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## MICROSILICA FILLER FOR POLYUREA SYSTEMS

Microsilica is widely used as a reinforcing filler due to its high commercial availability and low price, which plays a significant role in reducing production costs. It fills the empty volumes of the material and decreases the porosity, which in turn improves the mechanical properties of composites. Polyurea coatings modified with microsilica and aerosil were prepared using a spray-coating machine. The materials were characterised in terms of thermal stability (thermogravimetric analysis - TGA, differential scanning calorimetry - DSC), mechanical properties (tensile strength, Shore D scale hardness), and hydrophilic-hydrophobic properties. To confirm the structure of the obtained materials, FT-IR spectroscopy was used. SEM analysis was performed to assess the dispersion of the modifiers in the polyurea coatings. The physicochemical properties of the obtained compositions were measured after ageing the samples under different conditions, including storing at room temperature, curing for 5 and 14 days at 80°C and weathering for 500 h with UV irradiation in a weathering station. The collected results show that the addition of microsilica improves not only the mechanical properties, but also the thermal stability of the obtained composites.

**Keywords:** polyurea, coatings, fillers, microsilica, spray-coating

## MIKROKRZEMIONKOWY NAPELNIACZ DO SYSTEMÓW POLIMOCZNIKOWYCH

Mikrokrzemionka stosowana jest powszechnie jako napelniacz wzmacniający ze względu na dobrą komercyjną dostępność materiału oraz niską cenę, co w znacznym stopniu przyczynia się do obniżenia kosztów produkcji. Wypełnia wolne przestrzenie w materiale oraz zmniejsza porowatość, dzięki czemu wpływa na poprawę właściwości mechanicznych kompozytów. Powłoki polimocznikowe modyfikowane microsilicą oraz aerosilem otrzymano przy użyciu urządzenia do powlekania natryskowego. Materiały scharakteryzowano pod kątem stabilności termicznej (analiza termogravimetryczna TGA, różnicowa kalorymetria skaningowa DSC), właściwości mechanicznych (wytrzymałość na rozciąganie, pomiar twardości w skali Shore'a D), właściwości hydrofilowo-hydrofobowych. Do potwierdzenia struktury otrzymanych materiałów wykorzystano analizę spektroskopową FT-IR. Wykonano analizę SEM w celu określenia dyspersji modyfikatorów w powłokach polimocznikowych. Badania właściwości fizykochemicznych oraz mechanicznych przeprowadzono po kondycjonowaniu próbek w różnych warunkach, tj. temperatura pokojowa, wygrzewanie w temperaturze 80°C przez 5 dni oraz 14 dni, proces starzenia przez 500 godzin w komorze UV. Z przeprowadzonych badań wynika, że dodatek mikrokrzemionki do osnowy polimerowej poprawia nie tylko właściwości mechaniczne, ale i stabilność termiczną uzyskanych kompozytów.

**Słowa kluczowe:** polimocznik, powłoki, napelniacze, mikrokrzemionka, natrysk

## INTRODUCTION

Polymer modification is a subject of constant and wide research due to the need to broaden the spectrum of applications of existing materials for different branches of industry, and due to the possibility of creating new systems of unique properties [1]. Chemical modification, however, rarely translates to a reduction in production costs, and therefore in industrial processing, fillers are mostly used (mineral or synthetic) [2]. The addition of a filler may, and usually does have an impact on the mechanical and/or physicochemical properties of the polymer [3, 4].

The constantly broadening area of polyurea material applications is due to their huge utility potential. In 2013, the demand for polyurea products was estimated at 164 000 metric tonnes, and the diagnosis for 2020 is at least 225 000 metric tonnes [5]. Polyurea coatings are used mostly as anti-corrosion protection [6], among others for dams [7], fire protection water reservoirs [8], water treatment facilities [9], drinking water reservoirs [10], as well as breeding pens and swimming pools [11]. Applying the coating on industrial floors guarantees resistance to temperature changes [12] and me-

chanical damage [13]. Polyureas are also used as damping materials and protection of ramps, driveways and cargo spaces. Their high chemical resistance to bases, organic acids up to a 10% concentration, inorganic acids up to a 20% concentration and their salts makes them suitable for protecting tanks used to purify municipal sewage and some chemical wastes [14]. Polyurea coatings can be applied on different surfaces to prolong their lifespan [15], and to protect them against moisture, microorganisms and weeds. Spray-coating technology based on polyureas offers high quality products and a short application time [16].

### EXPERIMENTAL PROCEDURE

To obtain a polyurea coating the materials used were:

- a) an isocyanate component (Chemolan B), containing:
  - 50÷70% by weight of MDI (methylenediphenyl-4,4'-diisocyanate)
  - 10÷30 wt.% of the reaction mixture of methylenediphenyl -4,4'-diisocyanate and *o*-(*p*-isocyanatebenzyl)phenylisocyanate;

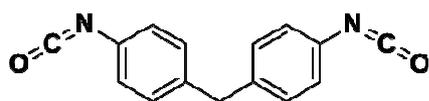


Fig. 1. MDI, methylenediphenyl-4,4'-diisocyanate

Rys. 1. MDI, 4,4'-diizocyanatodifenylometan

- b) an amine component being a 1:3 w/w ratio mixture of (accordingly):
  - Jeffamine D-2010 (Huntsman Holland BV)

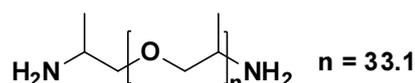


Fig. 2. Jeffamine D-2010

Rys. 2. Jeffamina D-2010

- Lonzacure DETDA 80LC (3,5-diethyltoluene-2,4-diamine) (LonzaLtd)

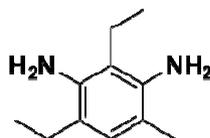


Fig. 3. Lonzacure® DETDA

Rys. 3. Lonzacure® DETDA

To modify the polyurea coating compositions, a microsilica mineral filler was used, which is a polymorphic, non-crystalline silicon dioxide, a type of silica fume. It is comprised of spherical particles of a diameter in the range of 20÷250 nm, and the mean diameter is 150 nm. The surface area measured by BET was around

24.9 m<sup>2</sup>/g. A transmission electron microscopy (TEM) micrograph is shown in Figure 4. Aerosil 200, hydrophilic fumed silica, produced by SiCl<sub>4</sub> flame hydrolysis, was used for the filler. It is characterised by very high purity, a high surface area (around 200 m<sup>2</sup>/g from BET) and creates agglomerates of which the original particles fall into the size range of 5÷50 nm.

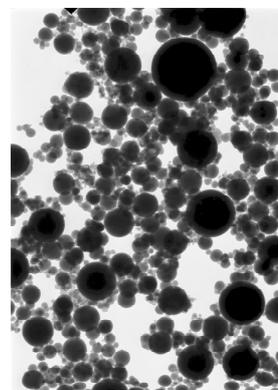


Fig. 4. TEM image of microsilica filler

Rys. 4. Zdjęcie TEM napelnacza microsilica

Polyurea samples were prepared using a spray-coating machine (Graco E 10 HP equipped with a fusion air-purge spray gun (AW2222, Graco). In all the runs, the block and hose heaters were maintained at a constant temperature of 70°C and the spraying operation was performed at 17.2 MPa (172 bar). The mixing ratio of A and B components was 1:1 (w/w). Polyurea films of a uniform thickness (2±0.4 mm) were obtained by spraying the formulation over a polycarbonate sheet. The curing time of the mixture was approximately 6 seconds, and after 30 seconds the material is dry. By such a described hydrodynamic method of spray coating, a reference (non-modified) sample was prepared, as well as samples of the systems mentioned below:

- polyurea with a microsilica additive,
- polyurea with an aerosil additive,
- polyurea with microsilica and liquid paraffin additives.

TABLE 1. Obtained polyurea compositions made by hydrodynamic spray coating

TABELA 1. Otrzymane układy polimocznikowe metodą natrysku hydrodynamicznego

Sample name	% filling (by weight)
Reference	-
Sample A	4% microsilica
Sample B	4% aerosil
Sample C	4% liquid paraffin 6% microsilica

The modified systems were obtained by mechanical mixing of the polyamine component with particular additives for 5 minutes for full homogenisation of the mixture.

## METHODOLOGY

The obtained coatings were characterized by FT-IR spectroscopy, contact angle analysis (hydrophobic-hydrophilic character), the Shore D scale hardness test, tensile strength test, electron microscopy with X-ray diffraction (SEM-EDS), thermogravimetric analysis (TG), and differential scanning calorimetry (DSC). Surface imaging was performed with a Quanta FEG 250 (FEI) instrument; SEM at 5 kV and EDS at 30 kV, respectively. For SEM of fractured samples, specimens were first frozen in liquid nitrogen and then fractured by hand using thick gloves.

Contact angle analyses were performed by the sessile drop technique at room temperature and atmospheric pressure, with a Krüss DSA100 goniometer. Three independent measurements were performed for each sample, each with a 5  $\mu\text{l}$  water drop, and the obtained results were averaged, which was done to reduce the impact of surface nonuniformity. Fourier transform-infrared (FT-IR) spectra were recorded on a Nicolet iS50 Fourier transform spectrophotometer (Thermo Fisher Scientific) equipped with a diamond ATR unit with a resolution of 0.09  $\text{cm}^{-1}$ . The spectra were collected in the 400–4000  $\text{cm}^{-1}$  range, 16 scans collected for each spectrum. Thermogravimetry was performed using a NETZSCH 209 F1 Libra gravimetric analyser. Samples of 5  $\pm$ 0.2 mg were cut from each granulate and placed in  $\text{Al}_2\text{O}_3$  crucibles. Measurements were conducted under nitrogen (flow of 20 ml/min) in the temperature range of 30–750°C and a 20°C/min temperature rise. Differential scanning calorimetry was performed using a NETZSCH 204 F1 Phoenix calorimeter. Samples of 6  $\pm$ 0.2 mg were cut from each granulate and placed in an aluminium crucible with a punched lid. The measurements were performed under nitrogen in the temperature range of –80–180°C and a 10°C/min temperature rise, and  $T_g$  was measured for the second heating cycle.

Measurements of the hardness were made with a Shore D scale round gauge durometer. The measurements were performed in accordance to the PN-EN ISO 868:2005 norm. For tensile strength tests the obtained materials were cut into type 1B dumbbell specimens in accordance with the EN ISO 527-2:1996 norm, with a CNC cutting machine. Tensile strength tests of the obtained specimens were performed on a universal testing machine INSTRON 5969 with a maximum load force of 50 kN. For the measurements, the traverse speed was set at 100 mm/min. The 1B dumbbell specimens were placed in an ATLAS UVTEST weathering station. The measurement was made according to the norm ISO 4892-3, and the measuring cycle according to ASTM G154:UV - irradiation 0.71  $\text{W}/\text{m}^2$  at 60°C for 4 h, condensation at 50°C for 4 h. The full time of measurement was 500 h. The total energy irradiated towards a sample during the whole experiment was 639  $\text{kJ}/\text{m}^2$ .

## RESULTS AND DISCUSSION

### FT-IR Spectroscopy

FT-IR was performed 3 and 30 days after applying the coatings (Fig. 5). After 3 days, a characteristic band at  $\sim 2277 \text{ cm}^{-1}$  coming from  $\text{N}=\text{C}=\text{O}$  group stretching was clearly visible. After 30 days full disappearance of the band was confirmed, which is due to full conversion of the remaining isocyanate groups. A band at  $\sim 1643 \text{ cm}^{-1}$  matches the  $>\text{C}=\text{O}$  of a urea group forming a hydrogen bond with the  $=\text{N}-\text{H}$  group of another urea moiety being in proximity. Furthermore, at  $\sim 1599 \text{ cm}^{-1}$  the **amide II** band is visible, and at  $\sim 1727 \text{ cm}^{-1}$ , the **amide I** band, being a free, non-bonded  $>\text{C}=\text{O}$  group. These absorption bands confirm the formation of urea moieties in the curing material of the prepared compositions. Moreover, absorption bands typical for polyetheramines are present, symmetrical  $\text{CH}_2-\text{O}-\text{CH}_2$  stretching at 924  $\text{cm}^{-1}$ ,  $\text{CH}_2-\text{O}-\text{CH}_2$  asymmetrical stretching at 1093  $\text{cm}^{-1}$ , and  $\text{C}-\text{N}$  stretching at 1016  $\text{cm}^{-1}$ . The band at 3332  $\text{cm}^{-1}$  comes from  $=\text{N}-\text{H}$  stretching of urea moieties.

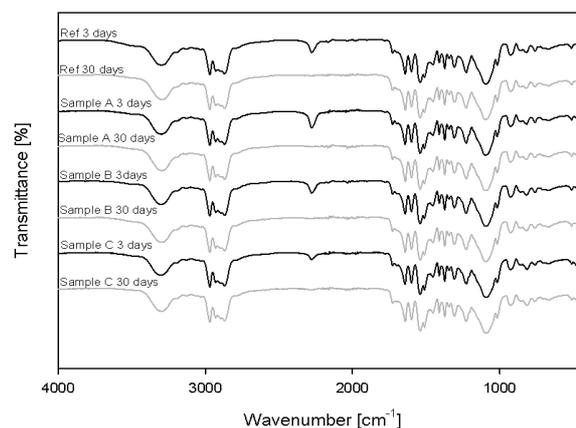


Fig. 5. FT-IR spectra of polyurea compositions 3 and 30 days after application

Rys. 5. Widma FT-IR układów polimocznikowych po 3 dniach oraz 30 dniach od naniesienia

### Thermogravimetric analysis - TGA

From the TGA curve, the temperatures of 1% mass loss were determined (Table 2, Fig. 6). For the reference sample, it was the lowest at 213.7°C. For the samples of modified compositions A-C, it was accordingly 254.6, 236.6 and 239.7°C, which translates to improvement of the degradation temperature in the range of 22.9–40.9°C. The temperature of the maximal mass loss rate of the reference sample was 363.8°C, and for the modified samples it was between 387.2–390.1°C, which is 23.4–26.3°C higher than that of the reference sample. On the DTG curves it is clearly visible that degradation of the reference sample is in the lowest temperature range (Fig. 7). The modified samples have two characteristic peaks, which corresponds to two-step degradation of the sample. The mass loss was obviously the highest for the reference sample at 99.93%. TG

analysis allowed the effect of the additives on the obtained compositions as thermal stabilising agents to be determined.

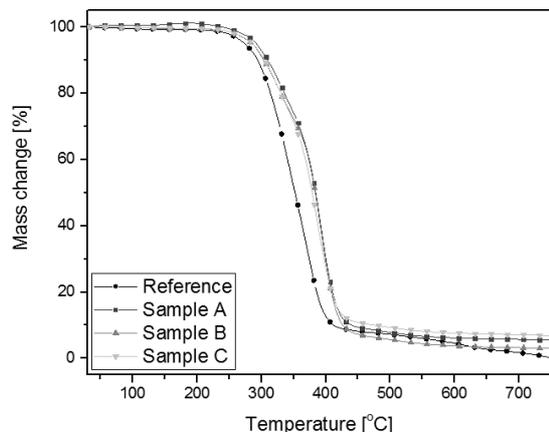


Fig. 6. Thermogravimetric curves of analysed polyurea compositions  
 Rys. 6. Krzywe termogravimetryczne badanych układów polimocznikowych

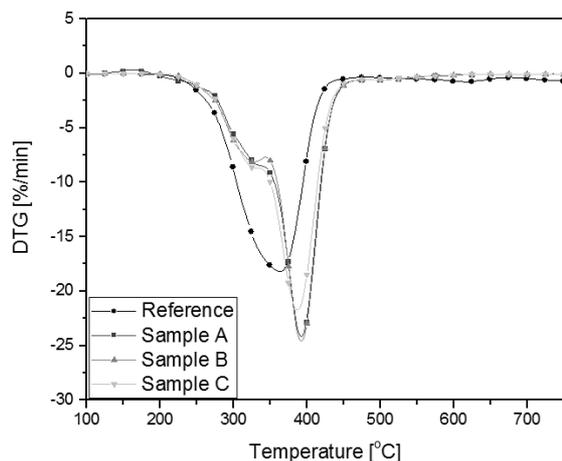


Fig. 7. Derivatographic curves of analysed polyurea compositions  
 Rys. 7. Krzywe derywatograficzne badanych układów polimocznikowych

TABLE 2. Temperatures and mass loss percentages from thermogravimetric and derivatographic curves of analysed polyurea compositions

TABELA 2. Temperatury oznaczone z krzywych termogravimetrycznych i derywatograficznych dla układów polimocznikowych

	Temperature of 1% mass loss [°]	Mass loss [%]	Temperature of maximal mass loss rate [°]
Reference	213.7	99.93	363.8
Sample A	254.6	94.53	390.1
Sample B	236.6	97.07	389.2
Sample C	239.7	93.16	387.2

### Differential scanning calorimetry - DSC

DSC analysis was performed to measure the phase transition temperatures for the obtained polyurea compositions. From the literature reports available, poly-

ureas are characterised by having two glass transition points.  $T_{g1}$  is the temperature of the soft segments glass transition (polyether segments), and  $T_{g2}$  is the glass transition of hard segments (isocyanate and aromatic segments).

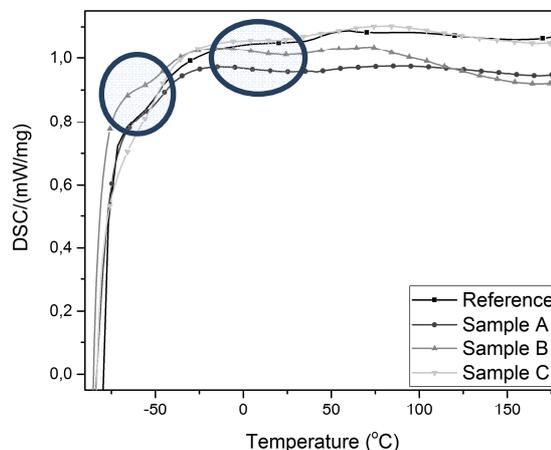


Fig. 8. DSC thermograms of obtained polyurea compositions  
 Rys. 8. Termogramy DSC otrzymanych kompozycji polimocznikowych

$T_{g1}$  is the lowest for the reference sample and equals  $-58.9^{\circ}\text{C}$  (Fig. 8). A similar temperature was measured for Sample A, modified with microsilica ( $-57.7^{\circ}\text{C}$ ). For Samples B and C, the  $T_{g1}$  was accordingly  $-46.3$  and  $-50.3^{\circ}\text{C}$ , which is  $12.6$  and  $8.6^{\circ}\text{C}$  in comparison to the reference. On the basis on the DSC curve analysis  $T_{g2}$  was also determined. The highest  $T_{g2}$  was measured for Samples B and C, which was  $42.7$  and  $42.6^{\circ}\text{C}$ , accordingly. The reference sample and Sample A were very similar in this manner, having a  $T_{g2}$  of  $39.4$  and  $39.7^{\circ}\text{C}$ . The dispersed modifiers reduce the mobility of the segments in the polyurea matrix, which in turn increases the  $T_g$  values.

### Mechanical tests

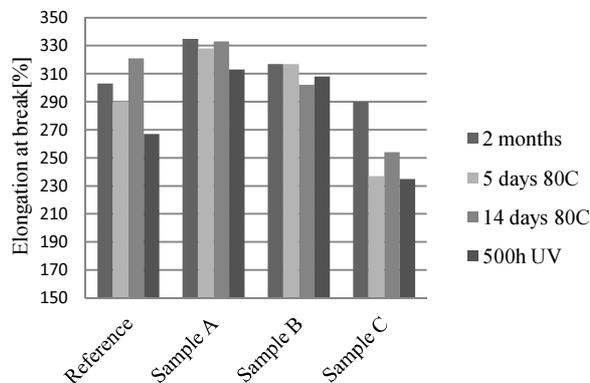


Fig. 9. Values of elongation at break for polyurea compositions. In the legend you are missing the degree sign - it should be  $80^{\circ}\text{C}$

Rys. 9. Wyniki pomiarów odkształcenia przy rozciąganiu dla układów polimocznikowych

Mechanical tests were performed on samples aged under different conditions, i.e. two months of storage at room temperature, post-curing for 5 and 14 days at 80°C, and weathering with UV irradiation for 500 h in a weathering station. Figure 9 presents the values of elongation at break of all the systems. The reference sample shows lower values than Samples A and B after 2 months of storage, as well as after ageing under different conditions. The best improvement of elongation at break was observed for the microsilica-filled system (sample A). For Samples A and B, the difference between the results for different ageing methods was small, with the biggest difference for the samples after weathering, as the weathering process causes degradation of the samples. For Sample C the values of elongation at break were lower than for the reference for all the methods of sample conditioning. It shows the weakening effect of the paraffin addition on the structure of the obtained composition.

Figure 10 presents the values of the tensile strength for the obtained compositions. Systems A and B show a higher tensile strength than the reference, and the highest values were observed for the samples conditioned at 80°C, which is due to post-curing of the compositions. What is more, weathering reduces the tensile strength of all the compositions due to material degradation, but still for Samples A and B this parameter remains higher than that of the reference. It shows improvement of the mechanical properties of the filler-modified polyurea compositions. For System C the results are the same as for the measurements of elongation at break - the addition of paraffin reduces the mechanical strength of the composition, showing the poor value of paraffin as a polyurea modifier.

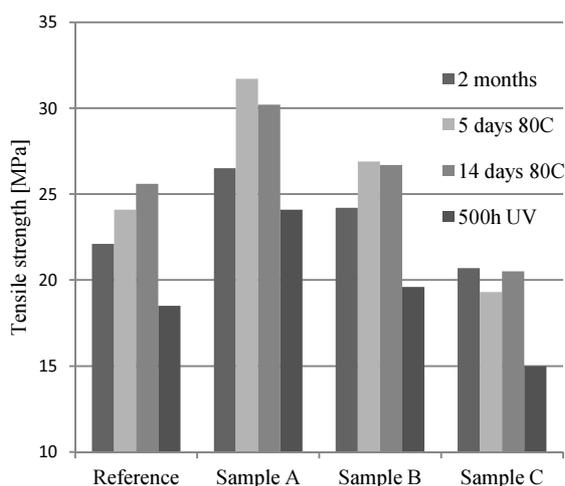


Fig. 10. Values of tensile strength for polyurea compositions

Rys. 10. Wyniki pomiarów naprężenia przy rozciąganiu dla kompozycji polimocznikowych

The mechanical analysis allowed the authors to verify the reinforcing effect of silica fillers on the mechanical parameters of Compositions A and B, and the weakening effect of liquid paraffin on Sample C.

## Shore hardness (D scale)

The measurements of Shore hardness showed that the additives did not have a very significant impact on the hardness of the obtained compositions, except for Samples B and C having a slightly lower hardness than the reference after two months of storage (3 and 4 points, accordingly) and samples all of the samples being slightly harder after heat-treatment (Fig. 11), which is due to curing of the compositions. After 14 days of post-curing, all of the compositions were harder than the reference, even System C containing liquid paraffin, which is due to the presence of microsilica. It goes in accordance with the fact that composition A, containing microsilica as the sole additive, showed the highest value of Shore hardness. There is visible loss of hardness after weathering of the samples, but all the measured values are  $\geq 51^{\circ}\text{Sh}$ , which still places the materials amongst very hard elastomers.

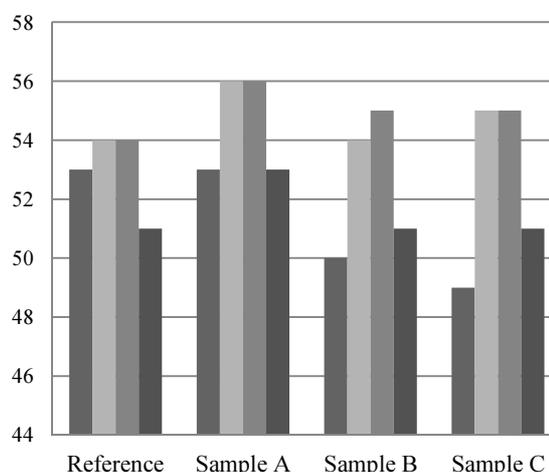


Fig. 11. Values of Shore D scale hardness measurements

Rys. 11. Wyniki pomiarów twardości badanych układów w skali Shore'a D

## Contact angle measurements

Measurements of the contact angle conducted after two months of storage at room temperature, and after 5 and 14 days at 80°C do not show significant changes in the hydrophobic-hydrophilic properties of the obtained polyurea compositions in comparison to the reference sample (Table 3, Fig. 12-14). However, differences can be seen after weathering the samples for 500 h with UV irradiation, when the samples undergo degradation due to free radical reactions on the material surface with moisture and oxygen from the air (Table 3, Fig. 15). The reference sample after exposure to UV showed a contact angle of  $39.1^{\circ}$ , which indicates a decrease in hydrophobic properties. On Samples A and B it was impossible to measure the contact angle, as water flowed on the surface of the specimens. The highest contact angle after weathering was measured for Sample C ( $64.0^{\circ}$ ). It was due to the presence of liquid paraffin, which worked as a hydrophobizing agent, more resistant to degradation than polyurea itself.

TABLE 3. Contact angles for polyurea coatings  
TABELA 3. Kąty zwilżania powłok polimocznikowych

Sample	Contact angle [°]			
	60 days	5 days 80°C	14 days 80°C	UV 500 h
Reference	74.6	76.1	73.7	39.1
Sample A	70.1	67.6	72.1	-
Sample B	73.2	76.7	78.7	-
Sample C	77.5	72.2	76.8	64.0

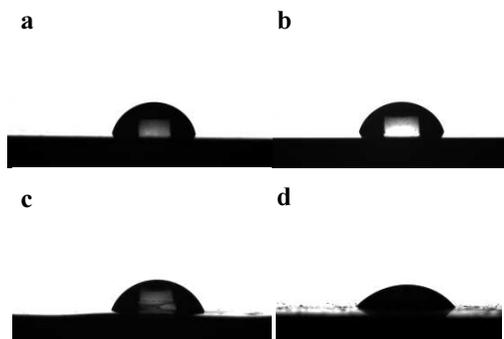


Fig. 12. Photographs water droplets on reference sample (a-d), from left: a) after 2 months, b) 5 days at 80°C, c) 14 days at 80°C, d) weathering for 500 h

Rys. 12. Zdjęcia kropli na próbce referencyjnej (a-d) od lewej: a) po 2 miesiącach, b) po 5 dniach w 80°C, c) po 14 dniach w 80°C, d) po starzeniu przez 500 h

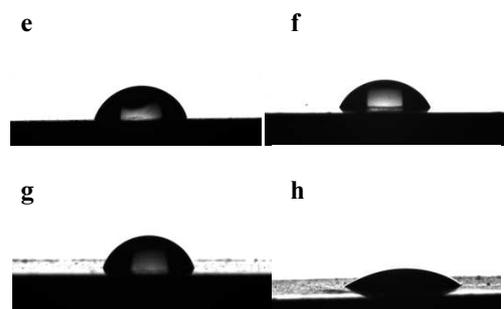


Fig. 13. Photographs of water droplets on Sample A (e-h), from left: e) after 2 months, f) 5 days at 80°C, g) 14 days at 80°C, h) weathering for 500 h

Rys. 13. Zdjęcia kropli na próbce A (e-h) od lewej: e) po 2 miesiącach, f) po 5 dniach w 80°C, g) po 14 dniach w 80°C, h) po starzeniu przez 500 h

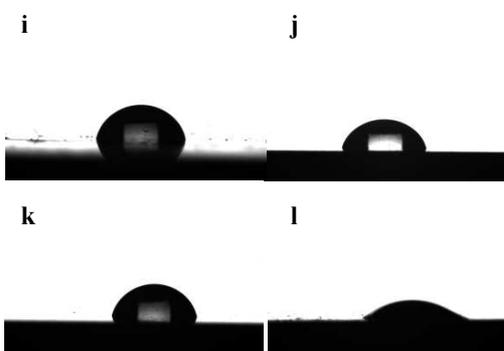


Fig. 14. Photographs of water droplets on Sample B (i-l), from left: i) after 2 months, j) 5 days at 80°C, k) 14 days at 80°C, l) weathering for 500 h

Rys. 14. Zdjęcia kropli na próbce B (i-l) od lewej: i) po 2 miesiącach, j) po 5 dniach w 80°C, k) po 14 dniach w 80°C, l) po starzeniu przez 500 h

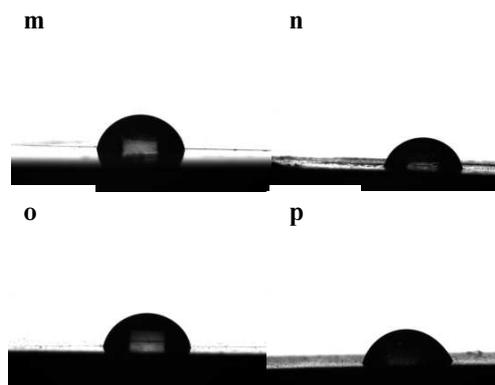


Fig. 15. Photographs of water droplets on Sample C (m-p), from left: m) after 2 months, n) 5 days at 80°C, o) 14 days at 80°C, p) weathering for 500 h

Rys. 15. Zdjęcia kropli na próbce C (m-p) od lewej: m) po 2 miesiącach, n) po 5 dniach w 80°C, o) po 14 dniach w 80°C, p) po starzeniu przez 500 h

### Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS)

The SEM micrographs present the dispersion of the fillers in the polyurea compositions (Figs. 16 and 17). Sample A modified with microsilica and Sample B modified with polyurea show tendencies to create agglomerates, which is visible on the micrographs and was confirmed by EDS (Fig. 16). The best dispersion was observed for Sample C. Furthermore, particles of cured polyurea can be seen on the coating samples. They are the most visible on the reference sample. EDS analysis confirmed that the visible particles were cured polyurea and not mineral additives (or contamination, for the reference sample). It may be explained by the extreme rate of curing reaction, which leads to the formation of cured polyurea particles in air and these particles stick to the surface of the curing material. In addition, SEM micrographs were taken of the fractured samples (Fig. 17). On the images, huge amounts of air bubbles are visible, which is characteristic for polyurea materials, as due to the very short time of initial curing (seconds) and specificity of the spray-coating technique required for polyurea systems, it is impossible to degas the compositions.

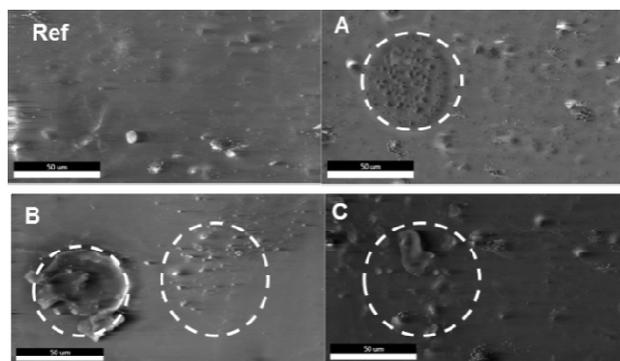


Fig. 16. SEM micrographs of polyurea compositions surfaces: Ref - reference, A - Sample A, B - Sample B, C - Sample C

Rys. 16. Zdjęcia SEM wierzchniej warstwy powłok polimocznikowych: Ref - układ bazowy, A - próbka A, B - próbka B, C - próbka C

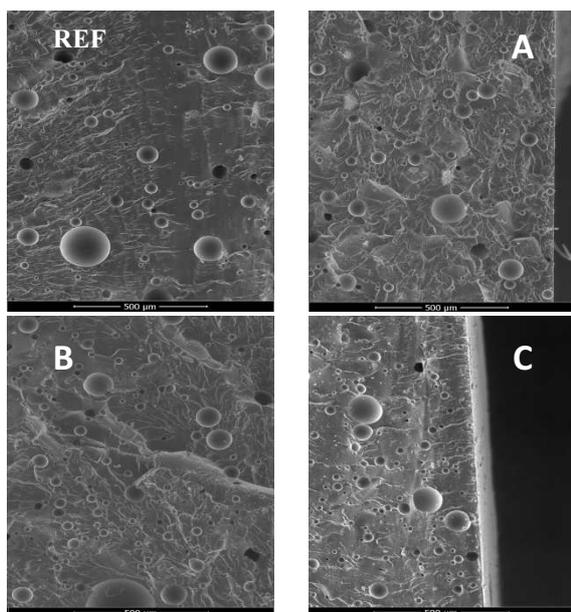


Fig. 17. SEM micrographs of fractured samples: Ref - reference, A - Sample A, B - Sample B, C - Sample C

Rys. 17. Zdjęcia SEM przelomów: Ref - układ bazowy, A - próbka A, B - próbka B, C - próbka C

## SUMMARY

Applying silica fillers, i.e. microsilica and Aerosil 200 resulted in improvement of the mechanical parameters of polyurea compositions, (elongation at break, tensile strength and hardness). Thermal analysis showed that the addition of modifiers significantly improves thermal stability. After 30 days of storage at room temperature, complete disappearance of the isocyanate and amine groups was observed, which translates into full curing of the systems, as was observed by FT-IR. SEM/EDS allowed the authors to prove that silica fillers form agglomerates within polyurea compositions, and the addition of paraffin improves the dispersion of the filler.

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