Influence of storage time on the useful properties of silicone pressure-sensitive adhesives*)

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Abstract: The influence of the storage time on the useful properties (cohesion, adhesion, stickiness) of silicone pressure-sensitive tapes (Si-PSA) was investigated. Two types of silicone resins PSA 529 and PSA 590 (Momentive, USA) were used and crosslinked with bis (2,4-dichlorobenzoyl) peroxide (DClBPO). There was no significant effect of tapes long-term storage (7 years) on their properties. The tapes based on PSA 590 resin were more resistant to aging than PSA 529.

Keywords: pressure-sensitive adhesives, silicone, self-adhesive tape, storage time.

Wpływ czasu przechowywania na właściwości użytkowe silikonowych klejów samoprzylepnych

Streszczenie: Zbadano wpływ czasu przechowywania na właściwości użytkowe (kohezja, adhezja, kleistość) silikonowych taśm samoprzylepnych (Si-PSA). Stosowano dwa rodzaje żywic silikonowych PSA 529 i PSA 590 (Momentive, USA), które sieciowano przy użyciu nadtlenku bis(2,4-dichlorobenzoilu) (DClBPO). Nie stwierdzono istotnego wpływu długotrwałego przechowywania (7 lat) taśm na ich właściwości. Większą odpornością na starzenie charakteryzowały się taśmy otrzymane na bazie żywicy PSA 590 niż PSA 529.

Słowa kluczowe: kleje samoprzylepne, silikony, taśmy samoprzylepne, czas przechowywania.

Self-adhesive materials in the international industry are called pressure-sensitive adhesives. Such adhesives adhere to its surface during a short contact with the substrate, without chemical reaction or physical transformation [1].

Polymers like acrylic polymers, SIS and SBS rubbers, polysiloxanes, polyurethanes, polyesters, polyethers, and EVA polymers are used in the technology of producing pressure-sensitive adhesives, which many times replace the standard techniques of joining materials, such as riveting, welding, or drilling. Increased demand for self-adhesive adhesives can be observed both in industry and everyday practice [2].

Silicone pressure-sensitive adhesives (Si-PSA) exhibit unique properties such as high flexibility of the Si-O-Si backbone, low intermolecular interactions, low surface tension, excellent thermal stability, and high UV transparency, making silicone PSA highly effective in extreme high and low temperatures, characterized by excellent electrical properties, chemical resistance, and exceptional weather resistance [3–4]. In most cases, in comparison with organic PSA, they show better performance properties. Traditional silicones consist of high molecular weight functional silicone polymers and siloxane resins. It is well known that the silicone pressure-sensitive adhesives are useful for special applications. Since the year 2000, there has been much interest in new uses for silicone PSA, especially in applications such as medical and industrial tapes [5–7].

Many researchers proved that silicone PSA are able to withstand the high processing temperatures and harsh conditions of modern industrial operations [5, 8].

Lin conducted various experiments to investigate the thermal stability of silicone PSA. It was observed that silicone polymers, including polydimethylsiloxane (PDMS), methyl silicone, *etc*., underwent significant thermal degradation in air at high temperatures. The thermal stability of the silicone PSA was inherently better than that of their corresponding silicone polymer components. None of the PSA silicone blends experienced more than moderate weight loss [9].

Aging tests for selective adhesive compositions were performed by Antosik *et al*. and excellent properties were exhibited. With increasing aging of the silicone PSA, low adhesion and tack were observed. However, aging did not affect the cohesion of the adhesive films at 20°C and 70°C [10].

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In this study, the influence of the storage time of self-adhesive tapes on their self-adhesive and useful properties was investigated. During experiments, the coated and protected adhesive films were stored at room temperature for 7 years. The properties of tapes were examined immediately after production and after 7 years of storage. In the available publications, no research was conducted so far in time to confirm the uniqueness of silicone pressure-sensitive adhesives.

EXPERIMENTAL PART

Materials

Commercial silicone resins PSA 529 and PSA 590 (Momentive, USA) were used to obtain the self-adhesive silicone tapes. Bis(2,4-dichlorobenzoyl)peroxide (DClBPO) produced by Peroxid-Chemie (Germany) was used as the crosslinker. To obtain a uniform composition of the adhesive, toluene was added to the resin with the addition of 0–3 wt% DClBPO and stirred until the mixture became homogeneous. Firstly, the appropriate amount of the crosslinking compound was weighed, and after that toluene was dosed in such an amount to obtain a 50% solution. After dissolving the crosslinker in toluene, pressure-sensitive adhesives PSA 529 or PSA 590 were added and mixed by hand until a homogeneous mixture was obtained. The composition containing 50 wt% of the polymer was coated with a polyester film with a thickness of 50 μm using a semi-automatic coater designed at the International Laboratory of Adhesives and Self-Adhesive Materials at the West Pomeranian University of Technology in Szczecin. The films coated in this way were crosslinked at a temperature of 110°C for 10 minutes, resulting in self-adhesive adhesive films with a basis weight of 45 g/m^2. The adhesive layer was then secured with a polyester film and cut. One-sided tapes obtained in this way were tested, measuring: cohesion at different temperatures, adhesion, tack, and the SAFT test. In order to study the aging process of silicone pressure-sensitive adhesives, all measurements were carried out after 1 hour and 7 years after receiving the tape. The tapes tested after 7 years were stored in stable conditions in an incubator at a temperature of 23°C and a humidity of 50 without exposure to UV radiation. Analogously the tape was prepared from silicone pressure-sensitive adhesive resins' composition and tested.

Methods

The peel adhesion of pressure-sensitive silicone adhesives was tested using a Zwick-Roell Z1 machine in accordance with the procedures of the international standard Association des Fabricants Europeens de Rubans Auto-Adhesifs (AFERA) 4001. A 2.5 cm wide adhesive tape was sticked to a steel plate under pressure 2 kg of hard rubber roller. The plate was placed in the jaws of a testing machine and the free end into the other jaw. The test measured the force with which the tape was peeled off the plate at a constant speed of 300 mm/min. The result was the average of three measurements. The steel plates used for the tests should be perfectly flat, 200 mm long, 50 mm wide and about 2 mm thick, made of polished stainless steel (of a Brinell hardness ranging from 130 to 200). They should contain the following elements: carbon <0.12%, nickel >8%, chromium >17% [11–12].

Tack was also measured using a Zwik-Roell Z1 testing machine according to the procedures of the International Standard Association des Fabricants Europeens de Rubans Auto-Adhesifs (AFERA) 4015. This method measured 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 × 2 cm) [13–14]. The steel plate had the same parameters as in case of peel adhesion.

The cohesion test was carried out according to the method of Fédération Internationale des Fabricants et Transformateurs d'Adhesifs et Thermocollants sur Papiers et Autres support (FINAT) FTM 8. A 2.5 × 2.5 cm sample of the tape was glued to a metal plate and then loaded with a 1 kg weight. During the test, the time needed to detach the tape sample from the metal plate

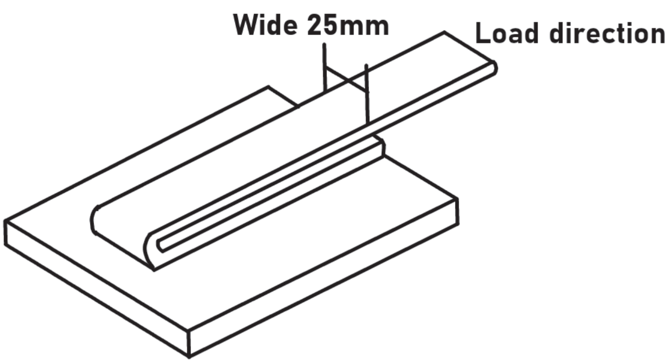

Fig. 1. Peel adhesion test at an angle of 90° and 180°

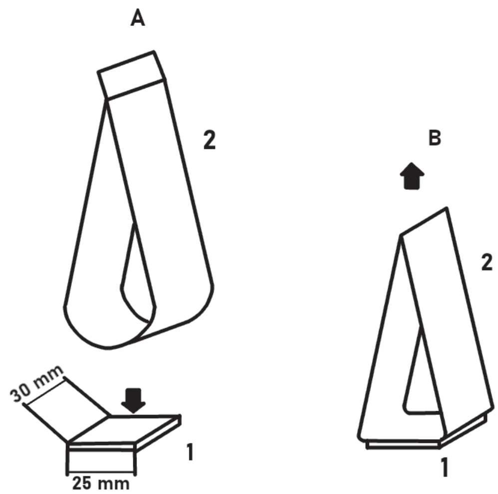

Fig. 2. Tack test scheme: a) sample (2) formed into a loop approaches the metal plate (1), b) after contact of the sample (2) with the plate (1), the plate is separated from the loop.

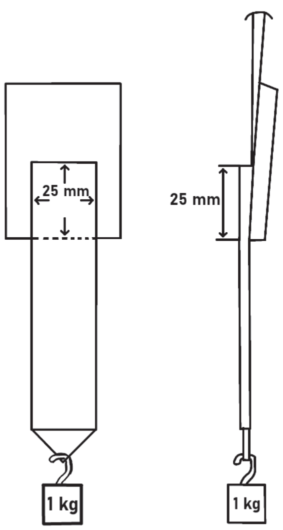

Fig. 3. Cohesion test

was measured. This test was carried out at room temperature and elevated temperature (70°C). The steel plate had the same parameters as in case of peel adhesion [15–16].

The SAFT test was also performed in the presented work. It was performed in a similar way to cohesion, except that the test temperature was increasing in time (from 20°C to 225°C). The test measured the time required to detach the sample from the metal plate. It was also a determination of the maximum operating temperature of a given sample of adhesive tape. The starting temperature for the test was room temperature: 22°C. The temperature was changing at a rate of 1°C per minute [17–18].

The obtained results were presented as an average value with standard deviations of at least five replicates. Where relevant, the data were subjected to one-way analysis of variance using ANOVA test.

RESULTS AND DISCUSSION

Table 1 shows the results for PSA 590 and PSA 529 commercial silicone adhesives, without the DClBPO crosslinking compound. In most cases, the values of the properties tested did not differ significantly between the tape stored for 7 years and the samples continuously tested immediately after producing. This confirms the information about the unique properties of Si-PSA described in the literature [5, 8–10, 16–19].

Table 2 shows the results of the cohesion at the temperature of 20°C depending on the amount of the compound used in crosslinking. In case of PSA 529, for all amounts of crosslinker, the maximum cohesion value of more than 72 hours was obtained immediately after the production of the tape, as well as after 7 years of storage. Similar values were also found for adhesive PSA 590. The cohesion value at 20°C was greater than 72 hours. The table also shows the cohesion results for the adhesives without crosslinker. It can be seen that adhesive PSA 590 had a higher cohesion value comparing to adhesive PSA 529 (without crosslinker). The obtained results are analogous to those presented in the literature for tapes examined immediately after production and stored for a shorter period of time (up to 9 months) [10, 20–21]. Maintaining the value for 7 years proves the high resistance of the materials.

Figure 4 shows the results of cohesion at 70°C for PSA 529. On the graph, we can observe the dependence of the cohesion on the amount of crosslinking compound. The values of cohesion increased with increasing of the content of crosslinking compound until a maximum at 2.5 wt% was reached. The cohesion results for samples after 7 years of storage are marked in red. They were higher comparing to the samples that were tested immediately after making the tape. Figure 5 shows the results of cohesion at 70°C for the second adhesive PSA 590. The results for tapes received immediately after preparation are marked in black, and for the content of 1.5 wt% of crosslinking compound and higher they showed the maximum values: over 72 hours. For tapes stored for 7 years, the values were similar, while the maximum value was obtained for 1 wt% of the crosslinking compound. It could be seen that adhesive PSA 590 had a better cohesion value than PSA 529. The tests confirmed previous observations that the PSA 529 resin exhibited lower cohesive properties comparing to the second tested resin. These results clearly translate into the results of cohesion at elevated temperature, both immediately after preparation and after seven years of storage [10, 20–21].

Figures 6 and 7 show the adhesion results for PSA 529 and PSA 590 as a function of the amount of crosslinker. In case of PSA 529, it could be observed that the adhesion value increased to the limit value for 2.5 wt%, while for 3.0 wt% the value dropped rapidly. For a tape sample stored for 7 years, the adhesion value increased to the limit

T a b l e 1. Performance of pressure-sensitive adhesives PSA 529 and PSA 590 without crosslinking compound

	Silicone resin	Cohesion		SAFT °C	Peel adhesion N	Tack N/25 mm
		Detach time at 20°C h	Detach time at 70°C h			
Immediately after production	PSA 529	18.03	0.18	77	9.82	3.61
After 7 years		25.45	0.17	89	9.27	6.25
Immediately after production	PSA 590	10.12	0.08	75	7.97	8.85
After 7 years		>72	5.6	87	8.29	9.13

T a b l e 2. Cohesion at 20°C for the tested tapes

	Silicone resin	DClBPO wt%	Detach time h
Immediately after production	PSA 529	0.0	18.03
		0.5	>72
		1.0	>72
		1.5	>72
		2.0	>72
		2.5	>72
		3.0	>72
After 7 years	PSA 529	0.0	25.45
		0.5	>72
		1.0	>72
		1.5	>72
		2.0	>72
		2.5	>72
		3.0	>72
Immediately after production	PSA 590	0.0	10.12
		0.5	>72
		1.0	>72
		1.5	>72
		2.0	>72
		2.5	>72
		3.0	>72
After 7 years	PSA 590	0.0	15.29
		0.5	>72
		1.0	>72
		1.5	>72
		2.0	>72
		2.5	>72
		3.0	>72

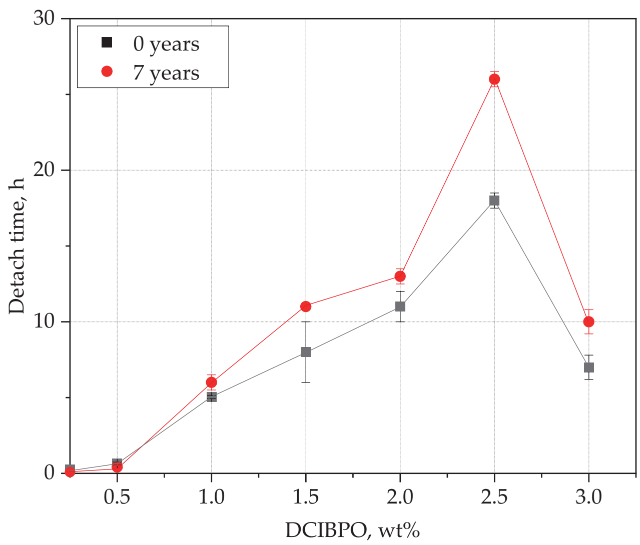

Fig. 4. Effect of DCIBPO content of detach time for PSA 529; cohesion at 70°C

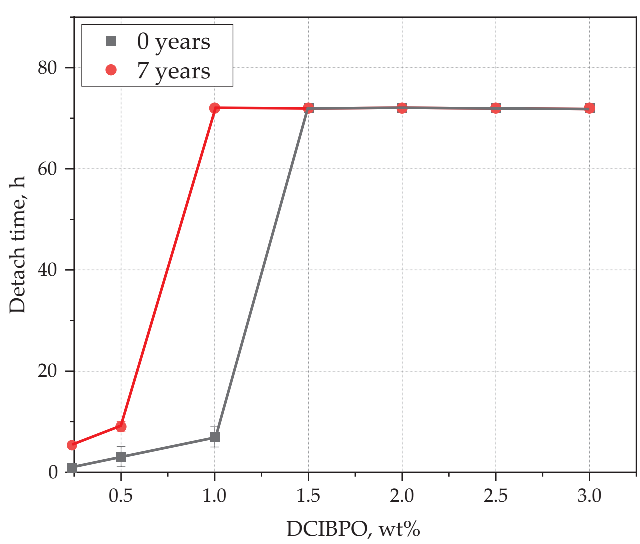

Fig. 5. Effect of DCIBPO content of detach time for PSA 590; cohesion at 70°C

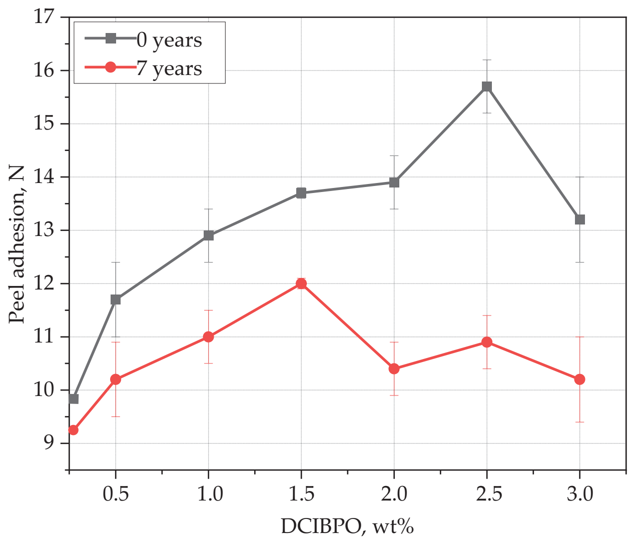

Fig. 6. Peel adhesion of PSA 529 tapes

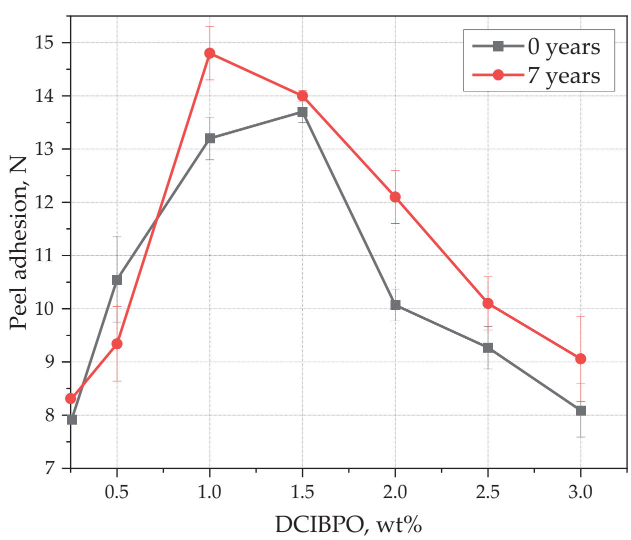

Fig. 7. Peel adhesion of PSA 590 tapes

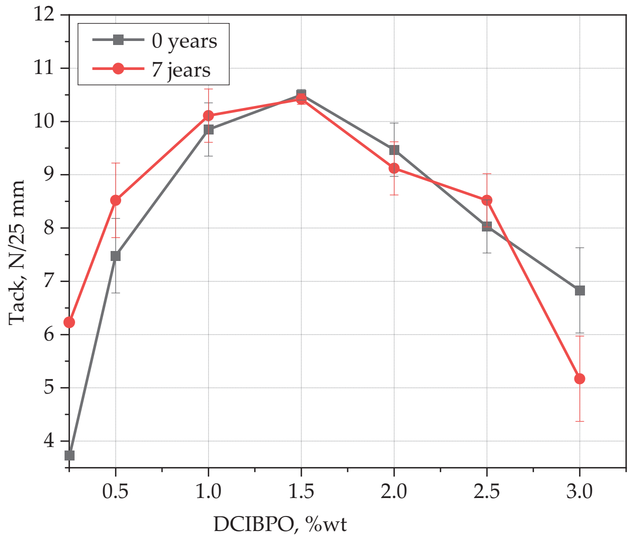

Fig. 8. Tack of PSA 529 tapes

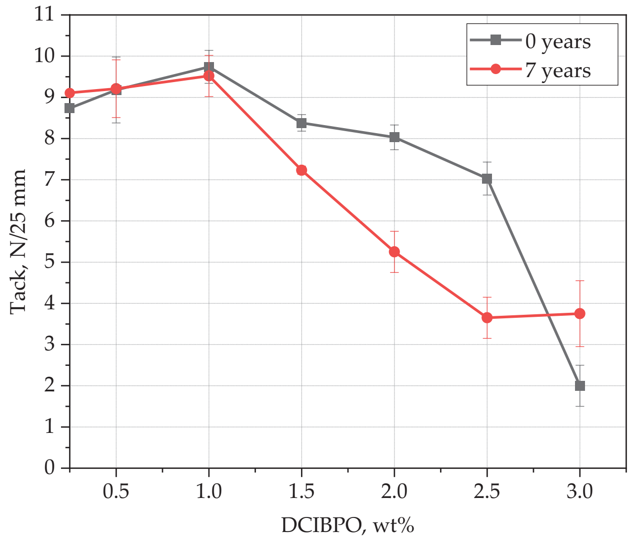

Fig. 9. Tack of PSA 590 tapes

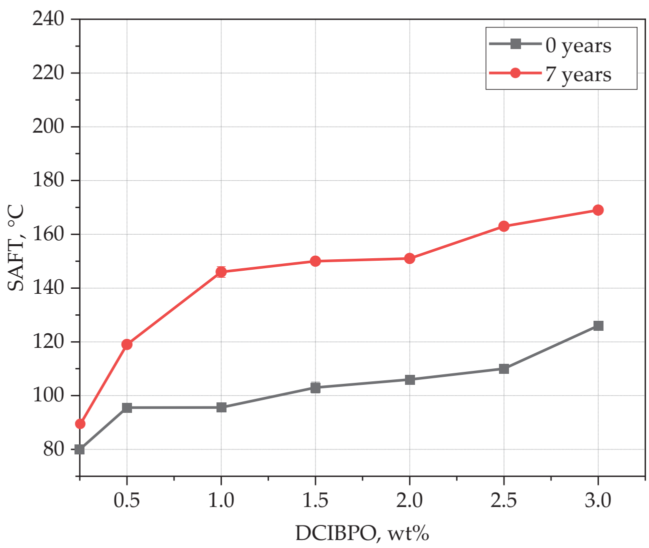

Fig. 10. Maximum working temperature for PSA 529

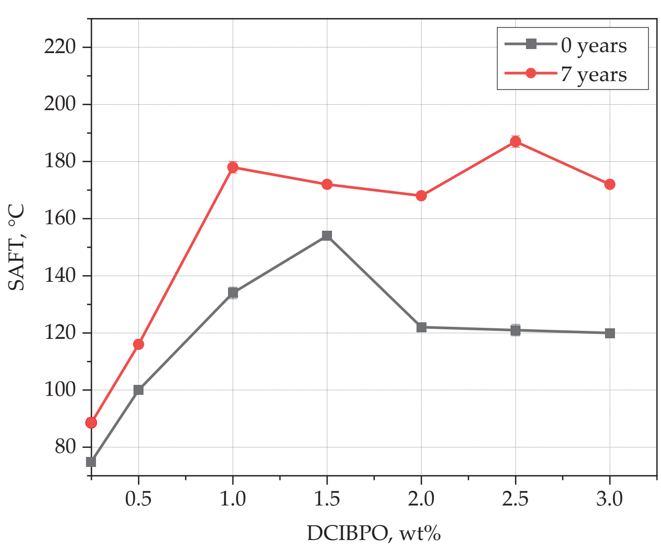

Fig. 11. Maximum working temperature for PSA 590

value for 1.5 wt% and then slightly decreased. With PSA 590, the results were similar. For the adhesive tested immediately after production, the adhesion value increased to the content of 1.5 wt%, and then decreased quite quickly. Likewise for a sample stored for 7 years: the value reached a maximum for 1 wt% and subsequent concentrations showed lower values. Two lines are marked in the graphs: the black line marked with 0 is the adhesion value without the DClBPO crosslinker for the sample tested immediately after preparation. On the other hand, the red line marked with 0 is the initial adhesion value, without the crosslinking compound, for the sample stored for 7 years. In virtually every case, an increase in the value of adhesion was observed, along with the share of the crosslinker. Even for 0.5 wt%, the values were higher than the initial value of adhesion (without crosslinking compound). The reduction of the adhesion value after 7 years for the PSA 529 resin proves the shift of the cohesive-adhesive balance towards cohesion. This effect is not noticeable for PSA 590 resin.

Figures 8 and 9 show tack values for the adhesives PSA 529 and PSA 590, respectively. In the first case, for both the tape tested immediately after production and the tape stored for 7 years at lower concentrations, the tack increased to the limit value for 1.5 wt%, followed by a decrease in this value. For the sample of the tape examined immediately after manufacturing, these values were higher than the initial value of the tack (samples without crosslinking compound – marked on the graph with a black line with the description 0), while for samples stored for 7 years, the values were usually also higher, but in one case: in case of 3.0 wt% this value was lower. In most cases, the storage time slightly affected the tack values. This property was the lowest variable during the test [10, 20, 22].

Another tested value was the maximum operating temperature determined using the SAFT test. During this test, the test temperature was raised from room temperature to 225°C. Figure 10 shows the results for PSA 529. In the graph it could be seen that the values of the samples stored for 7 years were higher comparing to the same samples tested immediately after production. The best values were obtained for the crosslinking compound in the amount of 3 wt%. In both cases the values were higher than the starting value, with no crosslinking. Figure 11 shows the results for adhesive PSA 590. The values were also higher comparing to the starting temperature (*i.e.* without crosslinking compound). In this case the samples after 7 years of storage showed higher values as well, while the maximum was obtained for the amount of the crosslinking compound of 2.5 wt%. For the adhesives tested immediately after production, the maximum value was observed at 1.5% by weight of crosslinker.

CONCLUSIONS

The article presents the effect of storage time (7 years) on the properties of Si-PSA self-adhesive tapes. There was no significant effect of their long-term storage on useful properties (cohesion, adhesion, stickiness). In the case of the content of the cross-linking compound above 1.5 wt% the stickiness of the samples decreased and increased with a smaller one. The self-adhesive tapes based on PSA 590 resin showed higher aging resistance than PSA 529. The unique properties of silicone adhesive tapes have been confirmed.

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