Influence of UV on the self-adhesive properties of silicone pressure-sensitive adhesives*)

Adrian Krzysztof Antosik [1), **)] (ORCID ID: 0000-0002-3954-6612), **Karolina Mozelewska**[1)] (0000-0001-8963-4349), **Konrad Gziut**[1)] (0000-0001-8663-5311)

DOI: https://doi.org/10.14314/polimery.2023.1.3

Abstract: The paper presents the results of research on the UV radiation influence on the self-adhesive properties of silicone adhesives. The adhesives were obtained by cross-linking commercial resins (PSA 590, Q2-7566) at the temperature of 110°C, using different amounts (0–3 wt%) of bis(2,4-dichlorobenzoyl) peroxide. Self-adhesive properties of adhesives such as adhesion, tack, and durability before and after aging were determined. The adhesives showed stable self-adhesive properties, however, the PSA 590 adhesive had a higher maximum operating temperature than the Q2-7566 adhesive.

Keywords: silicone pressure-sensitive adhesive, self-adhesive properties, adhesion, UV resistance.

Wpływ UV na właściwości samoprzylepne silikonowych klejów samoprzylepnych

Abstrakt: W pracy przedstawiono wyniki badań dotyczące wpływu promieniowania UV na właściwości samoprzylepne klejów silikonowych. Kleje otrzymano poprzez sieciowanie w temperaturze 110°C żywic komercyjnych (PSA 590, Q2-7566), stosując różne ilości (0-3% mas.) nadtlenku bis(2,4-dichlorobenzoilu). Oznaczono właściwości samoprzylepne klejów takie, jak adhezja, przyczepność oraz trwałość przed i po starzeniu. Kleje wykazywały stabilne właściwości samoprzylepne, przy czym klej otrzymany na bazie żywicy PSA 590 miał wyższą maksymalną temperaturę użytkowania niż klej na bazie żywicy Q2-7566.

Słowa kluczowe: silikonowe kleje samoprzylepne, właściwości samoprzylepne, adhezja, odporność na UV.

Silicones are semi-inorganic polymers (polyorganosiloxanes) that can be fluid, elastomeric, or resinous depending on the types or organic groups on the silicon atoms and the degree of cross-linking between the polymer chains. The silicone resins owe their high thermal stability to strong silicon - oxygen - silicon bonds. They exhibit unique properties such as high flexibility of the Si-O-Si skeleton, low intermolecular interactions, low surface tension, excellent thermal stability and high UV transparency, excellent electrical properties, chemical resistance, and excellent weather resistance. Silicones are used as a sealing materials. As one-component adhesives, they cure by absorbing moisture from the surrounding air. During curing, the appearance of a hardened silicone layer, the so-called skin that still has an uncured layer underneath which may take much longer to harden further by slow moisture absorption. Silicones are very flexible, even at low temperatures, down to -70°C [1–3]. One of the many specialized products obtained from them are silicone pressure-sensitive adhesives (Si-PSA).

Silicone adhesives are typically used as encapsulates, sealants or adhesives. They are exposed to UV radiation in many applications, *e.g.*, as sealants for blue LEDs or as adhesives for attaching a protective glass cover to solar cells. As a result of exposure to radiation, radicals are formed and then cross-linking reactions occur, which may cause brittleness and cracking leading to material degradation [4–6].

Transparent silicone adhesives are extremely versatile, and therefore technologically important materials. They show adhesion to many different surfaces and low shrinkage during curing. It is combined with high flexibility, good tensile strength, as well as resistance to weather conditions, ozone, chemicals, and abrasion. Moreover, they retain these properties over a wide temperature range from -100°C to 300°C. The self-adhesive and mechanical properties of silicone pressure-sensitive tapes depend largely on the type and concentration of the

1) West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Department of Chemical Organic Technology and Polymeric Materials, Pulaskiego 10, 70-322 Szczecin, Poland.

*) Material contained in this article was presented at the 64. Zjazd Naukowy Polskiego Towarzystwa Chemicznego (PTChem 2022), 11–16 September 2022, Lublin, Poland.

**) Author for correspondence:
adriankrzysztofantosik@gmail.com

cross-linking compound used. As the cross-link density of the adhesive increases, the cohesion of the obtained product generally increases, and the adhesion and tackiness decrease. The most common on the market are silicone resins that cross-link according to the free-radical mechanism [7-9]. In addition, silicone pressure sensitive adhesives are materials characterized by low surface tension, excellent thermal stability, and chemical resistance. Since their arrival in the market in 1960, silicone pressure sensitive adhesives have found many applications. They are used as tapes for joining materials with low surface energy, as well as in the electrical and electronics sectors, medical and health care and the automotive industry [10–12].

The aim of the work was to obtain silicone self-adhesive adhesives by thermal cross-linking of silicone resin with bis(2,4-dichlorobenzoyl) peroxide (DCIBPO). The effect of UV radiation on self-adhesive properties such as adhesion, tack and durability before and after aging as a function of DCIBPO was investigated.

EXPERIMENTAL PART

Materials

Colored transparent commercial silicone resin Dowsil Q2-7566 (Dow Corning, USA) was used. The solids content was 56 wt% and the viscosity was 20,000−80,000 mPa · s. Milky-opaque silicone resin PSA 590 was supplied by Momentive (USA).The solids content was 60 wt% and the viscosity was 18,000 mPas. Bis (2,4-dichlorobenzoyl) peroxide (DClBPO) was purchased from Gelest (USA) and was used as the crosslinking agent.

Preparation of one-sided self-adhesives tapes

In the first step, the silicone resin was mixed with varying amounts (0–3 wt%) of DCIBPO. The homogenized and deaerated composition was then covered with a 50 μm thick polyester film using a Byk slotted applicator (Altana AG, Germany). The cross-linking process was carried out at a temperature of 110°C for 10 minutes, thus obtaining self-adhesive adhesive tapes with a basis weight of 45 g/m^2.

Aging of silicone self-adhesive tapes

Accelerated aging was performed according to ASTM D904-99 in a QLAB, USA test chamber (UV-B 313 nm) (SERU program) QLAB, USA (420 nm). The three-stage aging process was carried out for 7 days according to the conditions presented in Table 1.

Table 1. Aging process conditions

Aging process	Conditions
First stage	UV, 63°C, 0.85 W/m^2, 4h
Second stage	50°C, 4h, condensation
Thered stage	UV, 63°C, 0.85 W/m^2, 24h

Methods

Peel adhesion to steel at 180° was determined in accordance with the Afera 4001 standard developed by the European Association des Fabricants Europeens de Rubans Auto-Adhesifs using a Zwick/Roell Z010 testing machine (Zwick/Roell, Germany). The adhesive tape, 2.5 cm wide, was sticked to the steel plate under the pressure of 2 kg hard rubber roller. The plate was placed in the jaws of the testing machine and the free end in the other jaws. The test measures the force with which the tape peels off the plate at a constant speed of 300 mm/min. The result is the average of three measurements. The steel plates used for the tests should be perfectly flat, 200 mm long, 50 mm wide and approximately 2 mm thick, made of polished stainless steel (with a Brinell hardness of 130 to 200). They should contain carbon (<0.12%), nickel (> 8%) and chromium (> 17%) [8, 13-16].

The loop method was used to determine the adhesion. Measurements were made in accordance with the Afera 4015 standard using a Zwick/Roell Z010 testing machine (Germany). This method measures the force to detach the tape from a metal plate without pressure. The contact area of the adhesive layer with the substrate during the test was 5 cm^2 (2.5 cm × 2 cm) [17–18]. The steel plate had the same parameters as in the case of peel adhesion.

Durability was determined in accordance with the Afera 4012 standard using a device that allows automatic measurement of the weld cracking time. In this method, a 2.5 × 2.5 cm tape sample was glued to a metal plate and then a 1 kg weight was placed on it. During the test, the time required for the sample to detach from the metal plate was measured. The test was carried out at room temperature and at 70°C.The steel plate had the same parameters as in the case of peel adhesion [8, 19–20].

The SAFT test was carried out in a similar way as the cohesion test, with the difference that the measurement was carried out in the temperature range from 20 to 225°C, at a heating rate of 1°C/min [8, 21, 22]. The time required for the sample to detach from the metal plate was measured. The maximum operating temperature of the adhesive has also been specified.

RESULTS AND DISCUSSION

The most important factor affecting the aging of self--adhesive products is the adhesive from which the sample is made. The film and the adhesive paper practically do not age. From the literature reports it can be concluded that the tape aging causes a decrease in the self-adhesive properties [7, 23].

In order to compare the effect of UV on self-adhesive tapes based on silicone adhesives, tests of their basic pro-

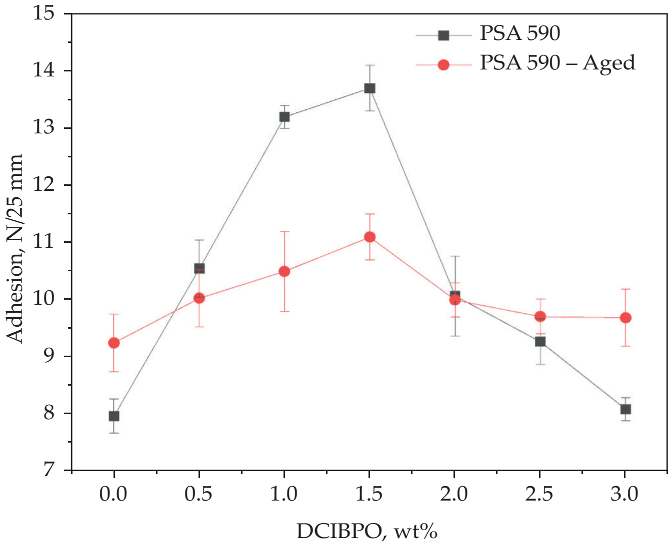

Fig. 1. Effect of DCIBPO on adhesion before and after aging of PSA 590 adhesives

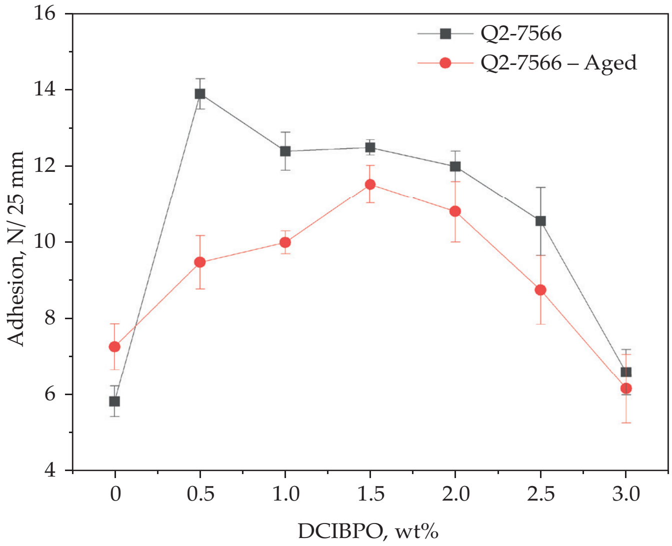

Fig. 2. Effect of DCIBPO on adhesion before and after aging of Q2-7566 adhesives

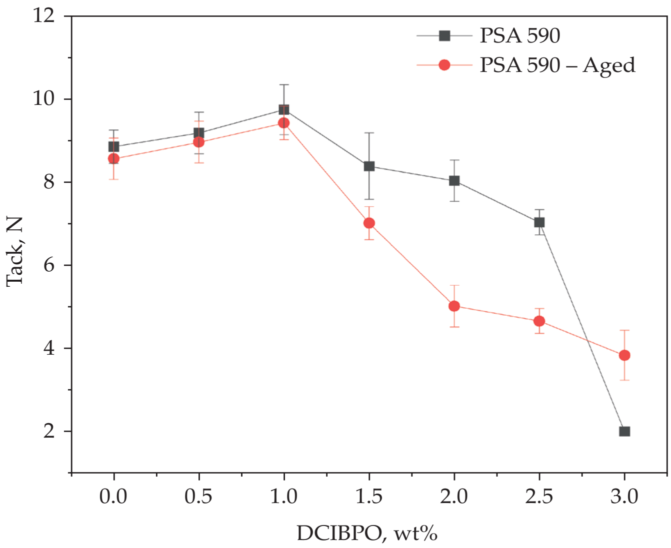

Fig. 3. Effect of DCIBPO on tack before and after aging of PSA 590 adhesives

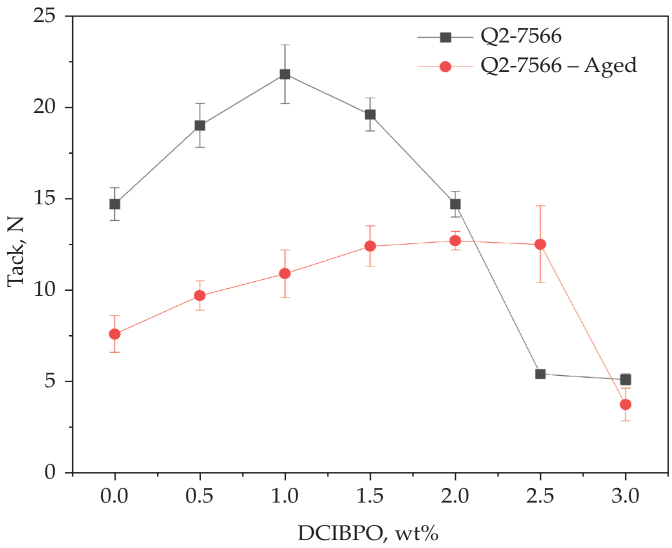

Fig. 4. Effect of DCIPBO on tack before and after aging of Q2-7566 adhesives

perties such as adhesion, cohesion and tack were selected. The tests were carried out on two selected resins (Dowsil Q2-7566, PSA 590). Based on our research, it was established that these resins hade the best performance properties and, being products of unrelated companies, wouldll enable confirmation of the proposed aging method effectiveness for products with different recipes, and thus it would be easier to show any imperfections.

Fig. 1 shows the results of the PSA 590 silicone resin adhesion before and after aging. The tests were carried out in conditions that stimulate the use of silicone adhesive tapes. They were exposed to changing environmental conditions, similar to the conditions in which the sample can be used (changes in humidity, temperature and insolation). As a result of the aging cycle, the adhesion decreased for all concentrations of the cross-linker. Only in the case of the sample without DCIPBO, the adhesion increased after aging. These results are in a good agreement with the literature review, which indicates that aging affects the properties of self-adhesive materials, manifested by a decrease in adhesion [24, 25]. In addition, it was found that the tape samples increased yellowness, which is not a positive aspect in the technology of producing adhesives and adhesive tapes. This was most likely due to the aging of the film used to make the adhesive tapes, not the adhesive itself.

Fig. 2 shows that in the case of cross-linked Q2-7566 adhesives, the adhesion after aging was lower than before aging. The exception was a sample of adhesive without the addtion of cross-linker. In addition, the uncrosslinked Q2-7566 adhesive had lower adhesion than the PSA 590 adhesive. The sample containing 0.5 wt% cross-linker had the maximum adhesion before aging and the sample containing 1.5 wt% cross-linker after aging.

The artificial aging method affects the adhesion of the tested adhesives, depending on the type of silicone resin and the amount of cross-linking agent. According to the literature, artificial aging reduces adhesives stiffness [26]. The reason for the decrease in adhesion may be the absorption of light with a wavelength below 400 nm, which may result in the bond breaking and oxidation of the side hydrocarbon groups [27]. It should also be noted that irradiation and water spraying are cyclical, so the temperature also cyclical, therefore the softening of both materials is a combination of all these effects.

Fig. 3 shows the tack results of the tested tapes made of PSA 590 resin. The tack increases with increasing of the cross-linking compound content to 1 wt% and then decreases. This phenomenon is quite popular in the technology of producing adhesives and self-adhesive materials and it is described in the literature [7, 8]. Comparing aged adhesive tapes, a decrease in tack is observed, which is consistent with the literature and quite predictable [28]. The drop in the tack may be caused by the aging conditions, which may damage the one-sided tape, as the samples are not completely resistant to them. Similar phenomena are observed for Q2-7566 resin (Fig. 4). For unaged samples, the tack increases to 21 N with increase of the cross-linker content to 1 wt%, and then decreases to approx. 6 N at 2.5 wt% cross-linker content.

On the other hand, after aging, a decrease in tack by up to half is observed (for 1 wt% of DCIBPO). Cyclic chan-

T a b l e 2. Effect of aging on durability and maximum operating temperature of PSA 590 adhesives

Sample	DClBPO, wt%	Durability, min		Max. operating temp., °C
		20°C	70°C	
PSA 590	0	607	5	75
PSA 590 – Aged		84	24	97
PSA 590	0.5	> 4320	186	116
PSA 590 – Aged		96	12	100
PSA 590	1	> 4320	426	134
PSA 590 – Aged		> 4320	> 4320	209
PSA 590	1.5	> 4320	> 4320	154
PSA 590 – Aged		> 4320	> 4320	208
PSA 590	2	> 4320	> 4320	123
PSA 590 – Aged		> 4320	> 4320	194
PSA 590	2.5	> 4320	> 4320	122
PSA 590 – Aged		> 4320	> 4320	188
PSA 590	3	> 4320	> 4320	121
PSA 590 – Aged		> 4320	> 4320	187

T a b l e 3. Effect of aging on durability and maximum operating temperature of Q2-7566 adhesives

Sample	DClBPO, wt%	Durability, min		Max. operating temp., °C
		20°C	70°C	
Q2 7566	0	749	9	86
Q2 7566 – Aged		78	6	87
Q2 7566	0.5	> 4320	144	123
Q2 7566 – Aged		354	72	83
Q2 7566	1	> 4320	492	129
Q2 7566 – Aged		1284	456	82
Q2 7566	1.5	> 4320	> 4320	133
Q2 7566 – Aged		> 4320	1500	89
Q2 7566	2	4320	> 4320	131
Q2 7566 – Aged		> 4320	> 4320	101
Q2 7566	2.5	> 4320	> 4320	105
Q2 7566 – Aged		> 4320	> 4320	102
Q2 7566	3	> 4320	> 4320	101
Q2 7566 – Aged		> 4320	> 4320	97

ges in temperature and humidity cause actual aging of the tape, and thus adhesive properties deterioration [7]. Tack for both unaged adhesives with a DCIBPO content of up to 2.5 wt% was higher than for the aged samples. In the case of PSA 590 resin, increase of the cross-linker content to 3 wt% resulted in greater tack of the sample after aging compared to the unaged one. This may be due to the fact that under the influence of elevated temperature, these samples could cross-link further, which created a very tightly cross-linked internal network and resulted in higher tack.

Tables 2 and 3 present the results of connection durability for PSA 590 and Q2-7566 adhesives, respectively. The addition of DCIBPO results in an increase in durability at 20°C up to 72 h. Besides, the non-crosslinked Q2-7566 adhesives had slightly higher cohesion than the PSA 590 adhesives. Artificial aging influenced the value of durability at 20°C, especially at low DCIBPO content. Very good durability (more than 72 hours) was observed for both adhesives with a cross-linker content of 1.5 wt%. However, for lower content of cross-linking agent, the durability was lower. Comparing the durability before and after aging, lower values were found with a lower content of cross-linker. On the other hand, for adhesives containing a larger amount of cross-linker (above 1.5 wt%), the durability after aging did not change. The reason for this may be the water absorption between the polymer chains, which facilitates their movement [7, 28, 29].

The addition of DCIBPO increases the thermal resistance of the adhesive, as evidenced by the higher maximum operating temperature in the SAFT test (Tabs. 2, 3). For both unaged resins, the maximum thermal resistance was obtained with a cross-linking agent content of 1.5 wt%. However, PSA 590 adhesives showed higher thermal resistance than Q2-7566 adhesives. Adged PSA 590 adhesives were characterized by a higher maximum operating temperature than Q2-7566 adhesives. The maximum service temperature of the aged PSA 590 adhesive containing 1–1.5 wt% DCIBPO was approximately 210°C. However, in the case of the Q2-7566 adhesive, the maximum working temperature after aging was much lower and ranged from 82 to102°C. This may be due to the increased content of water absorbed by the PSA 590 adhesive and the increased stiffness of the materials [28, 29].

CONCLUSIONS

The tested self-adhesive adhesives show high durability and strength after aging. The obtained results confirm the usefulness of silicone tapes as products for facade applications. However, there is a decrease in cohesion after aging, especially at low cross-linker content. Both adhesives showed stable self-adhesive properties. However, the PSA 590 resin adhesive had a higher maximum operating temperature than the Q2-7566 resin adhesive. This may be related to water infiltration, especially in bond boundary layers. And this, in turn, can promote an earlier loss of traction under constant load. Greater adhesion of the PSA 590 resin adhesive may result in cross-linking of the adhesive after aging, which increases the adhesive strength.

ACKNOWLEDGEMENT

The National Center for Research and Development (NCBiR) financed this research under the LIDER initiative. Project number LIDER/9/0028/L-11/19/NCBR/2020.

REFERENCES

[1] Benedek I.: Pressure-sensitive adhesives and applications. Marcel Dekker 2005 ISBN 0-8247-5059-4.
[2] Mirski Z., Piwowarczyk T.: *Przegląd Spawalniczy* **2008,** *8,* 12.
[3] Ho K. Y., Dodou K.: *International Journal of Pharmaceutics* **2007**, *333*, 24. https://doi.org/10.1016/j.ijpharm.2006.09.043
[4] Fischer H.R., Semprimoschnig C., Mooney C., *et al.*: *Polymer Degradation and Stability* **2013,** *98*, 3, 720. DOI: 10.1016/j.polymdegradstab.2012.12.022
[5] Cai C., Miller D. C., Tappan I. *et al.*: *Solar Energy Materials and Solar Cells* **2016,** *157*, 346, https://doi.org/10.1016/j.solmat.2016.05.065
[6] Mozelewska K., Czech Z., Bartkowiak M., *et al.*: *Materials* **2022,** *15,* 246. https://doi.org/10.3390/ma15010246
[7] Antosik A. K., Bednarczyk P., Czech Z.: *Polymer Bulletin* **2018,** *75,* 1141-DOI:10.1007/s00289-017-2083-2
[8] Antosik A. K., Mozelewska K. *Polimery* **2022,** *67,* 308. https://doi.org/10.14314/polimery.2022.7.4
[9] Mozelewska K., Antosik A. K.: *Materials* **2022,** 15, 5713. https://doi.org/10.3390/ma15165713
[10] Antosik A.K., Czech Z.: *Wiadomości Chemiczne* **2016,** *70*, 25.
[11] Mapari S., Mestry S., Mhaske S. T.: *Polymer Bulletin* **2021,** *78,* 4075. https://doi.org/10.1007/s00289-020-03305-1
[12] Antosik A. K., Makuch E., Gziut K.: *Journal of Polymer Research* **2022,** *29*. https://doi.org/10.1007/s10965-022-02981-z
[13] Sowa D., Czech Z., Byczyński Ł.: *International Journal of Adhesion and Adhesives* **2014,** *49,* 38. https://doi.org/10.1016/j.ijadhadh.2013.12.013
[14] Sasaki M., Fujita K., Adachi M., *et al.*: *International journal of adhesion and adhesives* **2008,** *28(7),* 372. https://doi.org/10.1016/j.ijadhadh.2007.11.002
[15] Hazama-cho K., Hachioji S., *ThreeBond Technical News* **1992,** *38,* 1.
[16] Shaomin S., Mengling L., Ally L.: *International Journal of Adhesion and Adhesives* **2013,** *41,* 98. https://doi.org/10.1016/j.ijadhadh.2012.10.011
[17] Tordjeman Ph., Papon E., Villenave J&J.: *Journal of Polymer Science Part B: Polymer Physics* **2000,** *38.9,* 1201.

[18] http://www.adhesivetest.com/resources/docs/FinatTestMethods.pdf (25.07.2022)
[19] Tiu B. D. B., Delparastan, P., Ney, M. R., *et al.*: *ACS applied materials & interfaces* **2019,** *11(31),* 28296. https://doi.org/10.1021/acsami.9b08429
[20] Antosik A. K., Mozelewska K., Piątek-Hnat M., *et al.*: *Journal of Thermal Analysis and Calorimetry* **2021,** 1. https://doi.org/10.14314/polimery.2022.7.4
[21] Antosik A.K., Mozelewska K., Czech Z. *et al.*: *Silicon* **2020**, *12*, 1887. https://doi.org/10.1007/s12633-019-00295-2
[22] Park H. W., Seo H. S., Kwon K., *et al.*: *Polymers* **2020**, *12(10),* 2410. https://doi.org/10.3390/polim12102410
[23] Czech Z., Kowalczyk A.: *Chemik* **2014,** *68*.1.
[24] Elsaka, Shaymaa E: *J Adhes Dent* **2014,** *16.6*, 531. doi: 10.3290/j.jad.a33198
[25] Savvilotidou M., Vassilopoulos A. P., Frigione M., *et al.*: *Construction and Building Materials* **2017,** *140*, 552. https://doi.org/10.1016/j.conbuildmat.2017.02.063
[26] Giese-Hinz J., Kothe C., Louter C., *et al.*: *International Journal of Adhesion and Adhesives* **2012,** *117*, 103019. https://doi.org/10.1016/j.ijadhadh.2021.103019
[27] Stazi F., Giampaoli M., Rossi,M., *et al.*: *Composite Structures* **2015,** *133*, 404. https://doi.org/10.1016/j.compstruct.2015.07.067
[28] Shuangyan X., Dillard D.,A., Dillard J., G.: *International Journal of Adhesion and Adhesives* **2003,** *23, 3*, 235 https://doi.org/10.1016/S0143-7496(03)00027-7
[29] Gregory J., Barany S. *Advances in colloid and interface science* **2011,** *169(1)*, 1. https://doi.org/10.1016/j.cis.2011.06.004

Received 30 XI 2022.