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Mechanical and thermo-mechanical properties of natural rubber composites filled with submicron- and nano-sized silica particles and prepared using glycolysate as a plasticizer

The main aim of this work was to examine the selected mechanical and thermo-mechanical properties of natural rubber/silica composites prepared using glycolysate as a plasticizer. Prepared composites contained different amounts of submicron- (10, 15, 20 or 25 pphr) or nano-particles (0.5, 0.75, 1.0 or 1.25 pphr). The tensile properties, tear resistance, hardness, abrasion resistance and resilience of prepared materials were determined. In addition, the thermo-mechanical properties (by Dynamic Mechanical Thermal Analysis) were determined for the samples characterized by the highest content of particulate filler. All results were compared with properties of reference samples (without silica particles).

Keywords: natural rubber, composites, submicron-sized silica, nano-sized silica, mechanical properties, dynamic mechanical properties, polyurethane glycolysate.

Właściwości mechaniczne i termomechaniczne kompozytów kauczuku naturalnego z krzemionką submikronową i nanokrzemionką, otrzymanych z użyciem glikolizatu poliuretanowego jako plastyfikatora

Celem niniejszej pracy było zbadanie wybranych właściwości mechanicznych oraz termomechanicznych kompozytów na osnowie kauczuku naturalnego, otrzymanych z użyciem glikolizatu poliuretanowego jako plastyfikatora. Kompozyty zawierały różne ilości submikronowej krzemionki (10, 15, 20 i 25 cz. mas. napełniacza na 100 cz. mas. kauczuku naturalnego) lub nanokrzemionki (0,5, 0,75, 1,0 i 1,25 cz. mas. napełniacza na 100 cz. mas. kauczuku naturalnego). Zbadano właściwości próbek wulkanizatów w statycznej próbie rozciągania, wytrzymałość na rozdzieranie, twardość, odbojność oraz ścieralność. Ponadto metodą DMA określono właściwości termomechaniczne kompozytów zawierających największą ilość napełniaczy. Otrzymane wyniki porównano z wynikami uzyskanymi dla wulkanizatu referencyjnego niezawierającego napełniaczy krzemionkowych.

Słowa kluczowe: kauczuk naturalny, kompozyty, submikronowe cząstki krzemionki, nanocząstki krzemionki, właściwości mechaniczne, właściwości mechaniczne dynamiczne, glikolizat poliuretanowy.

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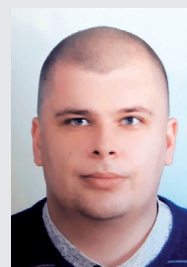
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Mgr inż. Kamila Błazek w 2015 roku ukończyła studia I stopnia na Wydziale Chemicznym Politechniki Gdańskiej – kierunek: Chemia. W 2016 roku ukończyła studia II stopnia na Wydziale Chemicznym Politechniki Gdańskiej – kierunek: Inżynieria Materiałowa, specjalność: Inżynieria Materiałów Polimerowych. Od 2016 roku jest słuchaczką Studium Doktoranckiego przy Wydziale Chemicznym Politechniki Gdańskiej. Specjalność: chemia i technologia polimerów, zwłaszcza poliuretanów otrzymywanych m.in. z wykorzystaniem substancji pochodzenia naturalnego (w tym bezizocyjanianowych poliuretanów).



1. Introduction

The inorganic fillers, e.g. carbon black, silica, talc, mica or calcium carbonate, are the most important and widely used fillers for the natural rubber composites [1–3]. The main advantage of using of mentioned fillers is reduction of cost of final materials. Some of mentioned fillers, i.e. silica and carbon black, are active fillers, which are responsible for the improving of the mechanical properties (e.g. tensile strength, tear strength and abrasion resistance) of rubber matrix composites [1, 4–6].

The content, size, structure, surface area and shape of fillers are the most important factors, which affect the mechanical properties of rubber composites [4, 7–9]. Silica particles are used as filler for natural rubber-based materials from many years, but still the influence of different types of silica particles (used separately or in the presence of other fillers) on the performance of rubber materials is investigated [10–14].

The growing amount of plastic waste produced every year resulted in development of mechanical and

chemical recycling methods of polymers. Recycling of polymers is resulted from requirements connected with the pollution prevention and the environment protection [15, 16]. In the case of polyurethanes (PUs), which are produced in form of flexible foams, rigid foams, coatings and elastomers, the total worldwide production in 2013 was equal nearly 16 mln tons, so the development of the cost-effective and environmental-friendly recycling technology is needed [17]. Polyurethane waste can be recycled by mechanical methods (i.e. grinding and applying as filler or pressing with a bonding agent) and chemical methods (mainly by e.g. glycolysis, hydrolysis or aminolysis). There is also possibility to the recovery of energy from polyurethanes waste (by e.g. incineration, gasification, and pyrolysis) [16]. The glycolysis is the chemical process which can be performed on the industrial scale, and involves the chemical decomposition of urethane groups by active hydrogen atoms presented in the structure of glycols. Glycolysis of polyurethanes is well described in the scientific literature and it is one of the most important chemical recycling method of polyurethane waste [17–25].

The main aim of this work was to examine the mechanical and thermo-mechanical properties of natural rubber/silica composites prepared using polyurethane glycolysate as a plasticizer. In this work, the silica particles with two different sizes (submicron- and nano-sized) were used. The tensile properties (tensile strength and elongation at break), tear resistance, hardness, abrasion resistance, resilience and thermo-mechanical properties (by Dynamic Mechanical Thermal Analysis) of prepared materials was determined. All results were compared with properties of reference samples (without silica particles).

2. Materials and preparation of composites

The two types of silica particles were used in this study – i.e. submicron sized silica particles Fransil 251 (Fransol, France) with a diameter equal to $0.2 \mu\text{m}$ and nanosilica Aerosil 200 (Evonik Industries, Germany) with a diameter 12 nm and specific surface area $200 \text{ m}^2/\text{g}$. Both fillers are shown in Fig. 1.

The polyurethane glycolysate was synthesized using polyurethane foam waste (PU) and 1,3-propanediol (PD). The reaction was conducted at PU/PD mass ratio equal 6:1 in the temperature $190 \text{ }^\circ\text{C}$ using potassium acetate as a catalyst. The schematic reaction is presented in Fig. 2. The polyurethane glycolysate was also successfully applied as a plasticizer in the case of lignin/natural rubber composites [26].

The ingredients – natural rubber (100 phr), stearic acid (3 phr), zinc oxide (5 phr), tetramethylthiuram (0.5 phr), submicron- or nano-sized silica particles, polyurethane glycolysate (2.5 phr) and sulfur (3 phr) were mixed in open two-roll laboratory mill at a friction ratio 1,08:1. The process of homogenization was carried out 15 min. The vulcanization was performed by using a hydraulic press at $150 \text{ }^\circ\text{C}$ under press 4,5-5 MPa and the vulcanization time was 10 min.

The prepared composites contained different amounts of applied submicron- (10, 15, 20 or 25 phr – coded as NRC-SP-10, NRC-SP-15, NRC-SP-20 or NRC-SP-25) and nano-particles (0.5, 0.75, 1.0 or 1.25 phr – coded as NRC-NP-0.5, NRC-NP-0.75, NRC-NP-1.0 or NRC-NP-1.25). The reference sample without silica particles (coded as REF) was also prepared.



Fig. 1. Comparison of silica fillers characterized by different particle size: a) submicron-sized silica ($0,2 \mu\text{m}$), b) nano-sized silica (12 nm)

Rys. 1. Porównanie wyglądu napełniaczy krzemionkowych o różnej wielkości cząstek: a) submikron ($0,2 \mu\text{m}$), b) nano (12 nm)

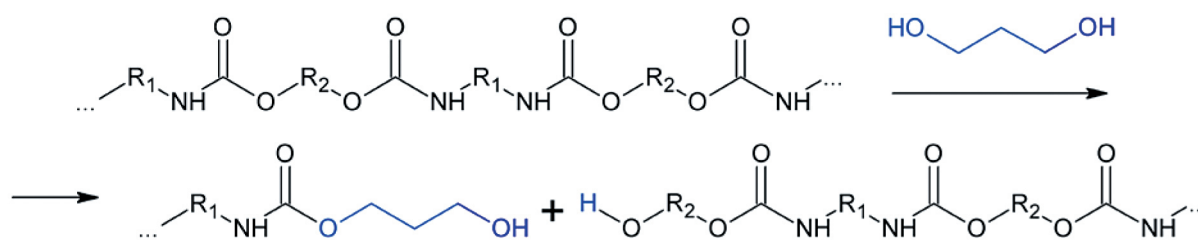


Fig. 2. Glycolysis of polyurethane using 1,3-propanediol
Rys. 2. Glikoliza poliuretanów z użyciem 1,3-propanediolu

3. Testing

The tensile properties (tensile strength and relative elongation at break) of the vulcanizates were determined, using universal testing machine Zwick/Roell Z020, according to ISO 37 standard. The cross-head speed was 300 mm/min. The test samples were prepared in a standard dumbbell shape, and all measurements were repeated five times.

The tear strength of the natural rubber composites were determined using universal testing machine Zwick/Roell Z020 in accordance to ISO 34-1 standard. The cross-head speed was 100 mm/min. The test samples were prepared in a crescent shape and with nick depth equal 1 mm, and all measurements were repeated five times.

The hardness was measured using Shore type A Durometer (Zwick/Roell) according to ISO 7619 in random ten points in one specimen.

The rebound resilience was determined with a Schob type machine using 6-mm-thick samples according to ISO 4662. All measurements were repeated ten times.

The abrasion resistance of the vulcanizates was determined using a Schopper-Schlobach apparatus with an APGi circulating roller and abrasive cloth No. 60.

Dynamic mechanical analysis was conducted using DMA Q800 analyzer (TA Instruments) with a frequency of 1 Hz and at heating rate of 4°C/min in the temperature range from -100 to 100 °C under nitrogen atmosphere.

4. Results and discussion

The mechanical properties of prepared composites are summarized in **Table 1** (vulcanizates with submicron-sized silica particles) and **Table 2** (vulcanizates with nano-sized silica particles).

The improvement of tensile strength of natural rubber composites was observed only for composites with submicron-sized silica particles. The highest values, i.e. 22.3 and 22.1 MPa, were observed for NRC-SP-10 and NRC-SP-15, respectively. Higher content of filler resulted in decreasing of tensile strength. In the case of elongation at break the decreasing trend with increasing content of both type silica particles is observed. The ability of inorganic fillers to form agglomerates at higher loadings of filler is responsible for decreasing of mechanical properties, and similar behavior was observed e.g. in the case of titanium dioxide/natural rubber composites [27].

Table 1. Mechanical properties of natural rubber composites with submicron-sized silica

Tabela 1. Właściwości mechaniczne wulkanizatu referencyjnego i kompozytów kauczuku naturalnego z submikronowymi cząstkami krzemionki

Materials	REF	NRC-SP-10	NRC-SP-15	NRC-SP-20	NRC-SP-25
Tensile strength [MPa]	20.3 ± 1.2	22.3 ± 0.6	22.1 ± 0.5	20.1 ± 0.9	20.2 ± 1.1
Elongation at break [%]	611.4 ± 23.1	620.4 ± 34.2	615.4 ± 12.5	603.4 ± 12.5	580.3 ± 24.7
Tear resistance [N/mm]	9.8 ± 1.4	9.8 ± 1.7	11.2 ± 0.6	13.0 ± 3.3	16.4 ± 3.6
Hardness [°Sh A]	42.7 ± 0.1	43.9 ± 0.3	44.6 ± 0.5	44.9 ± 0.3	45.2 ± 0.4
Rebound resilience [%]	63.0 ± 2.4	62.9 ± 1.7	61.8 ± 2.1	59.0 ± 1.7	58.5 ± 2.0
Abrasion resistance [cm ³]	0.207 ± 0.016	0.155 ± 0.0012	0.146 ± 0.012	0.140 ± 0.018	0.119 ± 0.011

Table 2. Mechanical properties of natural rubber composites with nano-sized silica particles (REF -- see Table 1)

Tabela 2. Właściwości mechaniczne wulkanizatu referencyjnego (REF – p. Tabela 1) i kompozytów kauczuku naturalnego z nanocząstkami krzemionki

Materials	NRC-NP-0.5	NRC-NP-0.75	NRC-NP-1.0	NRC-NP-1.25
Tensile strength [MPa]	17.9 ± 1.3	18.2 ± 0.9	19.0 ± 1.1	19.5 ± 1.5
Elongation at break [%]	624.1 ± 21.1	630.4 ± 34.6	604.3 ± 28.8	590.4 ± 27.4
Tear resistance [N/mm]	14.0 ± 2.0	12.4 ± 0.2	10.5 ± 1.6	9.1 ± 0.9
Hardness [°Sh A]	41.9 ± 0.6	41.3 ± 0.9	42.1 ± 0.6	42.3 ± 0.4
Rebound resilience [%]	64.7 ± 1.6	64.4 ± 1.8	63.0 ± 1.7	59.2 ± 0.8
Abrasion resistance [cm ³]	0.158 ± 0.016	0.131 ± 0.018	0.054 ± 0.020	0.041 ± 0.011

The most important factor, which affects the mechanical properties, is good dispersion of filler particles in polymer matrix. The well dispersed filler permit to uniform stress distribution and stress-concentration reduction, and this results in improvement of mechanical properties [4, 7–9, 28, 29].

In the case of submicron-sized silica particles/natural rubber composites tear resistance increasing with increasing content of filler (from 9.8 N/mm for NRC-SP-10 to 16.4 N/mm for NRC-SP-25), while for the nanosilica/natural rubber composites tear resistance reaches maximum value (14.0 N/mm) for the composites with the lowest applied amount of nanofiller (NRC-NP-0.5).

Natural rubber composites with submicron-sized and nano-sized silica particles exhibit improved abrasion resistance in comparison with the reference samples, and increasing trend with increasing content of silica particles was observed. The highest abrasion resistance was observed in the case of composites with silica nanoparticles (0.041 cm³ for NRC-NP-1.25), and this is probably connected with higher specific surface area of nanoparticles, in comparison to the submicron-sized particles. Also the good adhesion of nano-sized particles to the natural rubber chains can results in increase of abrasion resistance.

Applying of both fillers resulted in increasing of hardness and decreasing of resilience of prepared natural rubber composites, which can be resulted from the high hardness of applied fillers and good adhesion between particles surface and polymer chains.

The results of dynamic mechanical analysis for selected vulcanizates (REF, NRC-SP-25, NRC-

-NP-1.25) are presented in Fig. 3 (storage modulus vs. temperature), Fig. 4. (loss modulus vs. temperature) and Fig. 5. (damping factor vs. temperature).

Both applied fillers caused improvement of storage and loss modulus in the comparison to reference samples. Increase of storage modulus value is probably resulted from the presence of hard filler in rubber matrix, good dispersion of filler and interaction between particles surface and polymer chains. All mentioned factors caused an improvement of the composites stiffness. It can be attributed to good adhesion between the polymer matrix and particles surface resulting in effective load transfer from the rubber matrix to fillers. The applied plasticizer (polyurethane glycolysate) can also improve the dispersion of hydrophilic silica in rubber matrix and interaction (adhesion) between them. The higher values of storage and loss modulus was observed for the vulcanizates filled with submicron-sized silica particles and this can be resulted from higher content of inorganic filler (25 pphr for NRC-SP-25) in comparison to NRC-NP-1.25.

The glass transition temperature (T_g) was determined as a temperature at which tan delta reaches maximum value. The T_g of prepared vulcanizates increases in the sequence:

REF (-35.6 °C) < NRC-NP-1.25 (-35.4 °C) < NRC-SP-25 (-33.0 °C).

The presence of filler caused reduction of polymer chains movements, and this is connected with increasing of glass transition temperature. It can be resulted from the good interaction of polymer matrix and filler surface.

The highest T_g was observed for NRC-SP-25 material, which has the highest weight content of inorganic filler.

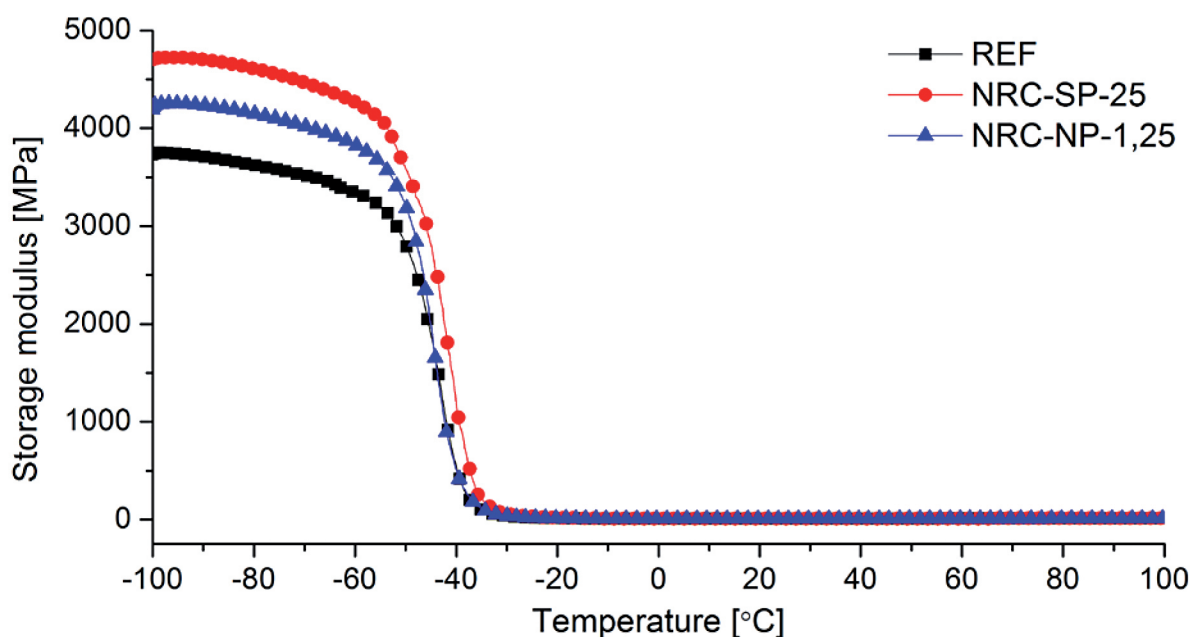


Fig. 3. Storage modulus of prepared vulcanizates as a function of temperature

Rys. 3. Moduł zachowawczy otrzymanych wulkanizatów w funkcji temperatury

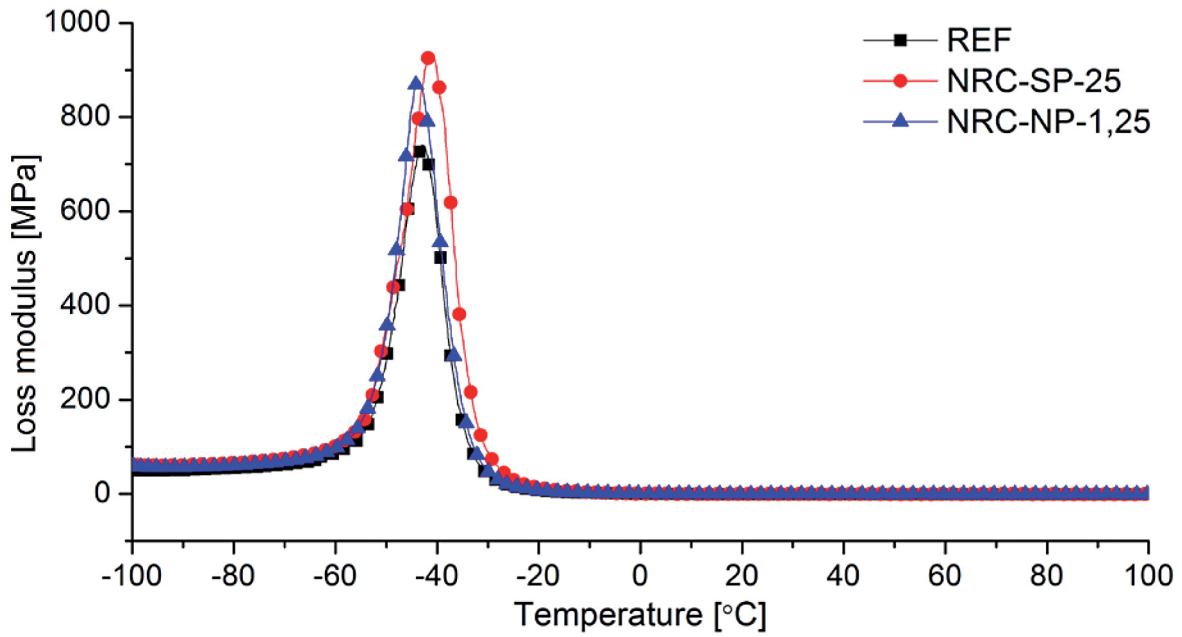


Fig. 4. Loss modulus of prepared vulcanizates as a function of temperature
Rys. 4. Moduł stratności otrzymanych wulkanizatów w funkcji temperatury

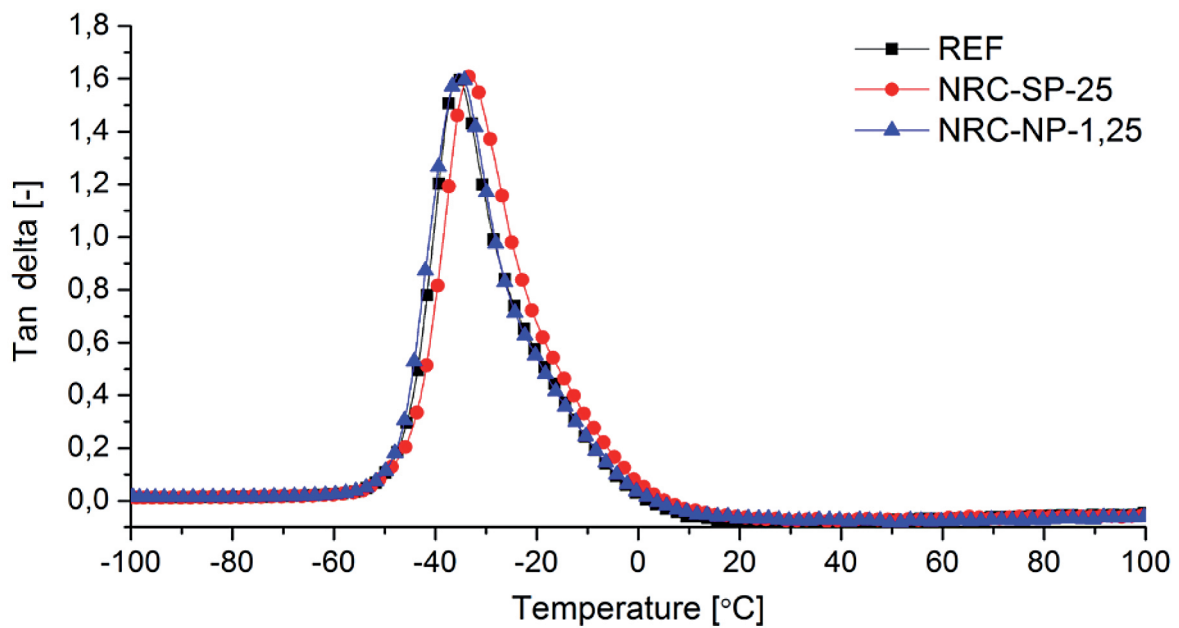


Fig. 5. Tan delta of prepared vulcanizates as a function of temperature
Rys. 5. Tangens delta otrzymanych wulkanizatów w funkcji temperatury

5. Summary

The natural rubber composites filled with submicron-sized and nano-sized particles were successfully prepared using polyurethane glycolysate as a plasticizer. The obtained results confirmed that applied product of polyurethanes chemical recycling has a good potential for the industrial applications. Moreover, the application of recycled material is beneficial from the environment protection point of view.

The size of silica particles affects the mechanical performance of obtained materials, which was especially visible in the case of abrasion resistance, which was the highest when the silica nanoparticles were applied as filler. The high specific surface area of silica nanoparticles permit to achieve specific mechanical properties at lower loadings of filler in comparison to natural rubber composites filled with submicron-sized particles.

References

1. *Guma. Poradnik inżyniera i technika*, WNT, Warszawa 1981.
2. *Poradnik technologa gumy*, IPGum „STOMIL”, Piastów 2003.
3. *Ogólna technologia gumy*, WNT, Warszawa 1972.
4. Wang M.J., *Rubber Chemistry and Technology*, 1998, **71**, 520–589.
5. Bokobza L., *Macromolecular Materials and Engineering*, 2004, **289**, 607–621.
6. Ansarifar A., Wang L., Ellis R.J., Kirtley S.P., Riyazuddin N., *Journal of Applied Polymer Science*, 2007, **105**, 322–332.
7. Rattanasom N., Prasertsri S., Ruangritnumchai T., *Polymer Testing*, 2009, **28**, 8–12.
8. Yang J., Tian M., Jia Q.X., Zhang L.Q., Li X.L., *Journal of Applied Polymer Science*, 2006, **102**, 4007–4015.
9. Orefice R.L., Hench L.L., Bennan A.B., *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, 2001, **23**, 1–8.
10. Idrus S.S., Ismail H., Palaniandy S., *Polymer Testing*, 2011, **30**, 251–259.
11. Kanking S., Niltui P., Wimolmala E., Sombatsompop N., *Materials and Design*, 2012, **41**, 74–82.
12. Ahmed K., Nizami S.S., Riza N.Z., *Journal of Advanced Research*, 2014, **5**, 165–173.
13. Prasertsri S., Rattanasom N., *Polymer Testing*, 2011, **30**, 515–526.
14. Thongsang S., Sombatsompop N., *Journal of Macromolecular Science, Part B Physics*, 2007, **46**, 825–840.
15. Datta J., Kopczyńska P., *Critical Reviews in Environmental Science and Technology*, 2016, **46**, 905–946.
16. Prociak A., Ryszkowska J., Rokicki G. (Ed.), *Materiały Poliuretanowe*, PWN, Warszawa 2014.
17. *Polyurethane (PU) Market Analysis by Product (Rigid Foam, Flexible Foam, Coatings, Adhesives & Sealants, Elastomers)*, by End-use (Furniture and Interiors, Construction, Electronics & Appliances, Automotive, Footwear, Packaging) and Segment Forecasts to 2020, Grand View Research, United States 2014.
18. Datta J., Rohn M., *Polimery*, 2007, **52**, 7–8, 579–582.
19. Datta J., Rohn M., *Polimery*, 2007, **52**, 9, 627–633.
20. Molero C., de Lucas A., Romero F., Rodríguez J.F., *Journal of Material Cycles and Waste Management*, 2009, **11**, 130–132.
21. Datta J., Haponiuk J.T., *Journal of Elastomers and Plastics*, 2011, **43**, 529–541.
22. Datta J., *Journal of Thermal Analysis and Calorimetry*, 2012, **109**, 517–520.
23. Datta J., Pasternak S., *Polimery*, 2005, **50**, 352–357.
24. Molero C., de Lucas A., Rodríguez J.F., *Polymer Degradation and Stability* 2006, **91**(2) 221–228.
25. H. Beneš H., Rösner J., Holler P., Synková H., Kotek J., Horák Z., *Polymers for Advanced Technologies*, 2007, **18**, 149–156.
26. Datta J., Parcheta P., Surówka J., *Industrial Crops and Products*, 2017, **95**, 675–685.
27. Datta J., Kosiorek P., Włoch M., *Iranian Polymer Journal*, 2016, **25**, 1021–1035.
28. Pinto D., Bernardo L., Amaro A., Lopes S., *Construction and Building Materials*, 2015, **95**, 596–524.
29. Hanemann T., Szabó D.V., *Materials*, 2010, **3**, 3468–3517.