles, as seen in **Figure 2**.

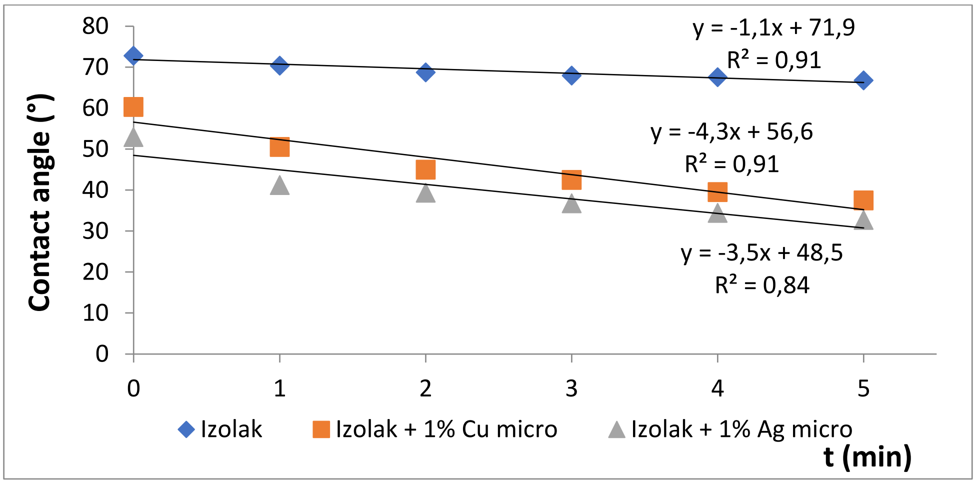

Figure 2 Hydrophobicity of epoxy coating Izolak modified with metal microparticles

The silver microparticle content had similar effect to the coefficient of friction as nanoparticles, as it likewise caused the coefficient of friction to increase faster from its initial value to the stable value of 0.6. This effect was stronger than with either nanoparticles. Copper microparticles, however, caused the coefficient of friction to increase slower, and also decreased the final stable value to 0.53. This indicates an increase in wear resistance of Izolak with 1% of copper microparticle, both the coating and the interface between coating and geopolymer and the penetrated geopolymer layer. The differences in coefficient of friction of Izolak modified with microparticles are specified in **Figure 3**.

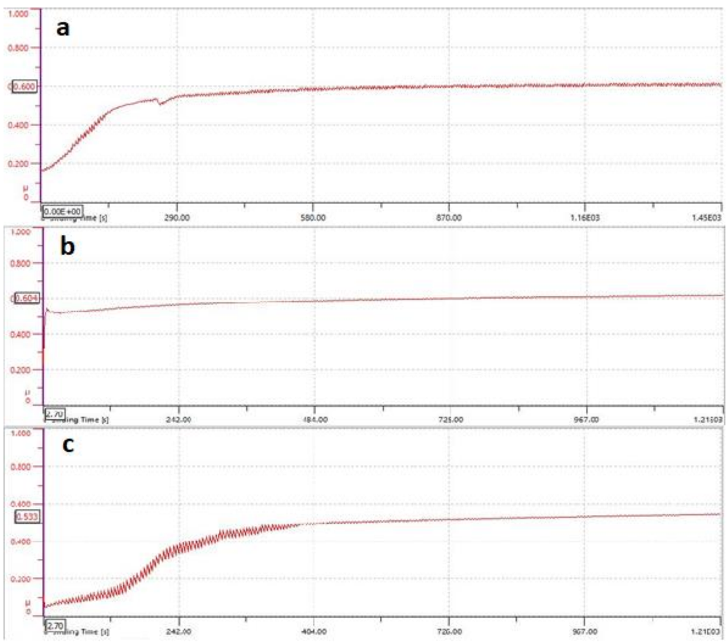

Figure 3 Coefficient of friction measurements for (a) unmodified epoxy coating Izolak, (b) epoxy coating Izolak modified with silver microparticles and (c) epoxy coating Izolak modified with copper microparticles

Confocal microscope analysis has confirmed the assumption of higher wear resistance of geopolymer coated with copper microparticles modified Izolak.The depth of groove created by tribological test is 22.9 μm for unmodified Izolak and 14.6 μm for Izolak modified with copper microparticles. There is also no major difference between the grooves, although cracks may be seen on the surface of Izolak modified with copper microparticles, as seen in **Figure 4**. These cracks were also present on the surface of Izolak modified with silver microparticles.

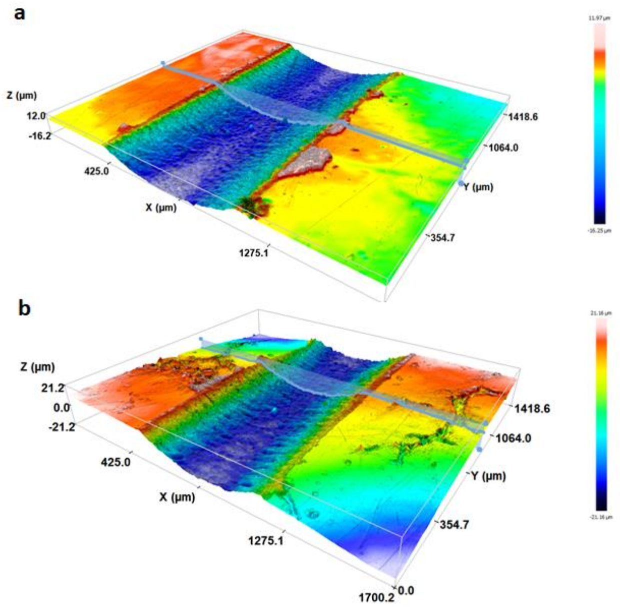

Figure 4 Confocal image of geopolymer surface with (a) unmodified epoxy coating Izolak (22.9 µm) and (b) epoxy coating Izolak modified with copper microparticles (14.6 µm)

Additionally, **Figure 5** shows the comparison of average coefficient of friction values for samples modified with nanoparticles and microparticles, as well as standard deviations. Higher value of standard deviation indicates slower initial growth of coefficient of friction, and is therefore higher for Izolak modified with copper microparticles.

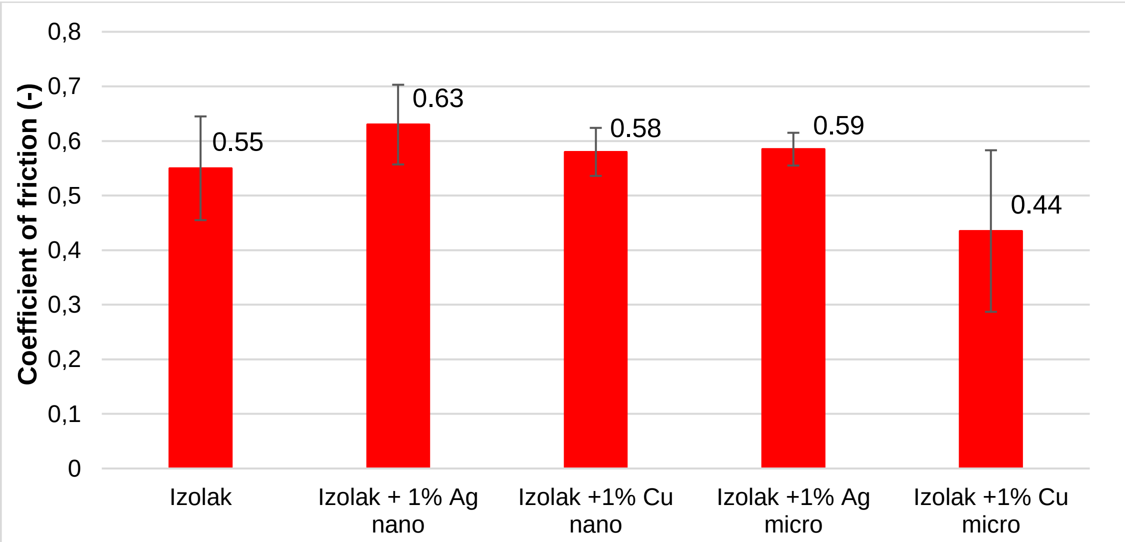

Figure 5 CoF comparison

3.2. Effect of plasma pretreatment

Plasma pretreatment had no effect on Izolak's wettability and only minimal effect on wettability of Repesil Aqua, as seen in **Figure 6**. The lack of effect on Izolak was expected, however, as it forms a uniform layer on the geopolymer surface to prevent water or other liquids from even coming into contact with it. The slight increase of hydrophobic properties of geopolymer surface coated with Repesil aqua after plasma treatment may be attributed to the increase in surface wettability and surface activation, which improved the bonding of the active component (siloxanes) to the surface layer of geopolymer.

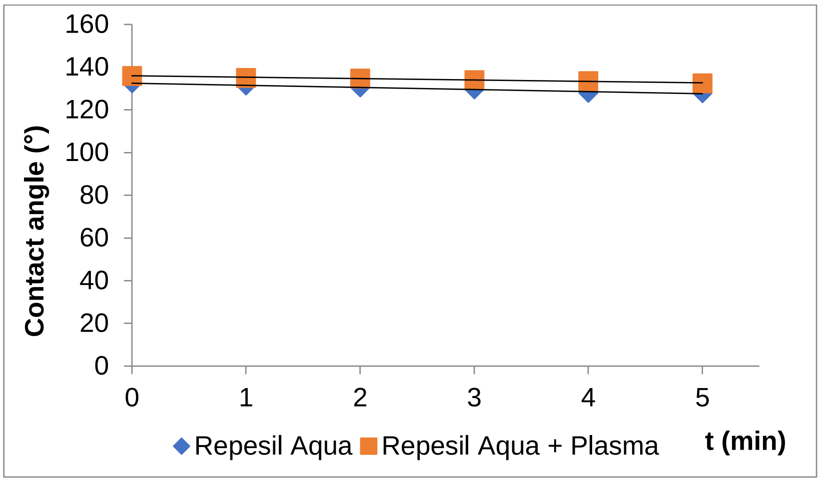

Figure 6 Hydrophobicity of Repesil aqua coated geopolymer surface with and without plasma pretreatment

The average value of coefficient of friction (**Figure 7**) was significantly lower after plasma activation (0.55 to 0.34), as well as the final value (0.6 to 0.34). The value of coefficient of friction at the end of measurement was also slightly lower than its maximum value. It may be caused by the gradual smoothing of the coating surface, which leads to a decrease in the value of the coefficient of friction. It may also be caused by improving the bonding of Izolak to the upper "penetrated" surface layer of geopolymer, which may lead to lower coefficient of friction and higher wear resistance when compared to both uncoated geopolymer and coating itself.

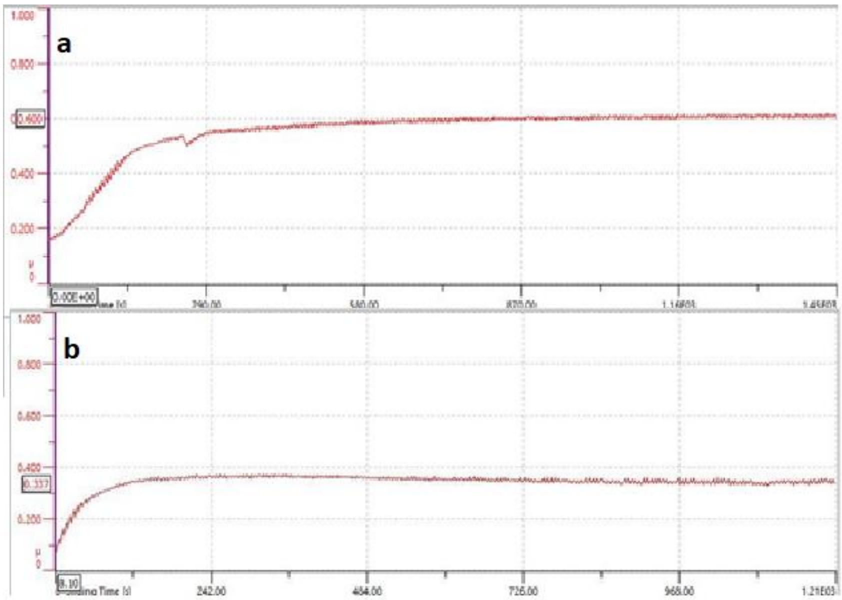

Figure 7 Coefficient of friction measurements for (a) Izolak applied on unmodified geopolymer surface and (b) Izolak applied on geopolymer surface modified by plasma pretreatment

The confocal analysis also shows increased wear resistance of geopolymer coated with Izolak after plasma pretreatment. The groove depth of sample coated without plasma pretreatment was 22.9 μm, while the groove depth of sample coated after plasma pretreatment was 7.4 μm. The difference between samples is shown in **Figure 8**.

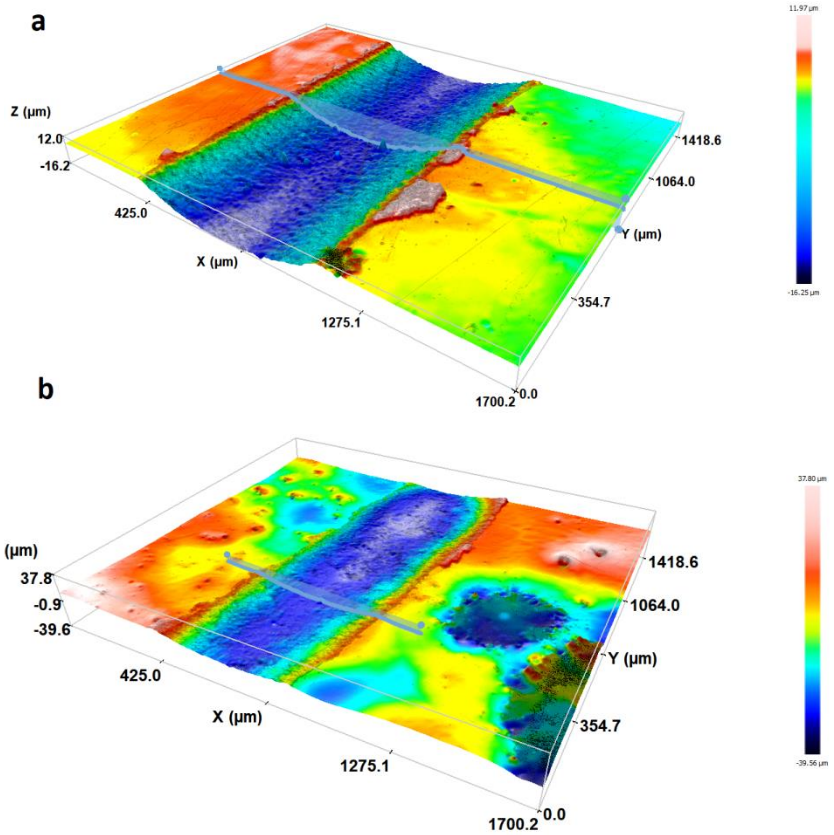

Figure 8 Confocal image of geopolymer surface coated with Izolak (a) without plasma pretreatment and (b) after plasma pretreatment

The effect of plasma pretreatment on tribological properties of geopolymer coated with Repesil Aqua was less significant, as the average coefficient of friction has increased only slightly (from 0.66 to 0.74), and did not change significantly in time (when compared to Izolak's properties), as seen in **Figure 9**.

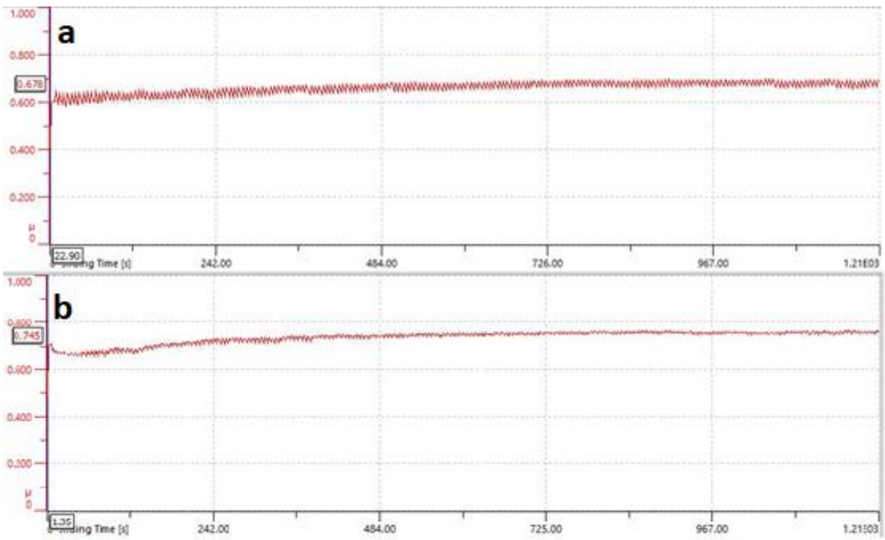

Figure 9 Coefficient of friction measurements for (a) Repesil Aqua applied on unmodified geopolymer surface and (b) Repesil Aqua applied on geopolymer surface modified by plasma pretreatment

However, despite the increased coefficient of friction, confocal analysis has still shown an increase to the wear resistance of sample treated by plasma, as the groove depth of untreated sample was 84.7 μm, while the groove depth on plasma treated sample was 56.8 μm. Both confocal images are shown in **Figure 10**. This effect is likely due to improved bonding of active component (siloxanes) to the geopolymer.

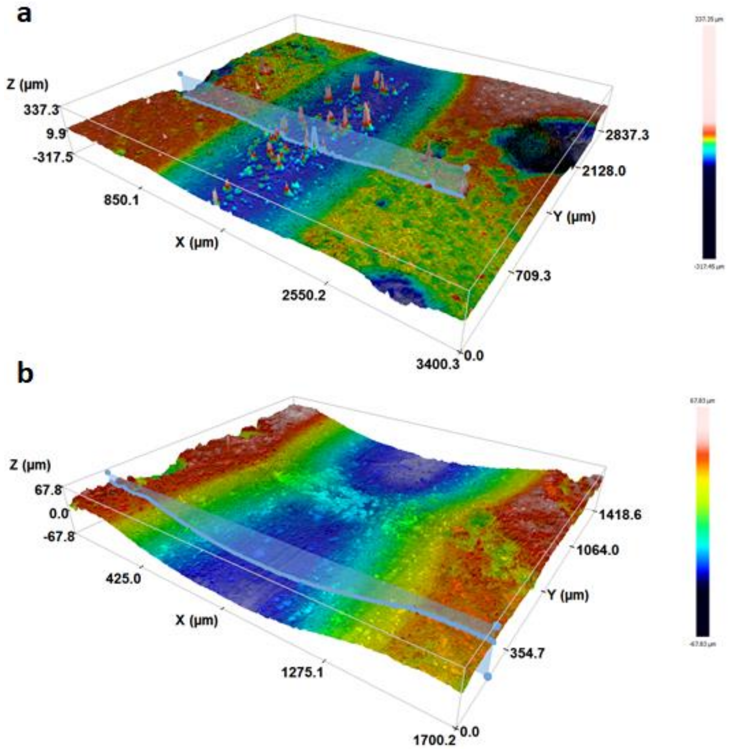

Figure 10 Confocal image of geopolymer surface coated with Repesil Aqua (a) without plasma pretreatment (84.7 μm) and (b) after plasma pretreatment (56.8 μm)

Additionally, **Figure 11** shows the comparison of average coefficient of friction values for samples treated by plasma, as well as standard deviations.

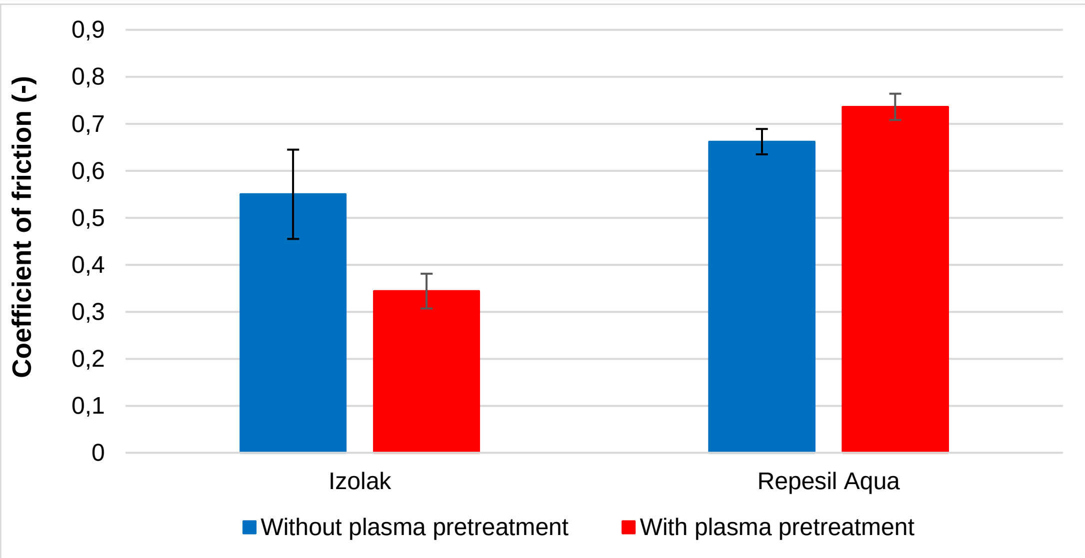

Figure 11 CoF comparison

4. CONCLUSION

This paper investigated silver and copper micro- and nanoparticles as a potential antimicrobial additive to epoxy based coatings and tested their effect on hydrophobic and tribological properties of the coating. Effect of plasma pretreatment of geopolymers on hydrophobic and tribological properties of both epoxy coatings and hydrophobic coatings was also investigated.

Nanoparticles have no effect on hydrophobic properties of epoxy coatings. Silver microparticles have a detrimental effect on both hydrophobic and tribological properties of epoxy coatings, while copper microparticles, while having slight detrimental effect on hydrophobic properties, improve the tribological properties of epoxy coatings, and are therefore a potential antimicrobial additive to epoxy based coatings.

Plasma pretreatment of geopolymers improves the wear resistance and tribological properties of both epoxy coatings and hydrophobic coatings on geopolymer, although it had little or no effect on hydrophobic properties.

Further studies should focus on testing the antimicrobial properties of epoxy coatings modified with copper microparticles, as well as their effect on geopolymer longevity in comparison to unmodified epoxy coatings.

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