Marta Dobrosielska[1], Daria Pakuła[2], Bogna Sztorch[2], Maciej Popiół[1], Bartosz Klonowski[1], Dariusz Brząkalski[3] Bogdan Marciniec[2], Robert E. Przekop[2]*

[1]*Teklon Sp. z o.o., ul. Świętego Marcina 29/8, 61-806 Poznań, Poland*
[2]*Adam Mickiewicz University in Poznań, Centre for Advanced Technologies, ul. Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland*
[3]*Adam Mickiewicz University in Poznań, Faculty of Chemistry, ul. Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland*
*Corresponding author. E-mail: rprzekop@amu.edu.pl

THE INFLUENCE OF SURFACE PHYSICOCHEMISTRY OF SOLID FILLERS ON DISPERSION IN POLYUREA SYSTEMS

Polyurea coatings are obtained by hydrodynamic spraying by means of high-pressure, spray-coatingequipment. A chemical reaction between the isocyanate and amine components occurs in the time of approximately 6 seconds, which enables use of the coated object almost immediately after coating application. Polyurea coating modification results in changes in their properties and a cost reduction. In this work modifiers such as expanded graphite, talc and chalk, which are inexpensive, easily commercially obtainable fillers were employed. The curing degree was measured by FT-IR spectroscopy, thermal stability by thermogravimetric analysis (TG) and phase transition temperatures by differential scanning calorimetry (DSC). For the systems stored under different conditions, the tensile strength and Shore hardness in the D scale were also measured. SEM/EDS analysis was performed to assess the dispersion of the modifiers in the polyurea coatings. To determine the hydrophobic-hydrophilic character, contact angle analyses were performed. The addition of the fillers improves some of the parameters, e.g. the thermal stability and mechanical properties.

Keywords: polyurea, coating, filler, modification, dispersion

WPŁYW FIZYKOCHEMII POWIERZCHNI NAPEŁNIACZY STAŁYCH NA DYSPERSJĘ W SYSTEMIE POLIMOCZNIKOWYM

Powłoki polimocznikowe otrzymywane są na drodze natrysku hydrodynamicznego za pomocą wysokociśnieniowych aparatów do powlekania natryskowego. Reakcja chemiczna pomiędzy składnikiem izocyjanianowym a aminowym następuje w czasie około 6 sekund, dzięki czemu możliwe jest użytkowanie powleczonego elementu niemal natychmiast po aplikacji. Modyfikacja powłok polimocznikowych powoduje zmianę ich właściwości oraz obniżenie kosztów produkcji. W pracy wykorzystano takie modyfikatory, jak grafit ekspandowany, talk oraz kredę, które są tanimi, łatwo dostępnymi komercyjnie napełniaczami. Stopień dosieciowania powłok badano za pomocą analizy spektroskopowej FT-IR, stabilność termiczną określono przy użyciu analizy termograwimetrycznej (TG), a temperatury przejść fazowych za pomocą skaningowej kalorymetrii różnicowej (DSC). Dla układów przechowywanych w różnych warunkach wykonano również badania odporności powłok na rozciąganie oraz zbadano twardość w skali Shore'a D. W celu określenia charakteru hydrofobowo-hydrofilowego przeprowadzono badania kąta zwilżania. Zbadano również dyspersję napełniaczy stałych w polimerze za pomocą skaningowej mikroskopii elektronowej (SEM) oraz określono skład chemiczny układów techniką EDS. Dodatek napełniaczy powoduje polepszenie niektórych parametrów, m.in. stabilności termicznej czy właściwości mechanicznych.

Słowa kluczowe: polimocznik, powłoka, napełniacz, modyfikacja, dyspersja

INTRODUCTION

Polyurea coatings were used on a large scale already in the 1980s in the USA [1]. A commercial version designed for the construction industry was introduced in 1987 [2]. Spray-coating application technology utilizing polyurea coatings offers high quality of the final product in a short time of application [3], even on large surfaces. The constantly increasing expansion of the area of interest in different industrial branches in polyureas shows the great application potential of these materials [4]. Protective coatings [5, 6], waterproofing the coated surfaces [7, 8] for reinforced concrete constructions, as well as steel ones, i.e. sheet metal rooftops, are some of the leading areas of application. The advanced technology of polyuria coating application and quick curing time allow the object to be put into service in a very short time after finishing the works [3]. These materials are also used as a protective coating against various destructive agents/factors [9] such as mechani-

cal wear [10-12], as well as chemical [13] and atmospheric corrosion [14]. It is an undisputable advantage that polyureas do not have a harmful impact on the environment and can be safely applied even on large surfaces [15]. They are fully ecological products [16] and may have contact with food and drinking water, which in turn makes polyurea materials widely used in the food, agricultural and livestock industries.

EXPERIMENTAL PROCEDURE

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 the A and B components was 1:1 (v/v). 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. Spray coating was performed perpendicularly to the surface, at a constant distance of 1.0÷1.2 m. To obtain the polyurea coatings, an isocyanate component (Fig. 1) and amine components (Figs. 2 and 3) were utilized. The isocyanate component (Chemolan B) comprised 50÷70% w/w MDI (methylenediphenyl-4,4'-diisocyanate) and a reaction mixture of methylenediphenyl-4,4'-diisocyanateand*o*-(*p*-isocyanatebenzyl)phenylisocyanate.
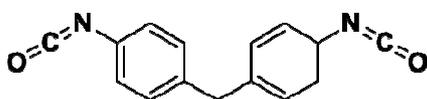
Fig. 1. MDI, methylenediphenyl-4,4'-diisocyanate
Rys. 1. MDI, diizocyjaniandifenylometan
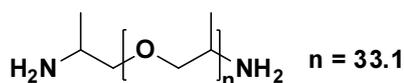
Fig. 2. Jeffamine D-2010
Rys. 2. Jeffamina D-2010
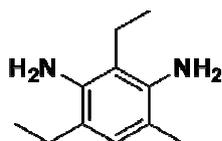
Fig. 3. Lonzacure® DETDA, 3,5-diethyltoluene-2,4-diamine
Rys. 3. Lonzacure® DETDA, 3,5-dietylotoluen-2,4-diamina

The amine components i.e. Jeffamine D-2010 α-amino-ω-2-aminopropylpoly(propylene glycol) (Huntsman Holland BV), a long-chain polyetheramine, and Lonzacure DETDA 80LC(3,5-diethyltoluene-2,4-

diamine) (LonzaLtd) were mixed in a 1:3 w/w ratio. The obtained modified polyurea coatings of the thickness 2 ±0.4 mm, as well as a reference, non-modified sample were prepared. A constant amount of the polyamine component, 3000 g, was mixed with different additives, i.e. talc, chalk and graphite in different weight ratios (summarized in Table 1), with a mechanical stirrer for five minutes to obtain a uniform mass with proper dispersion of the additives. The such prepared compositions were then transferred to the tanks of the spray-coating machine. After spraying, the coatings were cut into dumbbell specimens and aged (post-cured) under different conditions: for 60 days at RT, for 5 and 14 days at 80°C, or for 500 h in a weathering station.

TABLE 1. **Summary of prepared modified compositions**
TABELA 1. **Stosunki wagowe stosowanych dodatków**

	Additive	Mass percent of additive to mass of poryurea mixture [%]
Sample A	Chalk	5
Sample B	Expanded graphite	10
Sample C	Talc	7.5

METHODOLOGY

The obtained coatings were characterized by FT-IR spectroscopy, contact angle analysis (hydrophobic-hydrophilic character), Shore D scale hardness test, tensile strength test, electron microscopy with X-ray diffraction (SEM-EDS), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), and colorimetry. Surface imaging was performed with a Quanta FEG 250 (FEI) instrument; SEM at 5 kV and EDS at 30 kV, respectively. 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 witha 5 μl water droplet, 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 iS 50 Fourier transform spectrophotometer (Thermo Fisher Scientific) equipped with a diamond ATR unit with a resolution of 0.09 cm^{-1}. The spectra were collected in the 400÷4000 cm^{-1} range, 16 scans were collected for each spectrum. Thermogravimetry was performed using a NETZSCH 209 F1 Libra gravimetric analyser. Samples of 5 ±0.2 mg were cut from each granulate and placed in Al_2O_3 crucibles. The 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 ±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. Hardness measurements were taken with a Shore D scale round gauge durometer. The measurements were performed in accordance with the PN-EN ISO 868:2005 norm. For the tensile strength tests the obtained materials were cut into 1B dumbbell specimens, according to the EN ISO 527-2:1996 norm, with a CNC cutting machine. Tensile strength tests of the obtained specimens were performed on the universal testing machine INSTRON 5969 with a maximum load force of 50 kN. The traverse speed was set at100 mm/min for the measurements. Measurements of colour change were performed with an EnviSense NR60CP colorimeter with a silicon photodiode detector. A 4 mm aperture was used. The 1B dumbbell specimens were placed in an ATLAS UVTEST weathering station. The measurement was made according to norm ISO 4892-3, and the measuring cycle according to ASTM G154:UV - irradiation 0.71 W/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 kJ/m^2.

RESULTS AND DISCUSSION

Thermogravimetric analysis - TGA

Thermogravimetric analysis, presented in Figure 4, showed improved thermal stability for all of the modified coating compositions in comparison to the reference sample. The reference sample shows the lowest 1% mass loss temperature of 213.7°C (Table 2). The addition of modifiers resulted in an increase in thermal stability by 24.2÷26.1°C. The beginning of sample decomposition (onset) and the temperature of the maximal decomposition rate were both increased in comparison to the reference sample.

All the modified samples show similar decomposition temperatures, with the highest being 239.8°C for the sample filled with expanded graphite. The DTG curves (Fig. 4b) allow one to determine the fact that

decomposition of the reference sample occurs in a one-step process, whereas for the modified samples two steps are visible.

TABLE 2. **Temperatures determined from thermogravimetric and derivatographic curves for polyurea compositions**

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

	Total mass loss [%]	1% mass loss temp.[°C]	Decomp. onset [°C]	Maximal mass loss temp. [°C]
Sample A	96.3	237.9	330.7	389.7
Sample B	94.9	239.8	339.1	390.0
Sample C	96.7	238.0	334.9	390.2
Reference	99.93	213.7	289.4	363.8

Differential scanning calorimetry - DSC

DSC was applied to measure the temperatures of the phase transitions for the obtained compositions. A characteristic feature of polyurea materials is the occurrence of two glass transition temperatures. T_{g1} (around −50°C) is the glass transition temperature of the soft segments of the polymer, and T_{g2} (20÷50°C) corresponds to the glass transition temperature of the hard segments. The DSC analysis (Fig. 5) confirmed the literature reports, as for the reference sample two T_g points were indeed observed (T_{g1} = −58.9°C, T_{g2} = = 39.4°C). Modifying neat polyurea with chalk, expanded graphite and talc resulted in an increase in the glass transition temperatures. T_{g1} for Samples A, B and C was respectively −42.4, −44.0 and −50.3°C. Moreover, for the talc-modified sample, T_{g2} was also raised to 42.6°C. For the graphite- and chalk-modified systems, T_{g2} was not observed, probably due to the high homogeneity of the compositions. Over 125°C post-curing can be observed for every sample as an inflection of the curve.
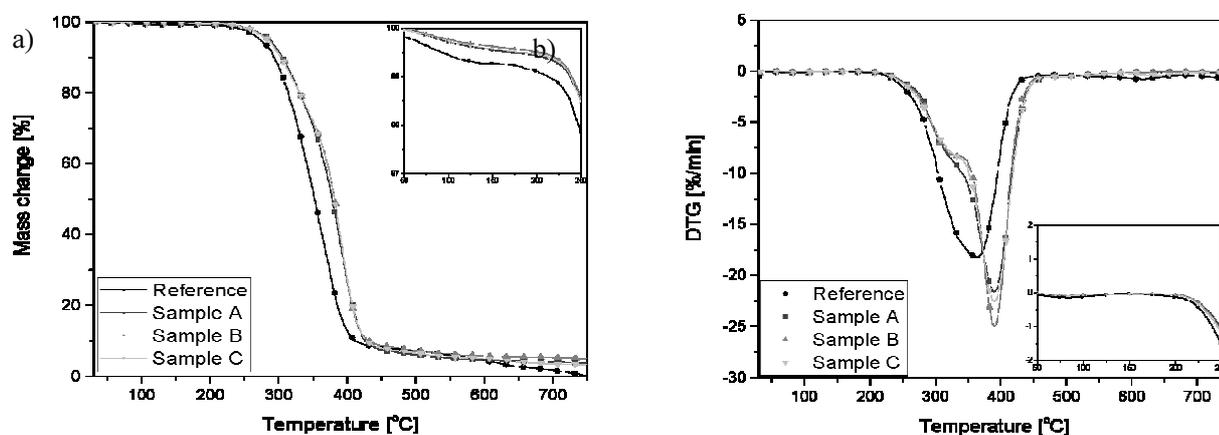
Fig. 4. Thermogravimetric (a) and derivatographic (b) curves of analysed polyurea compositions

Rys. 4. Termograwimetryczne (a) i derywatograficzne (b) krzywe analizowanych układów polimocznikowych
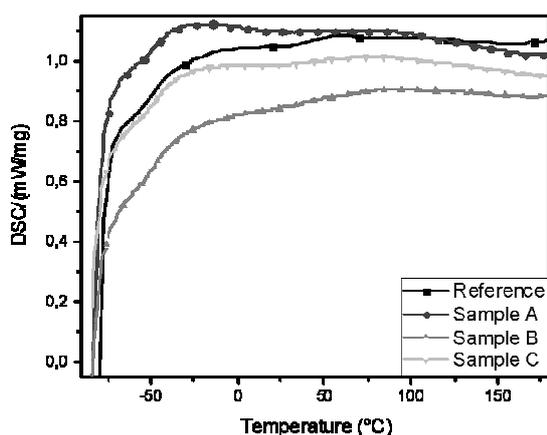
Fig. 5. DSC thermograms of obtained polyurea compositions
Rys. 5. Termogram DSC badanych powłok polimocznikowych

Shore hardness (D scale)

Figure 6 presents the results of hardness tests for all the compositions. Measurements in the Shore D scale are dedicated to materials with high levels of hardness and give values in the range of 25÷75. The measurements were performed for samples aged under different conditions. For the samples left for two months at room temperature, the highest measured hardness was that of the reference sample. Better results were obtained for the samples conditioned (post-cured) for 5 and 14 days in a laboratory drying oven at 80°C, where, except for the system containing graphite and conditioned for 5 days, all of the samples showed improved hardness in comparison to the reference sample. The best improvement was observed for the composition modified with chalk. After irradiating the samples with UV and treating them with varying humidity in the weathering chamber, the hardness decreased significantly. It is due to degradation of the material caused by UV radiation and free-radical reaction between the surface of the sample and water and oxygen from the air.
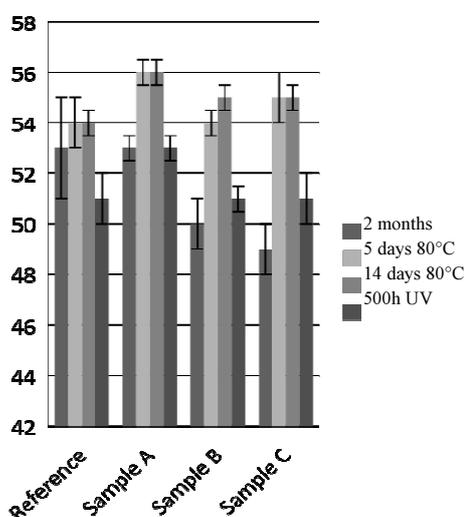
Fig. 6. Shore D scale hardness of obtained compositions
Rys. 6. Wyniki pomiarów twardości badanych układów w skali Shore'a D

Measurements of colour change parameters

Measurements of the colour change parameters were performed by the CIELab method for the samples conditioned at 80°C for 5 and 14 days as well as the samples after 500 hof UV irradiation. In Table 3 summarized intervals for the ΔE colour change parameter, and in Table 4 the resulting ΔE for the samples investigated 2 months after coating are presented. ΔE is calculated as follows:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

where: $\Delta L = L_1 - L_2$, $\Delta a = a_1 - a_2$, $\Delta b = b_1 - b_2$ represent the differences in particular colour parameters between two given samples.

The polyurea coatings were also measured for colour change after tensile strength tests. This was due to the fact that polyurea coatings under their working conditions are exposed to constant or repeatable stress. The reference system showed a visible colour change after a tensile test ($\Delta E = 3.97$), but much larger changes were observed for the systems containing chalk and talc, accordingly $\Delta E = 11.08$ and $\Delta E = 13.24$. The smallest colour change was noted for the composition modified with graphite ($\Delta E = 2.66$).

TABLE 3. **Intervals of ΔE colour change parameter**
TABELA 3. **Przedziały zmienności parametru ΔE**

Interval	Colour change
$0 < \Delta E < 1$	Invisible colour change
$1 < \Delta E < 2$	Very small colour change, only visible to an experienced observer
$2 < \Delta E < 3.5$	Medium colour change, visible to an in experienced observer
$3.5 < \Delta E < 5$	Colour change easily visible
$\Delta E > 5$	Great difference in colour change

TABLE 4. **Colour change of compositions after tensile test, after conditioning at 80°C, and after weathering test**
TABELA 4. **Wyniki analizy zmiany barwy badanych układów po wygrzewaniu w 80°C przez 5 oraz 14 dni oraz po komorze starzeniowej**

	After tensile test	ΔE after 5 days 80°C	ΔE after 14 days 80°C	ΔE after 500 h UV
Sample A	11.08	2.05	3.25	20.49
Sample B	2.66	0.22	2.12	5.76
Sample C	13.24	5.01	5.10	22.29
Reference	3.97	2.42	2.72	23.41

The polyurea systems after conditioning at 80°C for 5 and 14 days show mostly show a visible colour change in comparison to the non-conditioned samples. After weathering and UV irradiation, the measured colour changes are very significant, which is due to chemical reactions occurring on the surface of the materials. An important improvement was noted for the samples modified with graphite as a satisfactory decrease in colour change was obtained. The sample after conditioning for 5 days at 80°C may be considered impossible to observe a colour change with the naked eye, and even

after weathering and irradiating, the colour change is much less considerable that that of the rest of the samples, including the reference sample.

FT-IR Spectroscopy

Spectroscopic analysis was performed 3 days after the coating procedure, and after 30 days at room temperature it was repeated. For the systems measured after 3 days, there is a visible band of N=C=O group stretching at ~2277 cm^{-1}. After 30 days disappearance of the band was observed, which is connected to the occurrence of a reaction between the remaining isocyanate and amine groups. A band at ~1643 cm^{-1} corresponds to C=O moiety forming hydrogen bonds with an N-H group being in proximity, known as so-called "ordered bonding". More evidence on urea moiety formation is the band at ~1599 cm^{-1} (CO-N-H typical for secondary amides). In addition, the absorption at ~1727 cm^{-1} corresponds to free C=O. Polyetheramines are characterised by specific absorption bands visible on the spectra of the samples associated with ether moieties (CH$_2$-O-CH$_2$, symmetrical stretching at 924 cm^{-1}, asymmetrical stretching at 1093 cm^{-1}) and amine ones (C-N stretching at 1016 cm^{-1}). The band at 3332 cm^{-1} is associated with the N-H of urea moieties. The FT-IR analyses show no impact of the modifier on the absorption profile of the samples, but rather allow the full curing time of the compositions to be determined.
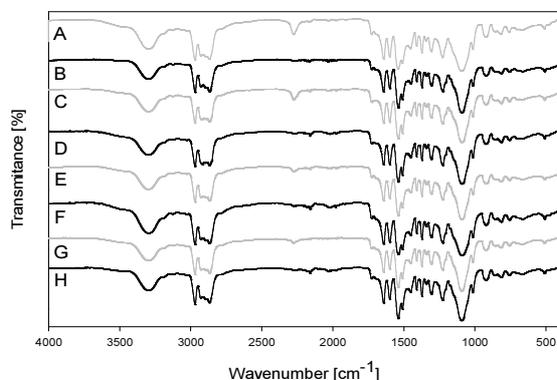
Fig. 7. FT-IR (A-H): A - Reference 3 days, B - Reference 30 days, C - Sample A 3 days, D - Sample A 30 days, E - Sample B 3 days, F - Sample B 30 days, G - Sample C 3 days, H - Sample C 30 days

Rys. 7. FT-IR (A-H): A - układ bazowy 3 dni, B - układ bazowy 30 dni, C - próbka A 3 dni, D - próbka A 30 dni, E - próbka B 3 dni, F - próbka B 30 dni, G - próbka C 3 dni, H - próbka C 30 dni

Hydrophobic properties investigation (contact angle)

Analyses of the contact angle were performed two months after the coating procedure, after 5 and 14 days of conditioning the samples at 80°C, and also after 500 h of weathering with irradiation (Table 6, Fig. 8). After two months at room temperature, the contact angle for the reference sample was 74.6°, and the addition of the hydrophobizing agent (talc) to the composition increased the contact angle by 13.1°. The analysis showed no significant changes for the samples conditioned at

80°C regardless of the conditioning time (Figs. 9 and 10). All of the resulting contact angles, except for those for the samples after weathering, fall into the range of 70÷90°, which is close to such typically hydrophobic objects.

After weathering and UV irradiation of the samples, the contact angle dropped significantly for all of the compositions, however they remained at much higher levels for the compositions containing chalk and especially talc (Fig. 11). On the other hand, for the samples containing graphite and the reference ones the contact angle dropped to 36.7° and 39.1° accordingly, the angles for chalk and talc dropped only to 63.4° and 75.0°. Analysis of the contact angle allowed the authors to confirm the stability of the polyurea coating regardless of the time of heat treatment, as well as the best hydrophobic properties of Composition C, where talc served the role of the hydrophobizing additive.

TABLE 6. **Contact angles of obtained samples**
TABELA 6. **Kąt zwilżania otrzymanych próbek**

	Contact angle [°]			
	60 days	5 days 80°C	14 days 80°C	UV 500 h
Sample A	74.5	80.9	79.2	63.4
Sample B	71.0	70.0	74.4	36.7
Sample C	87.7	81.9	89.7	75.0
Reference	74.6	76.1	73.7	39.1

Mechanical tests

Mechanical tests were performed to assess the mechanical properties of the obtained coatings, i.e. elongation at break and tensile strength (Fig. 13). The reference system after 2 months at room temperature is characterized by elongation at break of 300%, which shows good elasticity of the material. The composition modified with talc exhibited improved elongation at break of 340%. After post-curing of the samples at 80°C for 5 days, a small decrease in elongation at break can be seen for most of the compositions, but for all the filled compositions the results improved in comparison to the reference sample. Nonetheless, after 14 days of post-curing the reference system shows the highest value of elongation at break. Weathering and irradiation of the samples resulted in degradation of the sample filled with chalk and the reference one, which can be seen by a significant drop in the elongation at break value. The addition of talc to the composition (Sample C) results in an increase in elongation at break that even after weathering and irradiation remains at the level of over 340%, which shows good resistance to atmospheric conditions. Composition C also shows the highest values of tensile strength, both after 5 and 14 days of post-curingat 80°C, around 30 and 31 MPa, accordingly. These values are higher than those of the reference samples by up to 15%. The remaining samples show tensile strength values higher than those of the reference, and only after weathering and irradiation re-

sulting in a decrease in the parameter do they exhibit a tensile strength lower than the reference samples. Analysis of the mechanical data allowed the authors to determine that the talc-filled polyurea composition showed the best mechanical parameters for all the post-curing conditions.
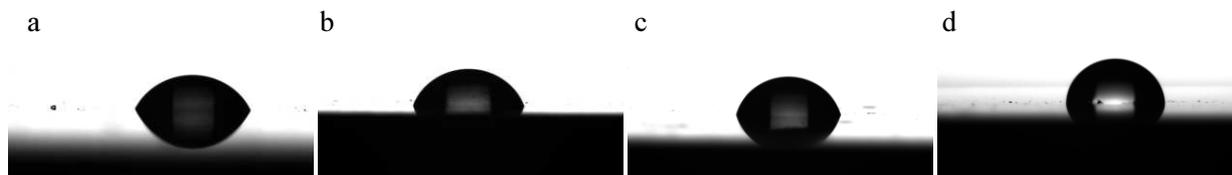
Fig. 8. Photographs of water droplets on polyurea compositions after 60 days of conditioning (a-d), from left: a) Reference, b) Sample A, c) Sample B, d) Sample C

Rys. 8. Zdjęcia kropli na badanych układach polimocznikowych po 60 dniach (a-d), od lewej: a) układ bazowy, b) próbka A, c) próbka B, d) próbka C

Fig. 9. Photographs of water droplets on polyurea compositions after 5 days of conditioning at 80ºC (e-h), from left: e) reference, f) Sample A, g) Sample B, h) Sample C

Rys. 9. Zdjęcia kropli na badanych układach polimocznikowych po 5 dniach w 80ºC (e-h), od lewej: e) układ bazowy, f) próbka B, g) próbka C, h) próbka C
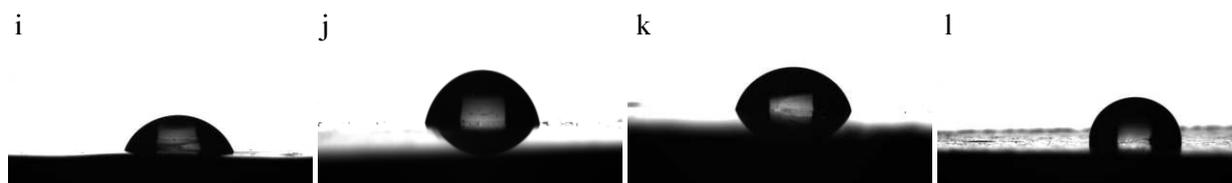
Fig. 10. Photographs of water droplets on polyurea compositions after 14 days of conditioning at 80ºC (i-l), from left: i) Reference, j) Sample A, k) Sample B, l) Sample C

Rys. 10. Zdjęcia kropli na badanych układach polimocznikowych po 14 dniach w 80ºC (i-l), od lewej: i) układ bazowy, j) próbka A, k) próbka B, l) próbka C
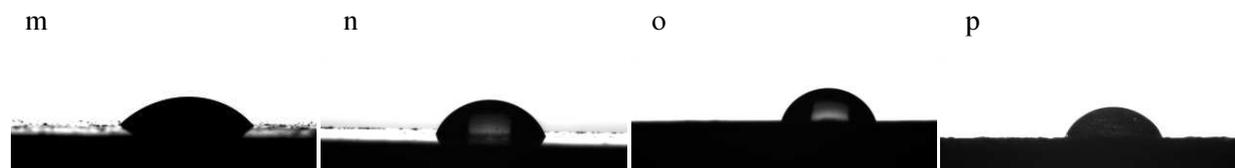
Fig. 11. Photographs of water droplets on polyurea compositions after 500 h in UV weathering station (m-p), from left: m) Reference, n) Sample A, o) Sample B, p) Sample C

Rys. 11. Zdjęcia kropli na badanych układach polimocznikowych po 500 h w komorze UV (m-p), od lewej: m) układ bazowy, n) próbka A, o) próbka B, p) próbka C
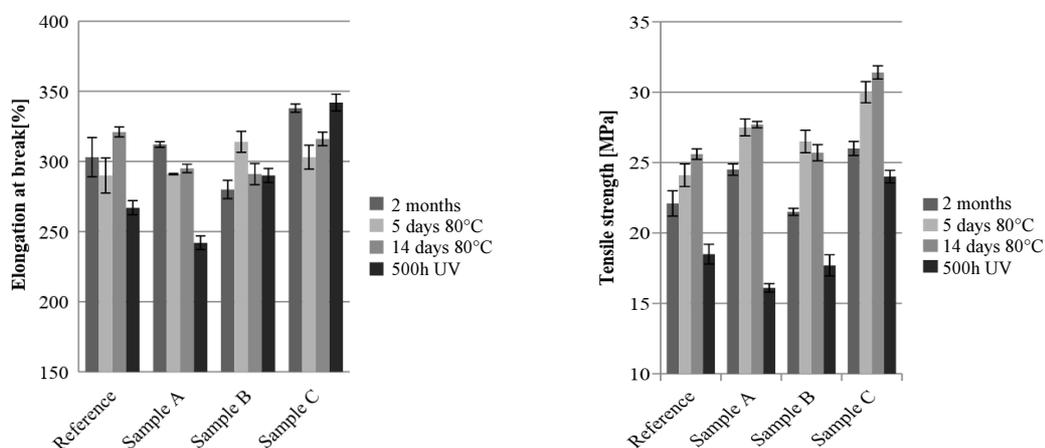
Fig. 12. Values of elongation at break and tensile strength for polyurea compositions

Rys. 12. Wartości odkształcenia oraz maksymalnego naprężenia przy zerwaniu dla układów polimocznikowych

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

SEM with EDS X-ray microanalysis was performed to assess the dispersion of the fillers in the polyurea compositions and analyse the chemical composition of the systems. SEM images of the fractured samples were taken (Fig. 13), where significant amounts of air bubbles can be seen, which is due to the lack of possibility to properly degas the composition before curing.

Additionally, micrographs of the the sample surfaces were taken as well (Fig. 14).

Good dispersion of the filler in the matrix was observed for Compositions A and C, modified with chalk and talc, respectively, while Composition B modified with graphite exhibited the best dispersion.

SUMMARY

Adding the fillers to polyurea improved the mechanical properties (i.e. elongation at break, tensile strength and hardness) for the compositions cured for 2 months at room temperature, as well as for the samples cured at the elevated temperature. Moreover, improvement of the thermal stability occurred. After 30 days of curing at room temperature, full conversion of the isocyanate and amine groups can be seen, which in turn confirms full curing of the products. The SEM/EDS analysis proves the good dispersion of the additives in the organic matrix, especially for the composition containing expanded graphite. No formation of filler particle agglomerates was observed, only the formation of cured polyurea particles due to the rapid nature of the curing reaction of the studied system.
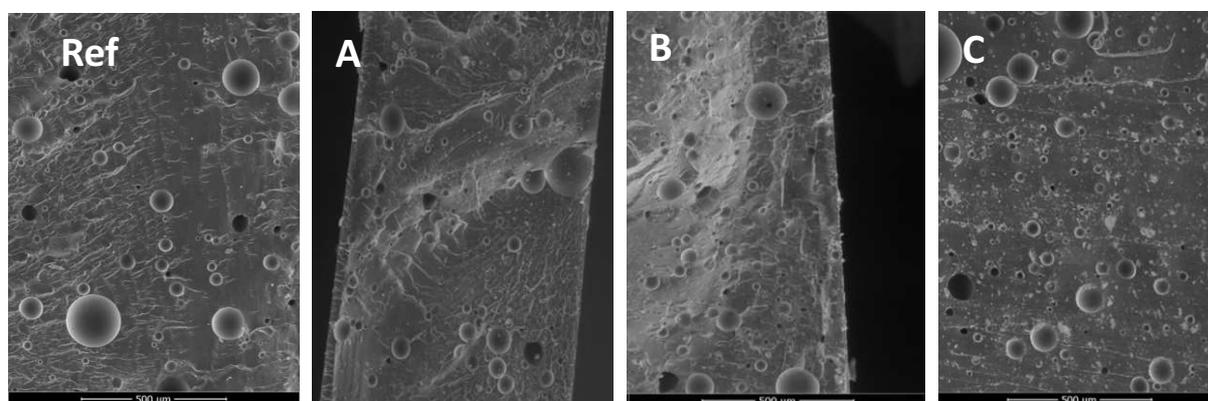
Fig. 13. SEM micrographs of fractured samples: Ref - reference, A - Sample A, B - Sample B, C - Sample C
Rys. 13. Zdjęcia SEM przełomów: Ref - układ bazowy, A - próbka A, B - próbka B, C - próbka C
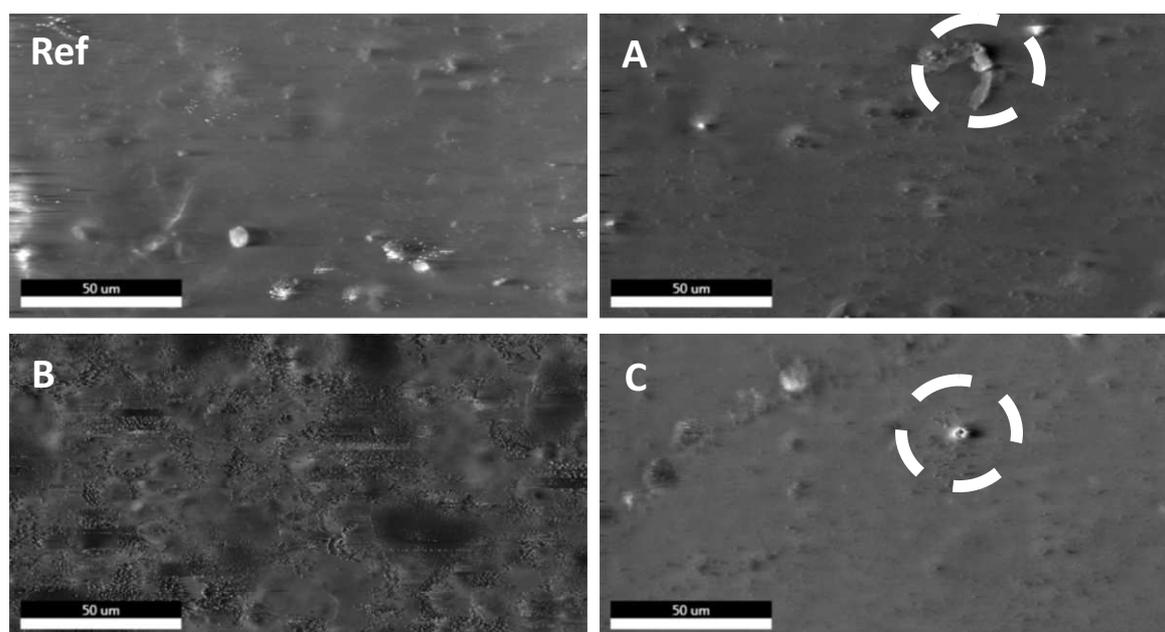
Fig. 14. SEM micrographsof sample surfaces: Ref - reference, A - Sample A, B - Sample B, C - Sample C
Rys. 14. Zdjęcia SEM powierzchni próbek: Ref - układ bazowy, A - próbka A, B - próbka B, C - próbka C

Acknowledgements

REFERENCES

[1] Mariappan T., Wilkie C.A., Thermal and fire retardant properties of polyurea, Polymer 2013, 58, 371-384.

[2] Choi T., Fragiadakis D., Roland C.M., Runt J., Microstructure and segmental dynamics of polyurea under uniaxial deformation, Macromolecules 2012, 45, 3581-3589.

[3] Dudley J., Primeaux II D.J., Fast-curing polyurea spray elastomers rapidly spreading in commercial use, Urethane Technology 2000, 17, 5, 37-40.

[4] Knop K., Nowoczesne powłoki polimocznikowe do ochrony konstrukcji żelbetonowych, Izolacje 2017, 9.

[5] Roland C.M., Twigg J. N., Vu Y., Mott P.H., High strain rate mechanical behavior of polyurea, Polymer 2007, 48, 574-578.

[6] He Y., Xie D., Zhang X., The structure, microphase-separated morphology, and property of polyurethanes and polyureas, J. Mater. Sci. 2014.

[7] Banera J., Maj M., Ubysz A., Powłoki polimocznikowe w budownictwie, Poznań 2017.

[8] Kernizan C., Lornimor J.J., Polyurea greases application case studies, White Paper, Lubrisense 2013, 14, 1-11.

[9] Tekalur, S.A., Shukla, A., Shivakumar, K.,. Blast resistance of polyurea based layered composite materials, Compos. Struct. 2008, 84, 271-281.

[10] Roland C.M., Twigg J.N., Vu Y., Mott P.H., High strain rate mechanical behavior of polyurea, Polymer 2007, 48, 574-578.

[11] Qiao J., Amirkhizi A.V., Schaaf K., Nemat-Nasser S., Wu G., Dynamic mechanical and ultrasonic properties of polyurea, Mechanics of Materials 2011, 43, 598-607.

[12] Grujicic M., Pandurangan B., King A.E., Runt J., Tarter J., Dillon G., Multi-length scale modeling and analysis of microstructure evolution and mechanical properties in polyurea, J. Mater. Sci. 2011, 46, 1767-1779.

[13] Toutanji H.A., Choi H., Wonga D., Gilbert J.A., Alldredge D.J., Applying a polyurea coating to high-performance organic cementitious materials, Construction and Building Materials 2013, 38, 1170-1179.

[14] Holzworth K., Jia Z., Amirkhizi A.V., Qiao J., Nemat--Nasser S., Effect of isocyanate content on thermal and mechanical properties of polyurea, Polymer 2013, 54, 3079--3085.

[15] Guan S.W., 100% solids polyurethane and polyurea coatings technology, Coatings World 2013, 49-58.

[16] Patent No.: US 7,001,948 B2.