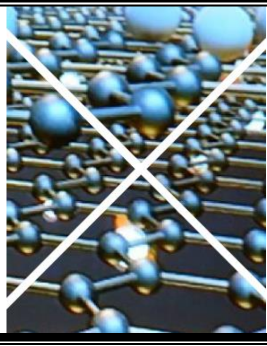
TIJMET, Vol. 004 (2021) 79-90

The International Journal of

Materials and Engineering Technology

ISSN: 2667-4033
TIJMET ID: 210401009 (12 pages)
Type of the Paper: Research Article
Received 21.10.2020 Revised: 09.04.2021 Accepted: 02.06.2021 Published (Online): 30.06.2021
Journal homepage: http://dergipark.gov.tr/tijmet



EVALUATION OF ANTISLIP PROPERTIES OF CERAMIC-POLYMER COMPOSITE COATING ON CERAMIC TILES

Neslihan TAMSÜ SELLİ[1a*], Fatma DUMAN[2b], Tuğçe YAGYEMEZ[2c]

[1a]Department of Materials Science and Engineering, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey
[2b, 2c]Eczacibasi Building Products Co. VitrA Innovation Center, 11300 Bozuyuk, Bilecik, Turkey
*ntamsu@gtu.edu.tr

Abstract

The objective of this work was to obtain polyurethane film that has antislip, mechanical, and chemical resistance properties on ceramic tiles. For this aim, different 2K polyurethane compositions were studied by NCO: OH ratio ranging from 0.7 and 1.4. The compositions that NCO: OH ratio is greater than or equal to 1 can not be applied on ceramic tiles. Water-resistance test, abrasion test, antislip test (DIN 51097 and 51130), UV resistance test, SEM/EDX analyses, stain resistance test (ISO 10545-14) were performed on other compositions. PU-3 composition was durable after keeping in water for 96 hours and 60000 cycles of abrasion test. According to the antislip test, the coated surface by PU-3 composition was R10B. After UV resistance and stain resistance tests, the change in color of the surface was appropriate ($\Delta E<0.5$). In SEM analysis it is seen that the granules used to obtain antislip properties were distributed randomly but homogeneously over the surface in PU-3. According to the test results, the PU-3 composition meets all desired values for high mechanical, chemical durability, and antislip level according to the standards.

Key Words: Antislip coating, polyurethane-ceramic composite, ceramic tiles.

1. Introduction

Floor ceramic tiles and porcelain tiles have high thermal shock resistance, high strength, physical and chemical inertness, hygiene, and easy to clean properties [1-3]. Also of these properties, antislip property of these tiles becomes critical especially for wet areas such as bathrooms, poolsides, and pool ladders [4, 5]. Particularly in Europe, accidents in wet areas have increased with the increase of the elderly population. Therefore, the reliability of the products used in this area is also important. In the present, the antislip property is provided by the crystalline phases in the glaze layer onto the tiles during production. Moreover, in the traditional production

How to cite this article:
Selli, N.T., Duman, F., Yagyemez, T., Evaluation of antislip properties of ceramic-polymer composite coating on ceramic tiles, The International Journal of Materials and Engineering Technology, 2021, 4(1): 79-90.

ORCID ID:
[a]0000-0002-1871-2925

method, the antislip property could not be added to the tiles after firing. After the production of the tiles, requirements of small quantities of antislip tiles for use in wet areas cause serious inefficiency in a production line. To add an antislip property to the tile surface, a polymeric coating can be applied on the tile surface after production as an antislip alternative. For this purpose, polymeric compositions with high mechanical and UV resistance has a critical role recently.

In the literature and patent surveys, polyurethane systems are remarkable considering the compatibility with ceramic substrates. Urethane chemistry began in the 1850s. In those years Wurtz and Hoffman studied a reaction involving the isocyanate and hydroxyl compound [6]. Dr. Otto Bayer found commercial use for the reaction in 1937, and the industry began to focus on polyester-based urethane polymers like fibers, foams, and coatings to compete with nylon. Initially, polyester, polyol compounds, and diisocyanates have been preferred. However, since the process difficulty, the cost has been increased considerably and for this reason, other materials have been sought instead of hydroxyl materials in the polyurethane industry [6, 7]. Polyurethanes, which are one of the most important polymer classes, are used commercially and contain diisocyanate and diol groups in various ratios and combinations in their structures. Polyurethanes range can be reached soft, linear elastomers to hard thermoset foams [8]. Polyurethane is frequently used for sound and thermal isolation, packaging materials, furniture, and decoration objects. The biggest advantage of polyurethane is that different products can be produced by changing the raw materials and constituents' ratios. Moreover, different forms and sizes of products can be produced easily [8-10]. In addition to this, there are some studies in the literature regarding the use of polyurethane coatings as coatings in literature. Sengupta et. al. [11], studied two-component polyurethane adhesive formulations and examined the effects of curing conditions on adhesion performance. Chen et. al. [12], gave detailed information about polyurethane coatings. They concentrated on solvent-based coating processes, polyisocyanates structures, polyols, catalysts, and solvents used in these structures. They worked on metal and polymer substrates. Ching et.al. [13], studied the effect of nano-silica filled polyurethane coating on propylene substrates. This study was mainly focused on the effect of acrylic-based polyurethane coating embedded with nano-silica on the wear and friction resistance of polypropylene substrate. Although there are general studies about polyurethanes in the literature, there is no specific study as polyurethane antislip coating on ceramic surfaces. Also, commercial anti-slip polyurethane products on the tiles are generally in the form of carpet/mattress applications laid on the tiles. Therefore, in this study, unlike the aforementioned studies and applications, the polyurethane composition was developed to provide anti-slip properties and was suitable for ceramic tile surfaces. This reveals the originality of this study.

2. Materials and Methods

2.1. Compositional Design

The precursors for the polyurethane coatings were Desmophen 650 MPa, a polyester resin with hydroxyl end groups, and Desmodur N3200, an aliphatic polyisocyanate resin, both of them were kindly supplied by Covestro. Dibutyltin dilaurate (DBTL (%95), Sigma Aldrich) was used as catalyst, ethanol and butanol were used as solvents for adjusting the viscosity of the composition. Tinuvin 1130 (BASF) and Tinuvin 292 (BASF) were used as light and UV stabilizers. To achieve the antislip property, the surface hardness of the coating was increased by using inorganic granules in the compositions. The particle size distribution of the inorganic granules was represented in

Table1. The concentration of the inorganic granules was 8 % by weight based on the total composition.

The product, which is resulting from the mixture of polyol system and isocyanate at a certain ratio and temperature with an exothermic reaction, is called polyurethane. The reaction proceeds roughly represented as in Fig. 1.

Table 1. Particle size distribution of the inorganic granules in the compositions.

Type of granules	Particle Size Distribution
Inorganic Granules	d10: 101,4 µm ±2 d50: 204,2 µm ±2 d90: 373,5 µm±2

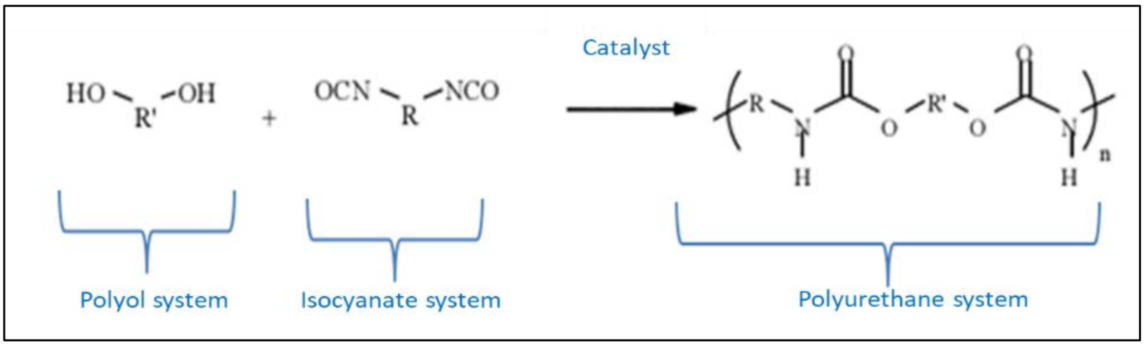


Figure 1. Schematic representation of polyurethane structure formation

The reaction forms a bond between the (OH) groups and the (NCO) in the two components, resulting in a completely different structure. The (OH) and (NCO) percentages in the composition make the resulting product rigid, semi-rigid, or flexible. In this study, two-component polyurethane compositions (NCO: OH) ratio was prepared in the range of 0.7-1.4. The coating systems are described in Table 2. Compositions are applied to the tile surfaces by roller brush and curing at room temperature is completed.

Table 2. The designation and composition details of antislip coating systems

Sample designation	NCO:OH ratio
PU-1	0.7
PU-2	0.8
PU-3	0.9
PU-4	1.0
PU-5	1.2
PU-6	1.4

2.2. Preparation of coating solutions and their application

For the first step, Desmophen 650 MPa was added to a mixture of solvents along with 0.1% of DBTL as a catalyst and stirred until a homogeneous solution was formed. Then the appropriate amount of inorganic granules were added (8 wt. %) and stirred for 30 minutes at the speed of 600 rpm and 1.0 wt. % Tinuvin 1130 and 0.5 wt. % Tinuvin 292 was added to the mixture and stirred for 10 minutes at the speed of 600 rpm and Mixture 1 was obtained (Fig. 2). The final coating solution was obtained after adding the appropriate amount of Desmodur N3200 and subsequently stirred for 10 minutes. The flow chart of composition preparation details was given in Fig. 2. The coating solution was applied on previously cleaned glazed/unglazed ceramic tile substrated by roller brush. After that, samples were kept for a week under normal ambient conditions to remove the solvent by evaporation and to allow the reactions of condensation to proceed fully. At the end of a waiting period, tests were carried out.

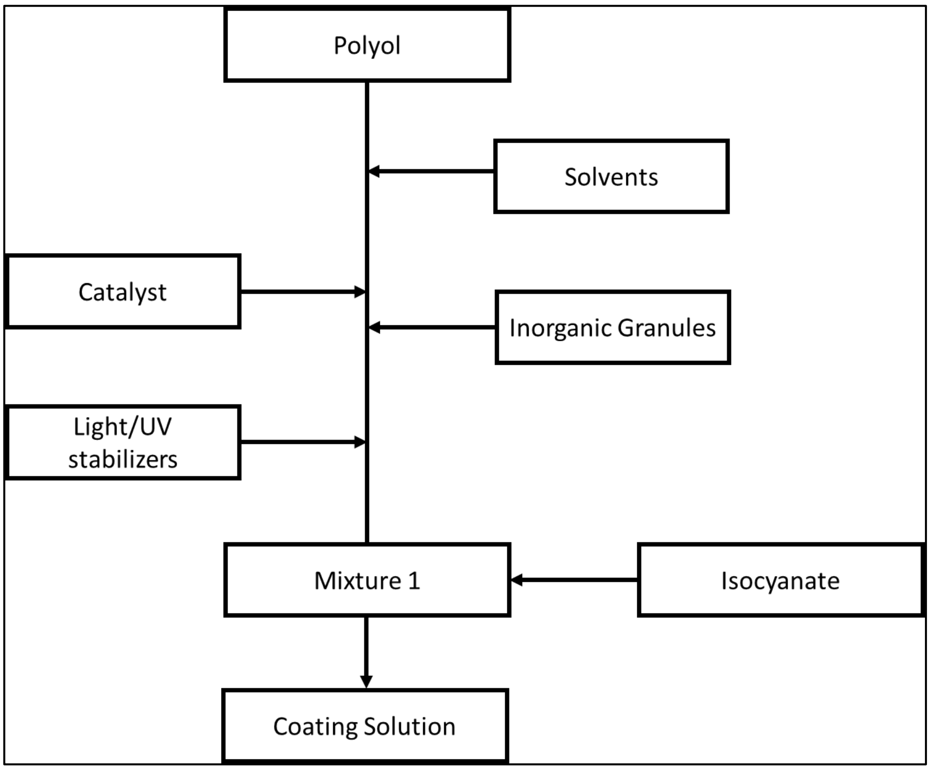


Figure 2. The flow chart of composition preparation

2.3. Coating Structural Analyses

Infrared spectroscopy (ATR-FTIR, Varian 1000 model) was utilized to investigate the chemical structure of coated samples. The polyurethane reactions were checked with peak intensities.

2.4. Water resistance of the coatings

The compositions were applied on tile and cured under room conditions for 7 days and subjected to a water resistance test. This test is done by dropping water on the surface of the tile for 96 hours. After this period is completed, the surface is checked and the coating must not be degraded.

2.5. Abrasion tests of the coatings

The coatings, which were passed the water resistance test, were subjected to a brush abrasion test. In this test, a hard brush is moved back and forth on the surface. The surface is checked at regular intervals whether the coating is removed from the surface (Fig.3). For this study, a 30.000 cycle is appropriate for these coatings.

2.6. Determination of the antislip degree of coated surfaces

A ramp test device was used to measure the antislip degree of the surfaces. The ramp tester is a laboratory-scale tester designed according to DIN 51097 and DIN 51130 standards and used to determine the antislip angles of the surfaces. The tester floor consists of a 60 cm wide and 200 cm long, flat and non-tilting surface with a slope adjustable from 0°to 45°. During the test according to DIN 51097 standard, 6 ± 1 Liter / minute test fluid is poured from the perforated pipe on the inclined plane tester and poured onto the sample surface. The person to walk on the sample starts the movement of the test device with the remote control. Standing upright, taking steps half a length forward and backward in the direction of water flowing, starting from the horizontal plane with a slope of about 1°/s moves on the surface to be tested (Fig. 4). It stops the device as it slides due to the increase in inclination during the person's walking and according to the surface characteristics. The inclination angle at which the person reaches the safe walking limit as a result of walking is determined by going forward and backward by repeating 10 times in the critical area from the protractor on the ramp tester.

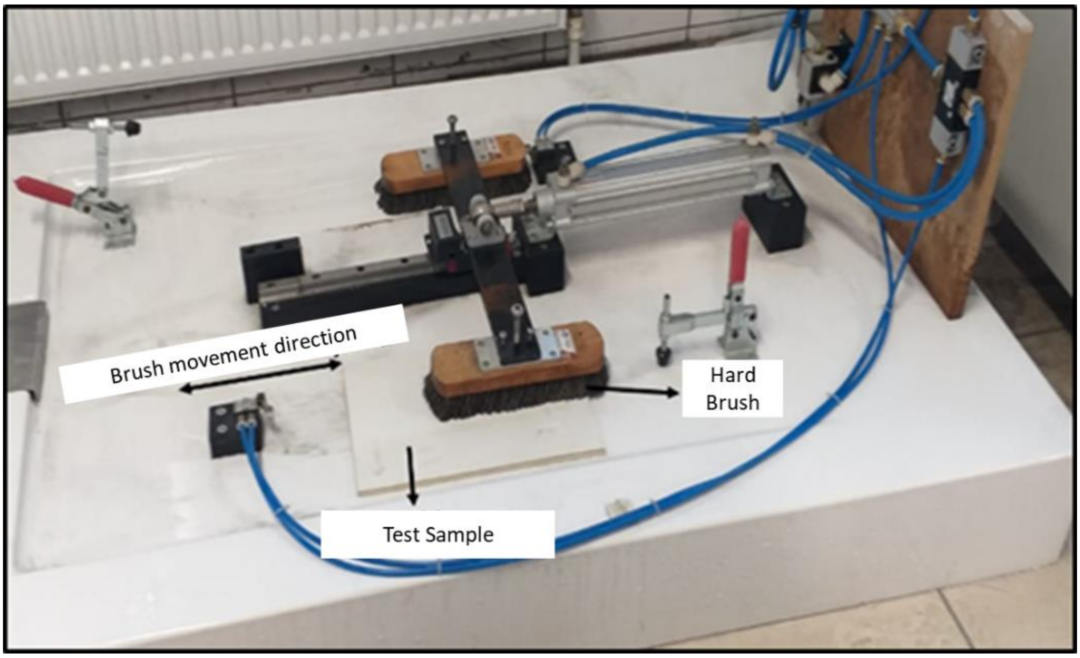


Figure 3. Brush abrasion test equipment

According to the DIN 51097 standard, the slip angles are classified as A, B and C, and the angular ranges of each code and the corresponding slip risk are given in Table 3. When the critical angle is higher than 12°, the risk of slipping is "high", when this angle greater than 18°, the risk of slipping is "medium", and finally when this value higher than 24°, the slipping risk is defined as "low".

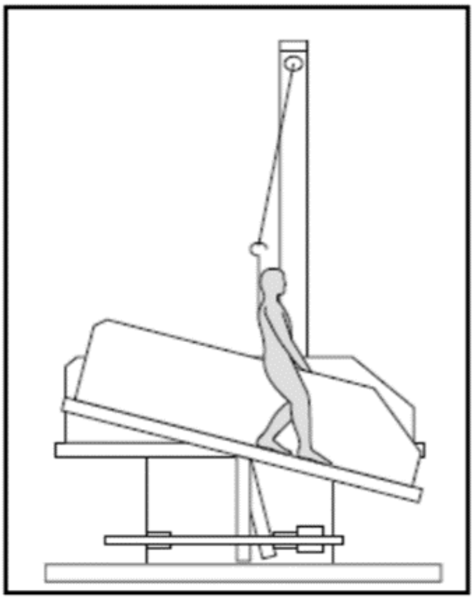


Figure 4. Ramp test equipment for determination of antislip degree [14]

Table 3. Determination and classification of antislip properties of the surfaces according to DIN51097.

Classification	Critical angle	Slip risk
A	≥12°	High
B	≥18°	Medium
C	≥24°	Low

Before starting the test process according to DIN 51130 standards, the temperature of the test chamber, shoe, lubricant and sole surface is ensured to be 23 °±5 ° C and the coated tiles to be tested are placed on the test platform. Tile surfaces placed on the test platform are cleaned before starting the test. 200 ml of machine oil is prepared to be applied to the sample surface. It is spread evenly on the sample surface with a brush. In the same way, the soles of the test shoes complying with the standards are lubricated with a brush. Test personnel wearing test shoes move on the specimen on the inclined plane tester starting from the horizontal plane back and forth in the upright position on the surface to be tested, with an inclination of approximately 1°/s. The critical angle is determined on the machine lubricated surface. The inclination angle at which the person reaches the safe walking limit is determined by repeating back and forth 10 times in the critical region and the data obtained are recorded. The sliding angles according to DIN 51130 are coded as R9, R10, R11, R12 and R13, and the angular ranges and corresponding fields of use of each code are given in Table 4. In this study, antislip target is determined as R10B.

2.7. UV resistance test for antislip coated surfaces

UV light test was performed to determine the UV resistance of the coatings. For this purpose, firstly L*, a*, b* and ΔE (color variation valeu) values of the reference were measured by spectrophotometer (Minolta CR-300 series chroma-meter). The samples were then incubated for 96 hours under UV light at a radiation intensity of 50 W/m^2 (300-400 nm wavelength) (Atlas Suntest XLS Plus) and L*, a*, b* color values were measured again. According to the test result, the total color difference value ΔE between the two measurements is expected to be 0.5 or less. Values below this value are not visible by eyes.

Table 4. Determination of slip risk by lubrication of dry areas, classification of test results according to application area

Classification	Critical angle	Slip risk
R9	6°-10°	High
R10	10,1°-19°	High and medium
R11	19,1°-27°	Medium and low
R12	27,1°-35°	Low
R13	>35°	Low

2.8. Microstructural analyses of the coated surfaces

The microstructure of the sample was investigated by means of scanning electron microscopy (SEM) (Supra Zeiss-50). The elemental compositions of the surfaces were analysed by means of electron dispersive analysis of X-Rays (EDX).

2.9. Stain resistance tests for antislip coated surfaces

ISO test method 10545-14 “Ceramic Tiles”-Part 14: Determination of Resistance to Stains” (1997) was used to determine stain resistance. The test method consists of maintaining various staining agents (green staining paste-chromium oxide particles in light oil, olive oil, and iodine solution) in contact with the working surface of the tile for an established predetermined amount of time, then cleaning with various agents and finally a visual inspection is done to detect any changes. The liquid stains and the iodine solutions were applied onto the tile with a pipette then covered with a watch glass.

The amount of staining was determined by visual inspection after each cleaning step:
1. mild washing with warm water,
2. washing with warm water plus a neutral detergent,
3. vigorous brushing with rotary brush equipment plus an alkaline detergent [16].
After washing the stains, the total color difference value ΔE between the coated and reference measurements is expected to be 0.5 or less.

3. Results and Discussion

In this study, 6 different two-component polyurethane compositions were studied. The compositions were prepared as indicated in Table 1. The progression of cross-linking of polyester resin with polyisocyanate was determined by FT-IR analysis of coatings. In the infrared spectrum (Fig. 4) there is a peak at 2270 cm^{-1}, which is related to the stretching vibration of isocyanate groups. After coating, the intensity of this peak decreases drastically in 96 hours at room temperature. After 96 hours no change in its intensity was observed. It means that 96 hours is enough time for curing the coating matrix.

Coating solutions were applied with a roller brush on the ceramic tiles. Composition details are given in Table 1. However, some problems were observed during the application of coatings especially for the NCO: OH ratio ≥of 1.0. While the PU-4 composition was applied by roller brush, the solution was not dispersed completely on the surface and flocculation occurred in the PU-5 composition, and gelation was observed for PU-6 composition (Fig. 5). An increase in the proportion of polyisocyanates causes a decrease in elongation of polyurethane, because of a decrease in the molecular weight per branch point. Thus the difficulty in application on tile can be observed. Besides, excess NCO results from a quasi prepolymer state that is used to describe a polyol–isocyanate adduct with free isocyanate contents between 16% and 32% by weight. These types of recipes are indicated as suitable for polyurethane foams in literature [15]. Because of these application problems, coatings were carried out with PU-1, PU-2, and PU-3 compositions, and coated samples were subjected water resistance test after one week of curing time.

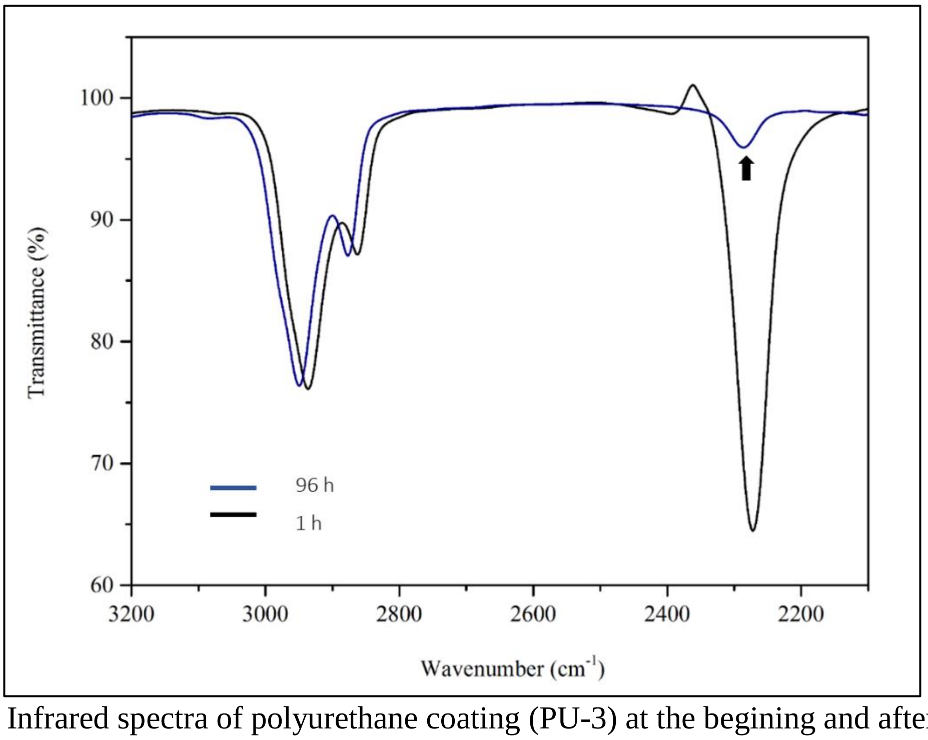


Figure 4. Infrared spectra of polyurethane coating (PU-3) at the begining and after 96 hours

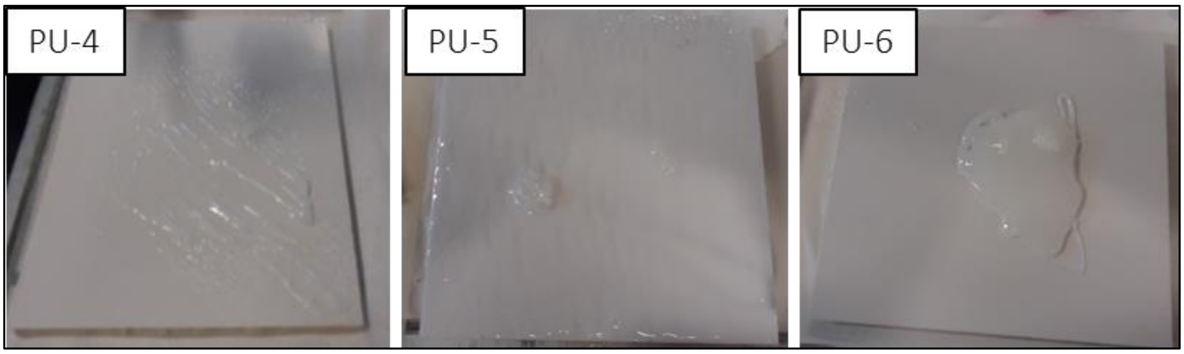


Figure 5. Applications of PU-4, PU-5 and PU-6 compostions on tile surface

Water-resistance tests of PU-1, PU-2, and PU-3 compositions are given in Table 4. It is seen that the coatings which are applied by PU-1 and PU-2 compositions are removed from the tile surface, therefore PU-1 and PU-2 compositions could not be suitable for antislip application on the wetting area. PU-3 composition with an (NCO-OH) ratio of 0.9 passed the water-resistance test.

Table 4. Water resistance test results of the coatings

Sample designation	(NCO:OH) ratio	Water resistance test results
PU-1	0.7	Pull off the coating
PU-2	0.8	Pull off the coating
PU-3	0.9	Passed

To determine the abrasion resistance of the coatings, a brush abrasion test was carried out for 3 compositions. The abrasion test result is given in Fig. 6. The graph showed that PU-1 and PU-2 compositions have not been shown the minumum wear resistance required for the coatings. PU-3 showed minimum required cycle, even after 60000 cycles coated surfaces did not abrade.

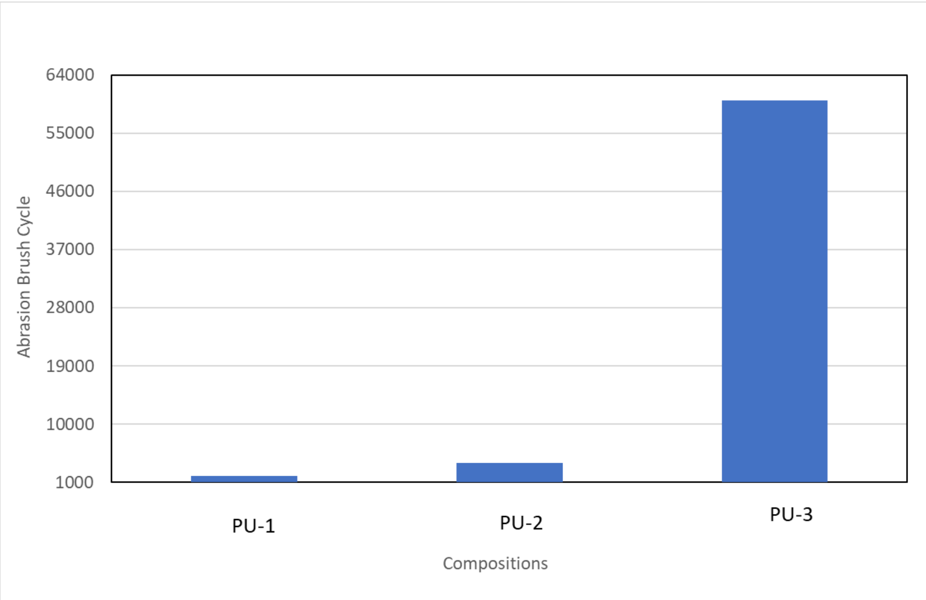


Figure 6. Abrasion resistance of the coatings depend on the compositions

Table 5. Antislip test results of the coated samples

Test	Coating Compositions	Antislip Test Results
Antislip Test	PU-1	R10-B
	PU-2	
	PU-3	

Antislip test samples prepared with PU-1, PU-2, and PU-3 compositions were also tested according to the DIN 51130 standard and their antislip grades were determined. The obtained results are given in Table 5. As indicated in Table 5, the tiles that are coated provide the target value. Furthermore, the degree of the antislip property could also be increased when the amount of granules added to the composition.

UV light tests were also performed on the UV light resistance of the coatings. The test results of the coated samples made with all three coatings are given in Table 6. Although PU-1 and PU-2 provide the desired antislip and UV resistance value, microstructure analysis, and other tests have been performed in the samples prepared with only PU-3 composition, since PU-1 and PU-2 could not pass the water-resistance test.

In figure 7, SEM micrographs of the coated samples with PU-3 composition are represented. It is seen from the microstructures that the granules used are distributed homogeneously over the surface in all the samples.

While microstructure images of the samples were taken, chemical analyzes (EDX) were also performed. In Fig. 7 (a), carbon and silicon peaks are observed in the EDX analysis from the area determined from the antislip coated surface (Fig. 7 (b)). The carbon peak belongs to the organic polymer coating and the silicon peak belongs to the silicon-doped granules (Fig. 8 (b)).

Table 6. UV resistance test results of the coated samples

Test	Coating Compositions	UV Resistance Test Results
UV Test	PU-1	$\Delta E \leq 0,5$
	PU-2	
	PU-3	

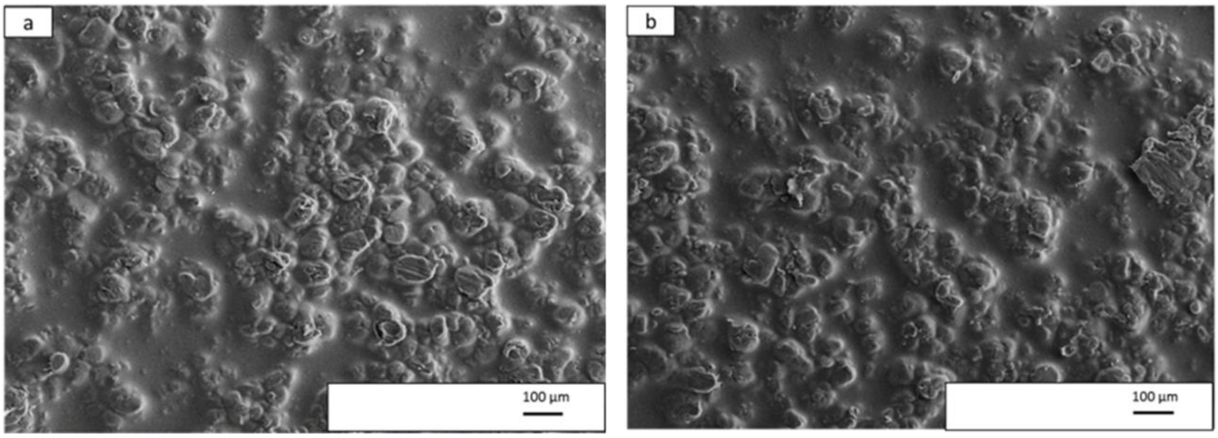


Figure 7. Electron microscopy images from different areas of tiles coated with PU-3 composition

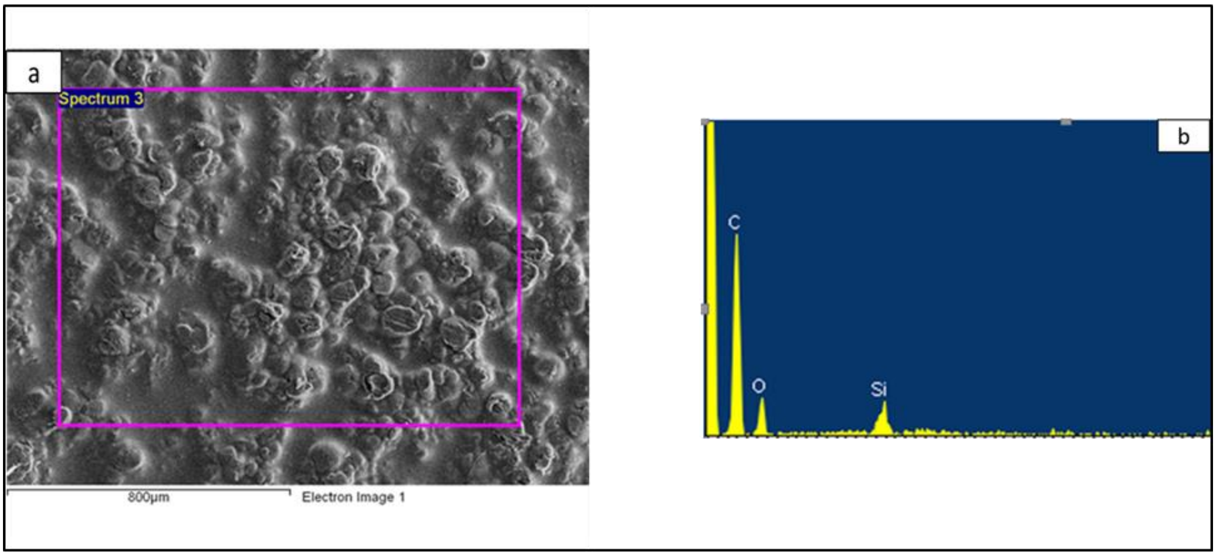


Figure 8. Samples coated with PU-3 composition a) microstructure images b) EDX analysis

According to EDX analysis from the "z" section, peaks of sodium, potassium, silicon, calcium, and magnesium belong to the clays and kaolin used in the composition (Fig. 9 (z)). According to the EDX analysis from the "y" section (Fig. 9 (y)), sodium, zircon, zinc, aluminum, calcium peaks belong to the glaze composition of the tiles (Fig. 9 (x)). Finally, the carbon peak in the EDX analyzes from the "x" region belongs to the organic coating and the silicon peak belongs to the inorganic particles in the coating. The average coating thickness is 65 ± 5µm (Fig. 9 (a), (b)).

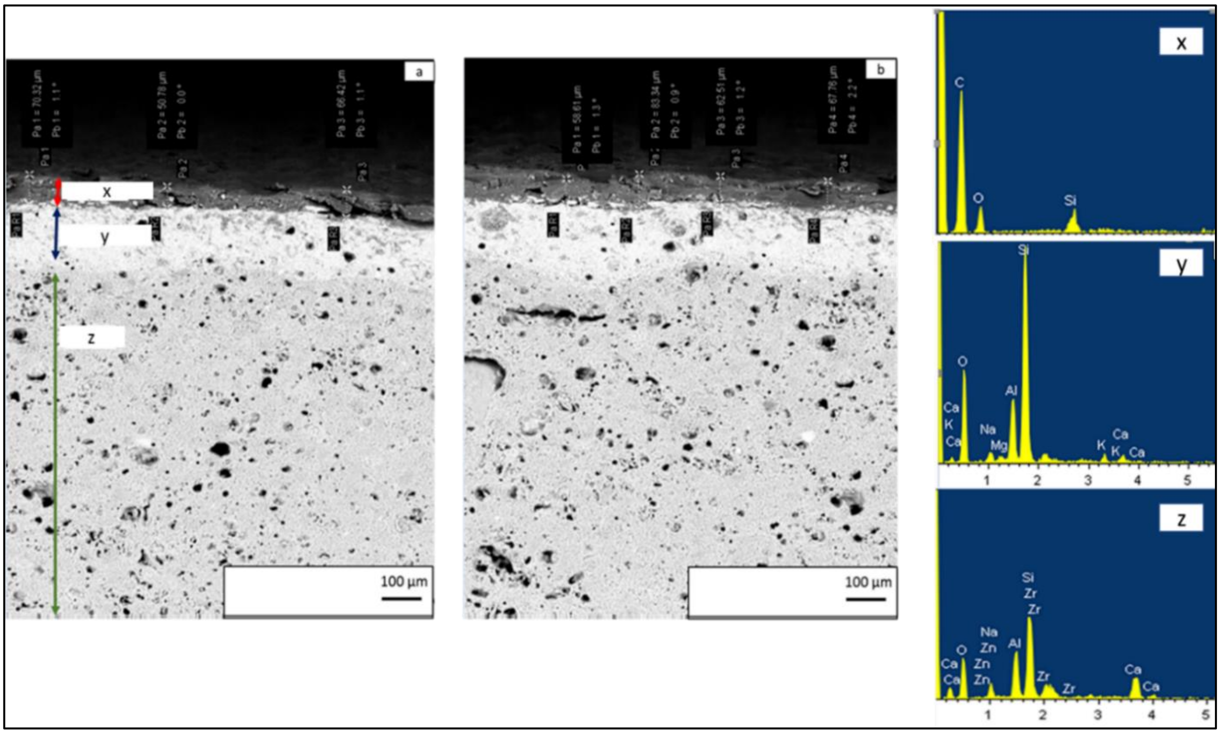


Figure 9. Cross-sectional images of tiles coated with PU-3 composition

Table 7. The staining test results of the surfaces coated with the PU-3 composition

Test	Coating Composition	Stains	Stain Resistance Test Results
Stain resistance test (ISO 10545-14)	PU-3	Chromium oxide	$\Delta E \leq 0,5$
		Olive oil	
		Iodine solution	

The staining test results of the surfaces coated with the PU-3 coating composition are given in Table 7. According to these results, after washing the stains, the total color difference value (DE) between the coated and reference measure is below 0.5.

CONCLUSIONS

In this study, a two-component polyurethane system is emphasized to improve the anti-slip tile composition. Different polyurethane compositions were prepared considering the (NCO: OH) ratio. When this ratio higher than 0.9, rheological problems were observed during the application of the solution on the tile surface. When the (NCO: OH) ratio less than 0.9, the coating did not adhere strongly to ceramic surfaces. The value of 0.9 for the (NCO: OH) ratio in this study is a critical result. Although the PU-1 and PU-2 compositions lower than this value had the desired anti-slip level and UV resistance value, they could not pass the water-resistance tests, so they did not adhere strongly to the ceramic substrates. PU-3 composition, which has this critical value (NCO: OH =0.9) among the prepared compositions, showed high mechanical and chemical resistance and achieved the targeted anti-slip value. The anti-slip level can be adjusted by controlling the amount of inorganic particles. It was observed that the inorganic granules were homogeneously distributed in the microstructure. The final coating thickness is determined as 65 ± 5µm. When all these results were evaluated, it has been seen that the developed PU-3 composition met all the targeted values. Since this application of such a composition has not been in the literature before, the study is rather original.

REFERENCES

1. Sanchez, E. Ibanez M.J., Porcelain Tile Microstructure: Implications for Polished Tile Properties, J. Eur. Cer. Soc. **2006**, 2533-2540.
2. Menezaggo, A.P.M., Paschoal, J.O.A., Evaluation of The Technical Properties of Porcelain Tile and Granite, Qualicer VII World Congress on Ceramic tile Quality, III Castelloon. **2002**, 211-230.
3. Esposito, L., The Reliability of Polished Porcelain Stoware Tiles, J. Eur. Cer. Soc. **2005**, 1487-1498.
4. Sanchez, E., Ibanez M.J., Porcelain Tile Polishing I.Wear Mechanism, Am. Cer. Soc. Bull. **2002**, 50-54.
5. Esposito, L., Tucci, A., Wear Resistance of Porcelain Stoneware of Porcelain Stoneware Tiles, Key Engineering Materials. **2002**, 1759-1762.
6. Aydin, H. Ekmekci, I. Isi Yalitim Malzemesi Olarak Poliuretan Köpüğün Fiziksel Ve Kimyasal Özellikleri Üretimi ve İncelenmesi, SAU Fen Bilimleri Enstitusu Dergisi. **2002,** 6(1):45-50.
7. Zlatanic, A., Cava, C., Zhang, W., Petrovic, Z.S., Effect of structure on properties of polyols and polyurethanes based on different vegetable oils, Journal of Polymer Science Part B: Polymer Physics. **2004,** 809-819.
8. Bektasoglu, S., Plastik İşleme Sanayi Ürünleri Raporu, T.C. Başbakanlık Dış Ticaret Müsteşarlığı Ihracatı Geliştirme Etüd Merkezi. **2005**.

9. Sadoh, T., Nakato, K., Surface Properties of Wood Physical and Sensory Aspects, Wood Science and Technology. **1987,** 111-120.
10. Beşergil, B., Polimer Kimyası, Gazi Kitabevi, Ankara. **2008**, 29-31.
11. Sengupta, A., Schreiber, H. P., Surface characteristics of polyurethane adhesive formulations, Journal of Adhesion Science and Technology. **1991**, 5(11):947-957.
12. Chen, A.T., Wojcik, R.T., Polyurethane coatings for metal and plastic substrates, Metal Finishing. **2000,** 98(6):143-154.
13. Ching, Y.C., Syamimie, N., Effect of Nanosilica Filled Polyurethane Composite Coating on Polypropylene Substrate, Journal of Nanomaterials. **2013**, 1-8.
14. Coskun, G., Sariisik, G., Dogal Taşlarin Sürtünme Katsayılarını (COF) Belirleyerek Yüzey Özelliklerinin Kayma Guvenlik Risk Analizi, Cumhuriyet Universitesi Fen Fakültesi Fen Bilimleri Dergisi (CFD). **2017,** 38(2).
15. Szycher, M., Structure–Property Relations in Polyurethanes from: Szycher's Handbook of Polyurethanes, CRC Press. **2012**, 41-85.