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PRIMER OR PRIMER-FREE GLUING – PROBLEMS OF ADHESIVES IN AUTOMOTIVE INDUSTRY

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The presented work aims at the comparison of physical and mechanical properties of commercially available black polyurethane adhesives designed for the glass bonding in automotive industry and at the assessment of adhesive systems with a primer. These adhesives require application and drying out of the appropriate polymer or a primer-free adhesive layer before bonding. UV stability is additionally measured in a view of the changing colours and mechanical properties.

Introduction

Today, adhesive bonding with pasty single-component (1K) polyurethane adhesives is a common standard in automotive industry. The appropriate surface is degreased with a solvent and a thin primer layer applied prior to bonding. Primers are isocyanate-based liquid(s), high-volatile and easy-to-dry agents,

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commonly filled with carbon particles for glazing. Primers are used for additional surface cleaning: it connects the remaining contaminants, such as oil and silicon, thus forming a substrate for good adhesive anchoring. The primer is laid on a painted body-work metal and on the bonded glass. After the primer dries out, the remaining adhesive is applied; usually, as a thicker layer of at least 3 mm.

Manufacturers obviously try — due to financial reasons and time limitations — to develop an adhesive that does not require application of the primer while retaining the same strength properties as adhesive systems with such a primer. This trend is seen in car manufacturers, but much more in the market sector focused on adhesives and sealants that are designed for car components and car-repair shops. Thus, one would benefit from the substantial simplification and a price reduction of the whole car glass changing due to a primer-free operation.

Bonded joints in automotive industry appear in many types according to their functional strain and construction aspects. We can say that the bonding has an additional and sealing function (bonding and sealing of bodyworks for the purpose of tightening, vibrations tamping, anticorrosion measures, application of reinforcement, etc.) or, in specific cases, it may replace the welding technology in construction strength welds.

Bodywork metal sheets have recently been joined by the resistance welding technology (namely: spot, seam, and projection welding). These technologies have certain drawbacks; e.g., problematic joining of different thickness and quality metal sheets or thermal influence on the welded area. Further problems are caused by zinc coating, functioning as an anticorrosive protection. Zinc adheres to the electrodes and the protective coating at the joints is largely reduced. This problem can be easily avoided by using the bonding technology [1-4].

The ratio between welding and bonding in automotive industry has been gradually changing in favour of bonding. Modern adhesives enabled manufacturers to reduce the spot welding by almost 50 %. Recently about 9 % of annual adhesives produced in the world are used in automotive industry and a recent type of car contains as much as 18 kg of adhesives. In the event of an accident, adhesives behave as a "bumper" — certain adhesives can even contribute to a passenger protection. Front glass is constructed to resist against a strong strain while appropriate adhesives contribute to the bodywork stiffness.

We have many types of adhesives in a wide range of price and varied properties. In automotive industry, the most frequently used are epoxide, polyurethane (PUR) acrylate, and cyanoacrylate adhesives. These adhesives are filled by different additives to improve their material properties, such as shear limit, strength limit or resistance against different loading, as well as the resistance against solvents and other negative impacts [5-8].

Besides different PUR adhesives, automotive industry employs silane-modified polyurethanes (SMP) as car-glass adhesives. Polymers modified this way combine an excellent PUR cohesion with silicone adhesion. Their modification is based on end groups of the N=C=O- type in the PUR prepolymer and aminosilane or an isocyanate-silane agent with silicon network-forming alkoxy groups. SMPs usually react with air humidity (with release of the respective alcohol), thus hardening the adhesive used. The pathway of the silane-modification is shown in Fig. 1.

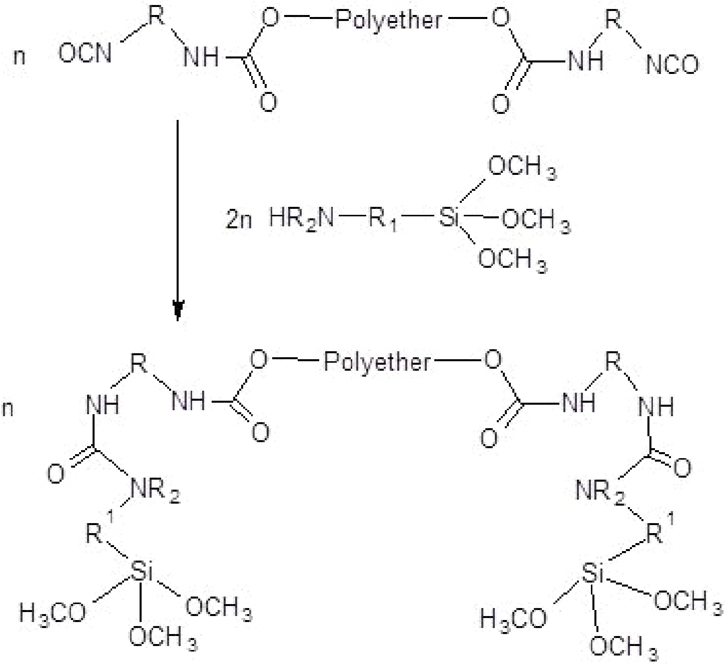

Fig. 1 Formation of an amino-silane modified PUR (dodat v JPG)

Modified silicone (MS) polymers are utilized nowadays as well. However, these adhesives lack the isocyanate group when being based on trimethoxysilane modified polyether polyols [9]. The hardening principle shown in Fig. 2 is the same as that for SMPs and MS polymers (with different adhesive skeleton and equal reactive groups). SMPs have a six-functional molecule (while MS polymers are only four-functional), exhibiting excellent adhesion to non-porous substrates and, moreover, when hardened, alcohol R-OH is released instead of CO_2 as the reaction of NCO- group with water for classical 1K PUR adhesives. So far, strength of silane-modified structures is lower than that of purely PUR adhesives.

The main objective of this work was to compare the adhesive systems requiring the primer and adhesives without need of primer for car glasses hardened by air humidity.

Their gluing efficiency was evaluated via mechanical properties (tensile strength and bonded joint shear strength on adherends metal/metal, glass/glass and metal/glass) and by means of optical properties when monitoring the colour changes by CIELAB method [11].

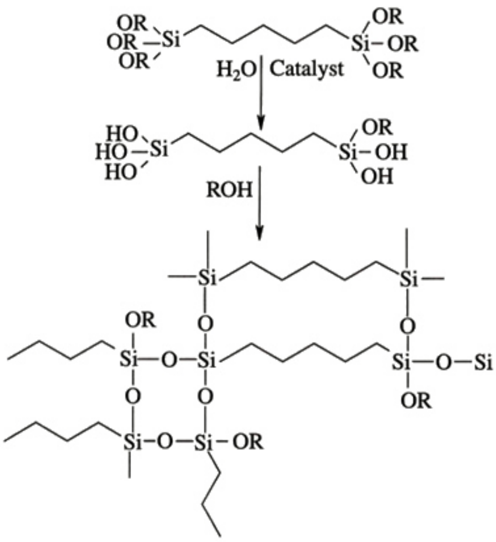

Fig. 2 STP and MS polymers networking [10]

Experimental

Materials

The samples of adhesives requiring the primer and samples of adhesives without primer for car glasses hardened by air humidity were supplied by company Matrix (Třebešov, ČR). Altogether four 1K adhesives without primer (PF) and three adhesive systems requiring primer (P) with the use of the respective primers (BETAPRIME 5500 and 5404) were tested and compared, namely: Teroson Terostat 9000 PL HMLC (Henkel) – silane-modified polyether polymer (PF); Teroson Terostat 9097 PL HMLC (Henkel) - PUR system on the MDI (PF); SIMP Seal 60 HV (N.P.T.S.r.l.) – silane finished polymer (PF); SikaTack GO! (Sika) - PUR system on the MDI (PF); BETASEAL 1517 (DOW) - PUR system (P); BETASEAL 1527 EP (DOW) - PUR system (P); 3M 590 (3M) – PUR system (P). Fig. 3 shows the samples of various primers used in this study.

Description of Bonding Procedure

Bonded areas were degreased with a solvent-wetted textile, glass ~~was~~ degreased by acetone, carbon steel with chloroform. In the case of adhesive systems with the primer, application of the primer layer was made, leaving the solvent to evaporate (for 10 min.). Then, the bonding was performed at ambient temperature using the adhesive device, joints overlay was set to 18×25 mm. To reach the constant thickness of a joint — i.e., 5 mm for the combination glass/glass, metal/glass,

Fig. 3 Sample primers for glass and metal

metal/metal and 0.15 mm for a thinner joint metal/metal — distance profiles of 0.6 mm Al metal U-form sheets and steel wires, respectively, were inserted into the bonded joint. After applying the adhesive to one bonded area and inserting the distance profile/wire, the second adherend was applied and loaded with 1kg weight. The joint was then bonded and hardened for minimally 28 days; then, the adhesive streaks were removed. Due to technical reasons, metal sheets (110 x 25 mm) were applied to the adhesive ends of metal/glass and glass/glass systems, while the overlap with the primer adherends was 70×25 mm. Distance plates complying with the joint thickness were applied to the ends of bonded joints in order to align the joint when clamped in a shredder.

The main objective of this study was to compare the adhesives while using a primer. Its influence was monitored via mechanical properties — by comparing the tensile strength according to ASTM 1708, bonded joints shear strength on adherends metal/metal, glass/glass and metal/glass in compliance with monitoring the colour changes after 500 hours-long exposure in QUV panel using CIELAB method (according to CSN EN 1465). Glass transition temperatures (T_g) were determined by means of the thermomechanical analysis (TMA) when using the TMA CX04R apparatus (R.M.I., Lázně Bohdaneč, the Czech Republic). Fig. 4 shows a bonded joint metal/glass and its typical model dimensions.

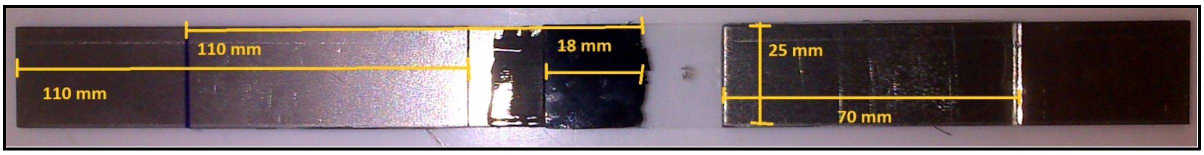

Fig. 4 Dimensions and picture of bonded joint metal/glass

Results and Discussion

The results of a study on the tensile resistance are given in Table I. As seen, the tensile strength was higher at P adhesives; all of them reaching 5.5 MPa. In the case of PF adhesives, only SikaTack GO! was closer to the limit; adhesive 3M 590 having shown the highest tensile strength, whereas the lowest value belonging to SIMP Seal 60. Elongation of all the tested adhesives had been relatively high, which was not surprising in regard to the requirement for elasticity of the adhesive designed to function as a flexible car glass sealant. Nevertheless, if compared directly, P adhesives showed better results; elongation of Betasel 1517 and 1527 EP attaining a maximum of 200 %, 3M 590 almost 300 %. Elongation of PF adhesives ranged from 100 % (SIMP Seal 60 and Teroson 9000) up to 160 % (Teroson 9097).

Table I Results of the tensile testing of black adhesives

Sample	Tensile modulus MPa	Tensile strength MPa	Tensile force N	Elongation %
Teroson 9000	3.96 ± 0.32	2.84 ± 0.34	26.82 ± 2.93	106.0 ± 20.0
Teroson 9097	2.33 ± 0.10	3.10 ± 0.20	32.53 ± 1.92	161.8 ± 10.6
SIMP Seal 60	3.52 ± 0.22	1.84 ± 0.24	18.67 ± 1.88	104.7 ± 16.6
Sika Tack Go!	5.50 ± 0.30	5.20 ± 0.25	55.72 ± 2.05	138.6 ± 6.7
Betaseal 1517	4.30 ± 0.17	5.82 ± 0.25	67.96 ± 6.07	211.8 ± 15.2
Betaseal 1527 EP	3.22 ± 0.10	5.54 ± 0.18	56.06 ± 4.54	199.7 ± 4.8
3M 590	2.58 ± 0.10	5.84 ± 0.30	52.13 ± 5.26	297.8 ± 25.4

Results of shear strength are summarized in Table II and Fig. 5. Joints with a 5 mm seam have a thickness typical for the given application; 0.15 mm being a standard value according to the CSN EN 1465. As far as shear strength is concerned, it has applied to each measurement higher at the thickness of 0.15 mm than at 5 mm. Shear strength decreased at 5 mm was sharp and it went down to 24-34 % of the original value (see Fig. 5). The lowest shear strength in both categories was reached at the PF adhesives; Teroson 9000 at 0.15 mm and SikaTack GO! at 5 mm. The greatest shear strength was reached at both thickness types with Betaseal 1527 EP. The Betasel adhesives exhibited more than two-fold shear strength compared to the value for other adhesives.

Table III shows the shear modulus and elasticity; graphic description of elasticity being shown in Fig. 6. The shear modulus in a thin seam revealed a large dispersion (140-520 MPa) in numerous adhesives. Nevertheless, as the shear strength had decreased, its values dramatically decreased with a thicker joint;

Table II Shear strength of black adhesives, adherends metal/metal at joint thickness of 0.15 and 5 mm

	Shear strength, MPa		Shear force, N	
Joint thickness	0.15 mm	5 mm	0.15 mm	5 mm
Teroson 9000	1.26 ± 0.17	0.30 ± 0.04	719.2 ± 58.5	180.5 ± 31.7
Teroson 9097	1.34 ± 0.13	0.28 ± 0.04	732.5 ± 71.0	174.2 ± 22.6
SIMP Seal 60	2.38 ± 0.09	0.79 ± 0.05	1 477.5 ± 59.9	496.0 ± 33.1
Sika Tack Go!	1.50 ± 0.08	0.19 ± 0.01	870.8 ± 48.5	120.5 ± 6.7
Betaseal 1517	5.50 ± 0.41	1.70 ± 0.18	3 258.1 ± 246.5	1 091.0 ± 114.5
Betaseal 1527 EP	6.71 ± 0.32	2.09 ± 0.06	3 946.9 ± 178.0	1 362.5 ± 43.6
3M 590	2.01 ± 0.22	0.61 ± 0.07	1 154.5 ± 135.6	389.2 ± 43.7

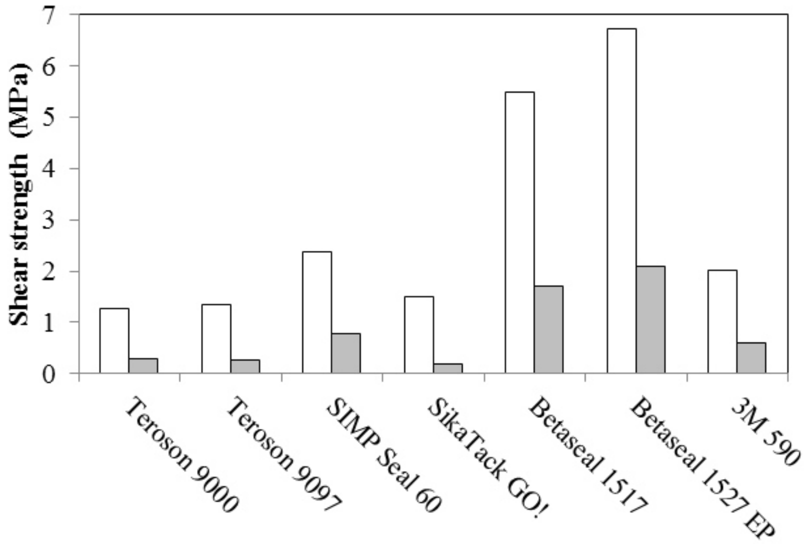

Fig. 5 Comparison of shear strength at joint thickness of 0.15 mm (white columns) and 5 mm (grey columns)

typically down to 20-30 MPa. The elongation, on the contrary and as expected, increased with the increased thickness, mostly at Betasel 1527 EP, the least at SikaTack GO! The shear resistance of the adhesives tested at metal/glass joint had also demonstrated that adhesive strength was unfortunately higher than the strength of the glass adherends; therefore, in all tests, the glass broke at the tension of max. 0.6 MPa (390N). Besides measuring the shear resistance of the adhesives, the way of joint breaking was assessed visually together with its shape after the test. The 0.15 mm joint exhibited mostly an adhesion failure, only Betaseal 1517 and 1527 EP corresponded to the cohesion failure. The 5 mm joint showed a pure adhesion failure at Sika Tack GO!, 3M 590, Teroson 9000 and 9097. Betaseal 1517 and Betaseal 1527 EP exhibited both adhesion and cohesion failures; the

Table III Shear modulus and elongation of black adhesives, adherends metal/metal at joint thickness of 0.15 and 5 mm

	Shear modulus, MPa		Elongation, %	
Joint thickness	0.15 mm	5 mm	0.15 mm	5 mm
Teroson 9000	286.5 ± 31.8	21.22 ± 1.19	0.62 ± 0.12	3.49 ± 0.22
Teroson 9097	141.9 ± 21.1	12.96 ± 1.99	1.41 ± 0.12	4.79 ± 0.81
SIMP Seal 60	178.9 ± 26.2	25.88 ± 1.41	2.78 ± 0.37	6.94 ± 0.88
Sika Tack Go!	401.4 ± 33.9	3.44 ± 1.11	0.56 ± 0.09	1.21 ± 0.27
Betaseal 1517	485.5 ± 59.9	30.28 ± 1.77	2.05 ± 0.18	4.56 ± 0.93
Betaseal 1527 EP	521.7 ± 51.9	24.02 ± 1.74	2.07 ± 0.20	11.60 ± 0.78
3M 590	356.8 ± 30.5	21.98 ± 1.49	0.82 ± 0.15	5.15 ± 1.14

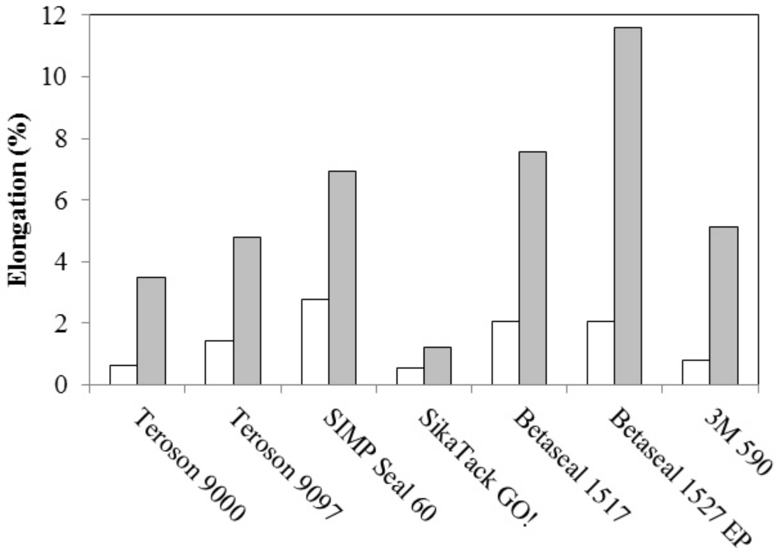

Fig. 6 Comparison of elongation at shear test for joint thickness of 0.15 mm (white columns) and 5 mm (grey columns)

only pure cohesion failure was ascertained for SIMP Seal 60.

Further, we focused on the measurement of colour changes of thin layers of adhesives by means of colour space $L^*a^*b^*$ (CIELAB) and the respective results (i.e. yellowing index) are shown in Tables IV and V. As demonstrated, the overall colour change ΔE did not concern P or PF adhesives but both the categories or, eventually, the change depended on a particular adhesive composition. Adhesives Betaseal 1527 EP (P) and Sika Tack GO! (PF) had fallen within the category of unacceptable, Betaseal 1517 and 3M 590 (P) showed the average results. The change in colour recognizable only with an experienced eye was seen for SIMP Seal 60 and Teroson 9000 (PF); related Teroson 9097 (PF) having almost invisible change.

Table IV Colour change according to CIELAB after 500 hours-long exposure in QUV panel

Sample	ΔL	Δa	Δb	ΔE^{a}
Teroson 9000	0.75 ± 0.13	0.07 ± 0.01	1.14 ± 0.08	1.36
Teroson 9097	–0.16 ± 0.49	–0.16 ± 0.02	0.62 ± 0.02	0.67
SIMP Seal 60	1.25 ± 0.74	–0.11 ± 0.01	0.09 ± 0.07	1.26
Sika Tack Go!	4.09 ± 0.08	0.82 ± 0.03	4.37 ± 0.04	6.05
Betaseal 1517	2.70 ± 0.34	0.03 ± 0.01	1.72 ± 0.01	3.20
Betaseal 1527 EP	5.75 ± 0.33	0.14 ± 0.03	4.09 ± 0.11	7.05
3M 590	–2.22 ± 0.38	0.09 ± 0.03	1.77 ± 0.11	2.84

[a] ΔE (overall colour change): 0-1 – non-rocognizable; 1-2 – recognized with an experienced eye; 2-3.5 – average; 3.5-5 – high; > 5 – unacceptable

Table V Index of black adhesives yellowing

Sample	Yellowing index (0 h)	Yellowing index (500 h)	Δ of yellowing index
Teroson 9000	2.2	6.98	4.78
Teroson 9097	3.36	5.92	2.56
SIMP Seal 60	–4.49	–4.03	0.46
SikaTack GO!	–13.52	6.44	19.96
Betaseal 1517	–0.36	6.58	6.94
Betaseal 1527 EP	–8.09	8.97	17.06
3M 590	0.53	8.37	7.84

The most significant change in measuring the yellowing index could be seen for the adhesive Sika Tack GO! (PF) followed by Betaseal 1527 EP (P), which corresponded to the results of colour changes. The least pronounced change in the yellowing index was then found out for the SIMP Seal 60, whereas the results in colour change were very satisfactory. The remaining adhesives moved within the yellowing interval 2.5 to 8.

Temperatures T_g of the black adhesives have been very low, which demonstrates a rubber-like character of the adhesives used and, across the spectre of adhesives, they were quite similar to each other (from –76.4 to –62.2 °C).

Conclusion

The above-indicated results have demonstrated that, between adhesives requiring the primer and adhesives without a need of primer, there exist substantial differences that vary according to the type tested. As mechanical properties of adhesives with primer are concerned, the tests performed have unambiguously proved better values compared to those showing a better tensile and shear resistance. Moreover, they did not dramatically lose the tensile strength after QUV exposition as the adhesives without primer mostly fell apart already at the ageing. In terms of the thin layer colour, adhesive systems with the primer comply with the standard, but most adhesives without primer have shown better values even when tested visually. Nevertheless, it is important to point out that the adhesives requiring primer have not been UV-protected by the primer that is normally used in this type of application. Taking into account the mechanical resistance, the adhesives without primer have failed in comparison with the adhesive systems with primer. The absence of the primer was evident, despite the fact that adhesives should be prepared for primer-free application.

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