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Experimental Analysis on the Curing and Adhesive Behaviour of Standard Moisture-cured and Fast-cured Polyurethanes used in Automotive Industry

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The subject of this experimental analysis is the comparison of polyurethane adhesives with regard to the improvement of quality and acceleration of production, which is associated with financial savings. The study was inspired by the real conditions of car window production. A moisture-cured one-component polyurethane adhesive is used as standard. Due to the risk of delamination of the glass, the use of heat-cured adhesives is excluded. In addition to the moisture-curing adhesive, a one-component polyurethane adhesive with a curing accelerator and a two-component polyurethane adhesive were tested. To compare the properties, the curing time and the force required to tear the bracket from the glass were assessed using a pull off test. Based on the results, it can be concluded that the two-component adhesive has the greatest potential, both in terms of curing speed, but also the mixing ratio satisfactory in real production. Ideally, it would be desirable to modify the hardness of the adhesive to make it more suitable for that application. However, the potential for financial savings is great in this type of production.

Keywords: Adhesion, Polyurethanes, Glass, Manufacturing Technology, Automotive Industry

1 Intoduction

Adhesives play an important role in the automotive industry. They enable the connection of various materials, and they are also used as seals around doors, windshields, and serve to attach interior and exterior elements. In glass automotive industry, adhesives are used to create a bond between glass surface and additional parts made of plastic or metal. [1–2] Joining a variety of materials is not particularly easy when gluing parts that must meet safety requirements. At the same time, there is an emphasis on the economic process. [3–5]

Commonly, the most used adhesives in the automotive glass industry are polyurethanes. Commonly used moisture-cured polyurethanes meet the required safety properties. However, from an economic point of view, the use of this type of adhesive is not advantageous. Curing moisture-cured polyurethanes is time consuming. Due to this, it is necessary to store glass with glued parts, which is demanding from the point of view of storage spaces and maintaining a suitable environment, especially temperature and humidity. For these reasons, the use of faster curing alternatives is suitable for reducing the costs associated with the long curing time of adhesives.

In addition to standard one-component polyurethanes, there are also two-component polyurethanes, or it is possible to add a curing accelerator to the one-component adhesive. In both alternatives, curing is accelerated, and these adhesives are called fast-curing polyurethanes. The principle of their curing is the reaction of two components, while the effect of moisture is greatly reduced. [6–7]

The aim of this work was to evaluate the currently widely used moisture-cured polyurethane adhesives containing one component and to compare it with possible alternatives that are suitable for the production of car windows. The reason for this research was to assess the properties of a one-component adhesive in combination with a curing accelerator and a two-component adhesive for use in real production for gluing holders to glass. One of the goals of this experiment was to evaluate the curing rate over time. Another goal was to evaluate the strength of adhesion and the type of joint failure when tearing the holders from the glass.

2 Background

Polyurethanes are chemically a combination of polyesters and polyamides. They are prepared from multifunctional isocyanates and substances containing hydroxyl groups. The production is from a mixture of both components either directly or in a solvent environment, where it is easier to dissipate the heat released during the exothermic reaction. The temperature in the reactor, the residence time in the molten state and the molar ratio of diisocyanate to diol affect the molar mass of the polymer produced. Furthermore, the polymers are linear or cross-linked. [8]

The most common are foam materials with a lightweight structure. They are formed by the reaction of diisocyanates, polyhydroxy compounds and water. The polyhydroxy compounds are in particular polyether alcohols (for example from ethylene oxide or propylene oxide) and polyester alcohols (for example obtained by reacting adipic acid with diethylene glycol). 4,4'-diphenylmethane diisocyanate is the most widely used to produce rigid foams, i.e., also for application in the automotive glass industry. The isocyanate groups react with the hydroxyl groups of the polyols to form urethane bonds connecting the carbon blocks of the polymer chains. Furthermore, the isocyanate groups also react with the hydroxyl groups of water to form carbon dioxide, which acts as a blowing agent. [8]

Moisture-cured polyurethanes require a relatively long time to cure to final hardness. Associated with this is the need for a long storage time, which makes production more expensive. In practice, the longer the product's time spent in production, the more expensive the production. For this reason, it is important to look for alternatives to moisture-cured adhesives.

The natural curing of polyurethanes takes place at normal temperatures, which are 25-30 °C, and at elevated humidity. The polymer reaction is exothermic and depends on temperature, moisture content, length, and heat dissipation. However, if there is moisture inside the mass (moist material), it acts as an impurity that prevents the chemical reaction. The reaction proceeds most rapidly in the first hour of the curing process. Then the reaction slows down because the polyurethane mass serves as an insulator and does not allow heat to escape to the surroundings. In 24 hours, about 50% of the mass is cured. Complete curing is usually completed within 72 hours. [9–11] The technical documentation of e.g., Betaseal™ polyurethane states a curing speed of more than 4 mm in 24 hours. Of course, it always depends on the adhesive layer and on the ambient conditions.

Thermal curing takes place, for example, at a temperature of 120 °C. Advantageously, a glass fibre-containing material can be used for this purpose, which acts as an accumulator and a heat source, which stimulates the curing process. Compared to the natural curing process, the thermal process is faster. In addition, moisture in the material is eliminated by heat, which has a positive effect on strength. However, during heating, there is a risk that the polyurethane will overheat and degrade. [12–13] In the automotive industry, this form of curing can be used to bond parts to glass that is tempered. When used on laminated glass, there is a risk of delamination and thus degradation of the final product. The heating temperature is thus limited by the heat resistance of the PVB film used.

Polyurethanes are formed by the reaction of various isocyanate and polyol types. [16] Adhesion to various surfaces is ensured by the urethane group. The crosslinking reaction takes place by polyaddition of the hydroxyl groups of the polyol and the isocyanate groups. [17] The reaction is determined by the ratio between the hydroxyl groups and the NCO-groups. [18–19] 2C polyurethanes consist of two parts – polyol and isocyanate. These are separated and mixed just before applying the glue on the surface of the glued part. Thanks to this, it is possible to modify the resin part in terms of viscosity, reaction rate, polarity, etc. Due to the trend of accelerating the process, fast-curing adhesives are widely used. [6, 19] For example, there are components that speed up the curing process. In addition, they can reduce the amount of volatile organic content. [17] The curing process of such polyurethane systems has been dealt with by several works. Fast-curing adhesives are also suitable for the characterization of reaction kinetics. [19] Water-based polyurethanes, which are used for coatings, for example, are also being investigated within these types of adhesives. [16] 2C adhesives offer a suitable alternative to 1C moisture cured adhesives. 2C adhesives are usually mixed in a ratio of 1 to 1. This area of adhesives is still being widely researched and various modifications for various applications are being tested. [6]

Adhesives consisting of one component and a booster, i.e., substance accelerating the curing process, are characterized by a short reaction time. The amount of booster is in percent units. For example, a ratio of 97 units of base adhesive to three units of booster is used. [7]

Glass and plastics, or metals, are difficult-to-bond surfaces, so chemical substances are used to form an intermediate layer enabling the bonding of these materials to the adhesive. These substances are called adhesion promoters or primers. Furthermore, before applying the primers, various cleaners and activators are used, which remove dust, grease, and other impurities from the surface of the bonded substrates. Specific adhesion promoters must be used for different materials. The composition of the primers can be modified to achieve the desired properties. Many studies are concerned with improving the specific requirements for the properties of these substances. In particular, the effect on adhesion and bond strength is investigated. [20–23]

3 Experiments

The basic step was to evaluate the current conditions in common production facilities, where moisture-curable polyurethane adhesives are used. This study makes it possible to evaluate the fluctuations of the monitored variables, which are temperature and humidity.

The conditions in the production hall are important to ensure a quality connection of materials. It is necessary to maintain certain stable conditions for the gluing process and especially for the subsequent hardening of the glue. Only after a perfect curing process is the quality of the product ensured. This is the reason why a certain temperature and humidity is monitored and maintained in the production area. The temperature should be between 20 °C and 35 °C. Humidity should be higher than 30% RH but not more than 70% RH. These values are usually recommended directly by the manufacturers or suppliers of adhesives and other chemicals or are verified by extensive tests.

The following tables show the measured values of humidity in Table 1 and temperature in Table 2 in a real production hall. These values were measured using a hygrometer and a thermometer located at the place where the additional parts are glued to the glass. The measurement was done in September 2019.

***Tab. 1** Values of humidity development in the production hall during the observed period, (Source: local hygrometer)*

Date	10/09	11/09	12/09	13/09	14/09	15/09	16/09	17/09	18/09	19/09	20/09	21/09
Time	%RH	%RH	%RH	%RH	%RH	%RH	%RH	%RH	%RH	%RH	%RH	%RH
0:00	52.1	47.3	42.0	42.5	45.9	43.3	43.9	43.6	45.0	45.8	43.9	51.4
3:00	51.3	44.8	44.9	43.1	46.6	42.9	43.0	43.7	41.9	44.7	45.2	46.4
6:00	51.2	44.3	43.6	41.7	47.8	43.7	42.4	44.7	40.9	42.5	45.9	42.4
9:00	50.3	47.5	43.2	46.6	46.3	43.9	43.4	46.8	43.6	43.2	47.2	46.8
12:00	49.7	47.6	44.3	45.1	41.4	43.4	47.8	42.0	44.2	45.0	47.0	44.1
15:00	47.0	43.3	43.2	42.7	42.4	44.6	44.8	40.3	45.0	40.5	45.0	46.8
18:00	43.5	44.9	43.5	46.5	38.2	40.7	44.2	42.3	44.3	38.9	41.9	44.9
21:00	48.3	46.3	43.8	45.2	38.5	45.4	46.6	46.3	46.3	42.9	49.0	46.6

***Tab. 2** Values of temperature development in the production hall during the observed period, (Source: local thermometer)*

Date	10/09	11/09	12/09	13/09	14/09	15/09	16/09	17/09	18/09	19/09	20/09	21/09
Time	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]	t [°C]
0:00	24.4	24.0	24.7	23.6	26.1	24.2	23.8	25.6	24.2	22.8	23.3	24.1
3:00	24.4	22.5	23.1	23.2	25.8	24.2	23.8	24.6	23.6	22.5	22.8	24.8
6:00	24.4	22.3	22.6	23.4	25.5	24.3	23.7	24.1	22.7	22.4	22.2	24.1
9:00	25.1	23.1	23.5	23.3	25.2	23.9	23.3	24.1	22.9	23.4	23.9	25.2
12:00	25.4	24.6	25.1	23.7	25.3	24.6	23.6	24.8	24.5	24.0	24.8	25.6
15:00	25.9	26.4	25.8	24.8	25.5	25.2	24.8	25.7	25.1	25.5	25.8	26.4
18:00	26.4	26.9	25.7	24.7	24.5	25.6	25.8	26.2	25.4	26.2	25.3	25.4
21:00	25.2	25.4	24.4	26.1	24.5	23.8	25.4	24.7	23.9	24.7	23.3	25.2

Evaluation of the measured data shows that the variability of the values was in the specification. The temperature ranged from 22.2 °C (lowest value) to 26.9 °C (maximum value) in the period. The average temperature was 24.5 °C. The lowest measured humidity in this period was 38.2% RH; the highest was 52.1% RH. The average humidity value was 44.7% RH.

Based on the determined real conditions, the curing of the prepared samples always took place at a temperature of 25 °C and a humidity of 45% RH, which were values corresponding to the measured data after rounding. In the case of a test with variable temperature and humidity, specific parameters are given in the methodology of the experiment.

3.1 Experiment with moisture cured 1C polyurethane adhesive

Betaseal™ adhesive from DOW® company was used for the experiment with the 1C polyurethane adhesive. Primers of the Betaprime™ series are used as adhesion promoters and Betaclean™ chemicals are used as cleaners.

According to the safety data sheet, the basic composition of the used Betaseal™ glue is in Table 3.

***Tab. 3** Composition of the 1C polyurethane sample Betaseal™, (Source: MSDS from DOW® company)*

Ingredient	CAS no.	Percentage [%]
1,2-Benzenedicarboxylic acid, di-C8-10-alkyl esters	71662-46-9	15.0 – 25.0
hydrotreated heavy naphtha (petroleum)	64742-48-9	1.0 – 5.0
4,4'-Diphenylmethane diisocyanate	101-68-8	0.1 – 1.0

The following is Table 4, which lists the selected properties of the adhesive based on the data in the technical documentation.

Tab. 4 *Selected properties of the 1C polyurethane sample Betaseal™, (Source: MSDS from DOW® company)*

Property	Value
density	1.23 g/cm^3 at 23 °C
solid contents	> 98%
viscosity (Extrusion, Ballan 4 mm nozzle, 4 bar)	10 – 14 g/min at 23 °C
processing temperature	10 – 40 °C
tack-free time	approx. 30 min at 23 °C/50% RH
cure rate	> 4 mm in 48 h at 23 °C/50% RH
tensile strength (DIN 53 504)	8 N/mm^2
elongation at break (DIN 53 504)	> 500%
lap shear resistance (EN 1465)	min. 4.5 N/mm^2 at 23 °C/50% RH, 7d, height of layer 2 mm
shore A hardness (DIN 53 505)	47-57

To evaluate the curing rate, block-shaped samples were prepared. The individual blocks were 1 cm high, 3 cm wide and 2 cm deep (Fig. 1). The samples cured in the chamber under defined conditions. These conditions included the specified humidity and the specified temperature. The aim was to determine the depth of the cured adhesive over time depending on the used conditions. The result was the depth [mm] of cured material from the surface to the inside of the mass. When reaching a depth of 15 millimetres, the block was 100% cured. The depth of cure was determined by measuring the solids in the block section (Fig. 3).

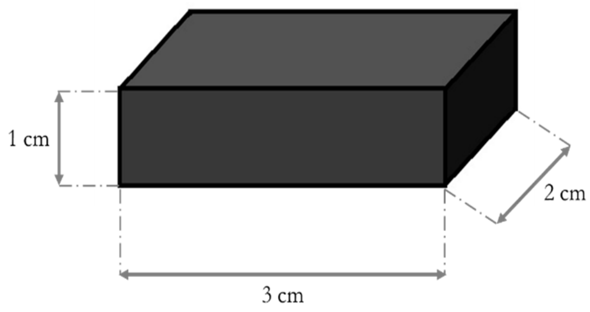

Fig. 1 *Illustrative representation of the tested block with the indicated dimensions - 1 cm height, 3 cm width, 2 cm depth*

Humidity and temperature values are given in the following Table 5. In the first case, one moisture value was chosen based on the real conditions in the production hall, and the effect of different temperature values on the cure rate was investigated. In the second case, one temperature value was chosen, and the effect of different humidity was tested.

Tab. 5 *Tested values. In case no. 1, the humidity was uniform, and the temperatures were different. In case no. 2 there was a uniform temperature and different humidity values*

Case no.	Humidity [% RH]	Temperature [°C]
1	45	10
		20
		25
		30
		35
2	30	25
	40	
	45	
	50	
	60	

The curing rate was evaluated after 0h, 1h, 2h, 3h, 4h, 8h, 24h, 48h and 72h. These values were chosen based on previous production experience. Five samples, i.e., blocks of polyurethane adhesive, were used for each combination of parameters and curing time. In total, 450 samples were evaluated.

Based on the results, the dependence of the curing rate on temperature and humidity after a constant curing time of 72 hours was determined. For the variable temperature, the humidity was constant and was set at 45% RH. In the case of variable humidity, on the other hand, a constant temperature of 25 °C was set.

In addition to the curing rate, other properties of these 1C moisture-curable polyurethane adhesives were tested. In the automotive industry, the key is the strength of the glued joint, which ensures safety and quality. For each glued part, certain requirements are set, which result from the standard of each customer, i.e., the car manufacturer, or from other general regulations. Standard DBL 7904 Adhesive bonds on components deals with the gluing of additional parts and their testing. Each customer defines their own requirements for the mechanical properties of the joint and the overall quality of the design. This article evaluates a model example inspired by real products.

The evaluated element is the strength of adhesion, respectively the force needed to break it. In addition to the monitored force value, the method of breaking the joint is particularly important. Failure of the joint can occur in such a way that the cohesion is broken, the adhesion is broken, or the glued material is damaged (e.g., the glass breaks or the plastic holder breaks).

In this experiment, the force required to tear off commonly used plastic holders was investigated. To adhere the test specimens, the glass was first cleaned with a special cleaner of the Betaclean™ series, an adhesive promoter called Betaprime™ was applied, specifically for glass. The surface of the plastic holder (material PA66 + 20% GF) was prepared by plasma treatment. Betaprime™ series for plastic materials. After the necessary ventilation, Betaseal™ glue was applied to the prepared surface of the holders. A total of twenty samples were prepared.

The parts were glued to a pre-prepared glass surface. Curing process followed under defined conditions, i.e., at 25 °C and 45% RH. The curing time was 96 hours, which ensured complete curing of the adhesive and perfect joint strength. The selected parameters were determined based on practice from the current production process and experience.

Joint geometry (Fig. 2) was chosen according to the real additional part, which is glued to car windows. It was a holder for moving the front door or the rear door glass, and it was a three-sided glued part. The joint area between the adhesive and the glass was 30.5 cm². All results of the measured force during the pull off test relate to this joint area.

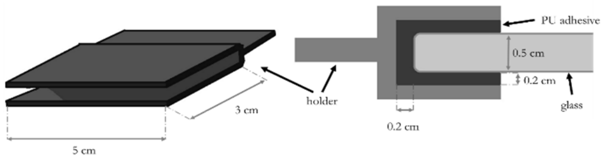

Fig. 2 *Illustrative representation of the holder with dimensions and the tested joint configuration*

The pull-off test of the holder was performed by attaching the tested sample to the pull machine. The holder was anchored to the moving mechanism of the machine so that it was in the axis of the sample when pulled. The movement of the mechanism was at a defined speed 100 mm/s according to real quality test requirements.

3.2 Experiment with 1C polyurethane adhesive with booster

Some 1C polyurethane adhesives can be used with an additive that is able to accelerate the speed of curing process. Usual amount of this additive is a few percent. For this experiment, Betamate™ series glue with of Betamate™ booster (additive) was used. The amount of additive in percentages of 1%, 2% and 3% was tested.

According to the technical data sheet, the basic information of the used Betamate™ and booster Betamate™ "Accel" is in Table 6.

Tab. 6 *Selected properties of the 1C adhesive Betamate™, booster "Accel" and the mixture (1C adhesive + booster), (Source: TDS from DOW® company)*

Property	Betamate™ adhesive	Betamate™ booster "Accel"
mixing ratio	99 – 97 parts	1 – 3 parts
basis	polyurethane prepolymer	polyol compound
density	1.25 g/cm³ at 23 °C	1.60 g/cm³ at 23 °C
solid contents	> 98%	> 98%

Property	Betamate™ adhesive + booster
processing temperature	50 – 60 °C
tack-free time	approx. 20 min at 23 °C/50% RH
cure rate	without booster > 2.7 mm in 24 h at 23 °C/50% RH with booster 24 – 48 h (depends on mixing ratio)
tensile strength (DIN 53 504)	> 5 N/mm²
elongation at break (DIN 53 504)	approx. 300%
lap shear resistance (EN 1465)	> 4 N/mm² at 23 °C/50% RH, 7days
G-Modulus	> 2.2 MPa at 10% strain after 7 days, 23 °C

The booster was used in an amount corresponding to 3%. Sample control time intervals were set at 20 min, 30 min, 40 min, 50 min, 60 min and 120 min. These values have been based on the fact that it is a fast-curing polymer, so the reaction was expected to be completed within 24 to 48 hours, depending on the mixing ratio. The depth from the surface towards the mass of tested block (Fig. 1), into which the solid hardened part intervened, was evaluated.

Another part of this experiment was to determine the dependence of the tear force on the amount of booster over time. The amounts of used additive were 1%, 2% and 3%. The same brackets and joint configuration as for the 1C polyurethane adhesive (Fig. 2) were used also for this test. The sample preparation conditions were standard, i.e., the same conditions as during normal production. The temperature was 25 °C and the humidity was 45% RH. The curing time was 96 hours to be able to compare with the first experiment.

To evaluate the strength of adhesion, twenty holders were used for a tearing test and for evaluation of the type of joint failure. All samples were prepared under the same conditions as in the previous experiment.

3.3 Experiment with 2C polyurethane adhesive

The last series of experiments was performed with a 2C adhesive from Weicon® from the Easy-Mix series. It is a high-strength fast-curing structured adhesive. Curing is fast and controlled because of a two-component system. The gluing process is thus almost independent of the layer thickness, air humidity and ambient temperature. Manual strength is after 10 minutes, mechanical strength after 30 minutes and final strength is reached after 12 hours.

According to the technical data sheet, the basic information about the properties of the used 2C adhesive is in Table 7.

Tab. 7 *Selected properties of the 2C polyurethane sample, (Source: TDS from Weicon® company)*

Property	Value
mixing ratio	1:1
density	1.30 – 1.35 g/cm³ at 23 °C
pot life, 20 °C	240 s
hand strength (35% of strength)	10 min
mechanical strength (50% of strength)	30 min
final strength (100% of strength)	12 h
tensile strength (ISO 527)	20 N/mm²
elongation at break (ISO 527)	31%
shore D hardness (DIN EN ISO 868)	68

As in previous experiments, the curing rate over time was evaluated here. The inspection time interval was adapted to the expected curing process. The measurements took place after 5 min, 10 min, 20 min, 30 min, 60 min and 120 min due to the fact that the mechanical strength is reached after only 30 minutes. The depth of cure was determined on a section of a polyurethane block sample (Fig. 1).

The dependence of the tear strength at the time of hardening was also determined. The samples corresponded to the standard preparation and conditions used throughout this work.

The last part of this experiment with 2C polyurethane adhesive was to evaluate the strength of adhesion during tearing and the type of joint failure according to standard DIN EN ISO 10365. A total of twenty samples of holders glued to the glass were prepared under the same conditions and same materials have been used. Curing was again under standard conditions, i.e., at 25 °C and 45% RH. The curing time was 96 hours to ensure the same conditions as in the previous experiments. The brackets were pulled off and the force was measured. The form of the failure was investigated to evaluate the overall properties.

4 Results

4.1 Results of the experiment with 1C polyurethane adhesive

A total of 450 samples were used to evaluate the curing rate. Five samples were used for each combination of temperature and humidity. Each sample was tested for the defined parameters by a destructive method in which a cut was made through a block of adhesive. For each sample, the depth from the surface towards the mass, in which the material had already hardened, was measured (Fig. 3).

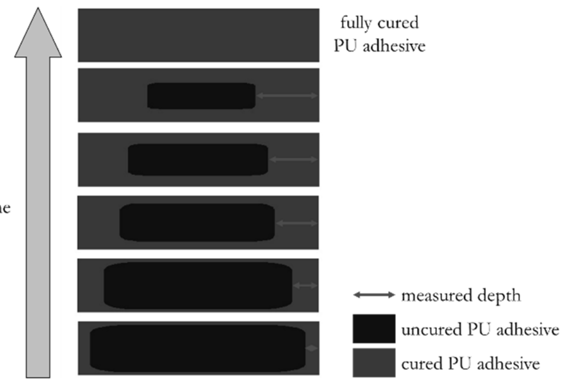

Fig. 3 *Illustrative depiction of the curing process over time. Representation of cured adhesive (light grey), uncured adhesive (dark grey), and measured depth of cure (red arrows)*

The average results for the curing rate test under defined conditions are given in the tables below. Table 8 shows the results for the first test with constant humidity and variable temperature. Table 9 summarizes the results of the second test with constant temperature and different humidity.

Tab. 8 *The average depth of cured 1C polyurethane adhesive [mm]. Conditions during the curing: 45% RH, different temperature*

45% RH					
	Temperature [°C]				
Time [h]	10	20	25	30	35
0	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
1	0.0 ± 0.04	0.3 ± 0.05	0.4 ± 0.08	0.5 ± 0.05	0.7 ± 0.05
2	0.4 ± 0.04	0.6 ± 0.12	0.8 ± 0.07	1.0 ± 0.06	1.2 ± 0.06
3	0.6 ± 0.05	1.0 ± 0.14	1.1 ± 0.10	1.4 ± 0.09	1.5 ± 0.05
4	0.9 ± 0.06	1.2 ± 0.06	1.6 ± 0.16	1.9 ± 0.10	2.1 ± 0.11
8	1.3 ± 0.06	1.8 ± 0.09	2.2 ± 0.12	2.5 ± 0.09	2.9 ± 0.08
24	2.9 ± 0.09	3.8 ± 0.08	4.1 ± 0.14	4.4 ± 0.16	4.7 ± 0.10
48	3.5 ± 0.12	4.6 ± 0.10	5.0 ± 0.16	5.6 ± 0.15	6.1 ± 0.12
72	3.5 ± 0.05	5.2 ± 0.19	6.0 ± 0.19	6.8 ± 0.17	7.6 ± 0.10
	mm	mm	mm	mm	mm

Tab. 9 *The average depth of cured 1C polyurethane adhesive [mm]. Conditions during the curing: 25 °C, different humidity*

	25 °C				
	Humidity [% RH]				
Time [h]	30	40	45	50	60
0	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
1	0.5 ± 0.05	0.7 ± 0.05	0.7 ± 0.05	0.9 ± 0.05	1.0 ± 0.04
2	0.9 ± 0.05	1.1 ± 0.10	1.1 ± 0.07	1.2 ± 0.07	1.4 ± 0.09
3	1.2 ± 0.06	1.4 ± 0.06	1.5 ± 0.04	1.5 ± 0.08	1.8 ± 0.07
4	1.6 ± 0.07	1.8 ± 0.06	1.9 ± 0.09	2.1 ± 0.10	2.4 ± 0.08
8	2.1 ± 0.11	2.3 ± 0.14	2.6 ± 0.08	2.8 ± 0.12	3.3 ± 0.14
24	3.9 ± 0.10	4.3 ± 0.10	4.5 ± 0.10	4.7 ± 0.07	5.1 ± 0.14
48	5.0 ± 0.15	5.7 ± 0.12	5.9 ± 0.11	6.1 ± 0.12	7.0 ± 0.13
72	6.3 ± 0.15	7.2 ± 0.17	7.3 ± 0.19	7.8 ± 0.14	8.6 ± 0.19
	mm	mm	mm	mm	mm

For a constant humidity value of 45% RH and for a uniform curing time of 72 hours, a temperature dependence of the curing depth was created (Fig. 4). For a given range of temperature values from 10 °C to 35 °C, this was a linear dependence.

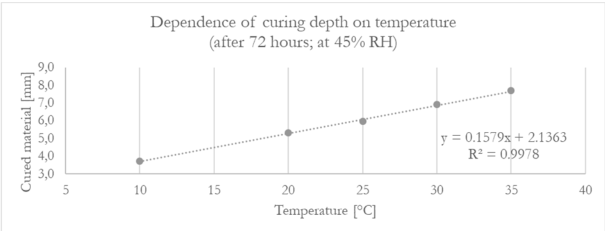

Fig. 4 *Dependence of curing depth on temperature in range 10 °C to 35 °C (constant humidity 45% RH and curing time 72 hours)*

For the constant temperature value of 25 °C and for a uniform curing time of 72 hours, the dependence of the curing depth on the humidity was created (Fig. 5). For a given range of humidity values from 30% RH to 60% RH, this was an exponential dependence.

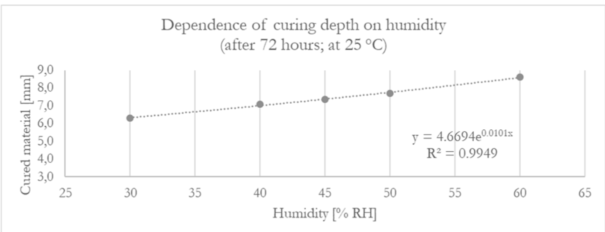

Fig. 5 *Dependence of curing depth on humidity in range 30% RH to 60% RH (constant temperature 25 °C and curing time 72 hours)*

The following Table 10 summarizes the values of the force needed to interrupt adhesion or cohesion. To ensure correct results, twenty holders (Fig. 2) as samples were used for this test. The test was performed as real products are evaluated. Thus, the parameters were 45% RH, 25 °C and cured for 96 hours. The values were measured using the tear force meter software. The minimum requirement for a positive final evaluation is a tear force of at least 1200 N and there must be a cohesive failure of the joint.

Tab. 10 *Values measured during the pull off test. Twenty samples with 1C moisture cured adhesive were tested and type of the failure according to standard DIN EN ISO 10365 was studied for each sample. The joint area between the glass and the adhesive was 30.5 cm². A sample with a negative rating is highlighted in red*

Sample no.	**Pull-off Force [N]**	**Type of failure**
1	3374	CF (cracked bracket)
2	4076	CF (cracked bracket)
3	4438	CF (cracked bracket)
4	3337	CF (cracked bracket)
5	3864	CF (cracked bracket)
6	3915	CF (cracked bracket)
7	3508	CF (cracked bracket)
8	3307	CF (cracked bracket)
9	3608	CF (cracked bracket)
10	4011	CF (cracked bracket)
11	3282	CF (cracked bracket)
12	2575	50% CF of the glue, 50% AF (glue – bracket)
13	3826	CF (cracked bracket)
14	4177	CF (cracked bracket)
15	4063	CF (cracked bracket)
16	3443	CF (cracked bracket)
17	3654	CF (cracked bracket)
18	3632	CF (cracked bracket)
19	3703	CF (cracked bracket)
20	3908	CF (cracked bracket)
average	**3685**	

4.2 Results of the experiment with 1C polyurethane adhesive with booster

From the experiment with 1C polyurethane in combination with a booster in the amount of 3%, the depths of the cured material were evaluated as a function of time. As it was a fast-curing polyurethane, the time interval has been set within minutes. The summary of results is in Table 11.

Tab. 11 *Summary of average measured values of cured 1C polyurethane with booster 3% material depth for a uniform temperature and humidity in a defined time*

Time [min]	Depth of cured material [mm]
0	0.00
20	2.50
30	4.70
40	5.80
50	8.10
60	9.00
120	15.00

The second part of the experiment with 1C polyurethane adhesive mixed with a booster concerned the evaluation of the effect of the amount of additive on the tear strength after a defined curing time. Holders (Fig. 2) glued to the glass were used as samples. The manufacturer's recommended amounts, which ranged from 1% to 3%, were tested. A summary of the results is given in Table 12.

Tab. 12 *Summary of measured pull-off force values in a defined time and comparison of the results with booster amount 1%, 2% and 3%. The joint area between the glass and the adhesive was 30.5 cm²*

Time [min]	Pull-off Force [N]		
	booster 1%	booster 2%	booster 3%
0	0	0	0
1	0	72	147
2	52	465	963
3	209	1034	1463
4	418	1551	1832
8	993	2172	2352
24	1777	2637	2873
48	2090	2896	2979
72	2613	3051	3136

To ensure comparability of results, the test with this adhesive was performed again. In this case, only a 3% booster was used. The conditions for sample preparation and testing were the same as in the previous case. The table of summary results Table 13 is designed as in the previous experiment. Again, the same parameters and conditions were used. The minimum value of the tear force and the method of breaking the bond was also valid in this evaluation.

Tab. 13 *Values measured during the pull off test. Twenty samples with 1C adhesive and booster were tested, and type of the failure according to standard DIN EN ISO 10365 was studied for each sample. The joint area between the glass and the adhesive was 30.5 cm². Samples with a negative rating are highlighted in red*

Sample no.	Pull-off Force [N]	Type of failure
1	3853	CF (cracked bracket)
2	4278	CF (cracked bracket)
3	4352	CF (cracked glass)
4	6285	CF (cracked glass)
5	5933	CF (cracked glass)
6	3637	20% CF of the glue, 80% AF (primer)
7	4096	CF (cracked glass)
8	6872	CF (cracked glass)
9	3810	10% CF of the glue, 90% AF (primer)
10	4144	CF (cracked bracket)
11	4711	CF (cracked bracket)
12	4304	CF (cracked bracket)
13	4548	CF (cracked bracket)
14	4276	CF (cracked bracket)
15	5213	CF (cracked bracket)
16	3057	20% CF of the glue, 80% AF (primer)
17	3495	20% CF of the glue, 80% AF (primer)
18	6388	CF (cracked glass)
19	3901	CF (cracked bracket)
20	5610	CF (cracked bracket)
average	**4638**	

4.3 Results of the experiment with 2C polyurethane adhesive

In an experiment with a 2C polyurethane adhesive, the depth of the cured material was evaluated as a function of time. The minute time interval was chosen with respect to the rate of the ongoing curing reaction. The summary of results is in Table 14.

Tab. 14 *Summary of average measured values of cured 2C polyurethane material depth for a uniform temperature and humidity in a defined time*

Time [min]	Depth of cured material [mm]
0	0.00
5	8.66
10	12.70
20	14.20
30	15.00
60	15.00
120	15.00

The second part of the experiment with 2C polyurethane adhesive included the evaluation of the tear strength after a defined curing time. A summary of the results is given in Table 15.

Tab. 15 *Summary of measured force values in a defined time. The joint area between the glass and the adhesive was 30.5 cm²*

Time [min]	Pull-off Force [N]
0	0
1	2063
2	2639
3	2930
4	3136
8	3634
24	4712
48	4963
72	4954

Twenty brackets were subjected to the same adhesion test to maintain comparability of results with previous experiments. The results are summarized in a Table 16. The measured tear strength and the type of bond failure were taken into account when evaluating the adhesion.

Tab. 16 *Values measured during the pull off test. Twenty samples with 2C adhesive were tested and type of the failure according to standard DIN EN ISO 10365 was studied for each sample. The joint area between the glass and the adhesive was 30.5 cm². Samples with a negative rating are highlighted in red*

Sample no.	Pull-off Force [N]	Type of failure
1	7051	100% AF (glue/primer – bracket)
2	6820	CF (cracked bracket)
3	7543	100% AF (glue/primer – bracket)
4	7252	100% AF (glue/primer – bracket)
5	5707	CF (cracked bracket)
6	6710	CF (cracked bracket)
7	7081	100% AF (glue/primer – bracket)
8	6590	CF (cracked bracket)
9	4183	CF (cracked bracket)
10	5547	CF (cracked bracket)
11	5045	CF (cracked bracket)
12	3440	CF (cracked bracket)
13	4895	CF (cracked bracket)
14	4152	CF (cracked bracket)
15	7262	100% AF (glue/primer – bracket)
16	5757	CF (cracked bracket)
17	6550	100% AF (glue/primer – bracket)
18	7131	100% AF (glue/primer – bracket)
19	6941	100% AF (glue/primer – bracket)
20	5998	CF (cracked bracket)
average	**6083**	

5 Discussion

5.1 Summary of results

To be able to compare the samples in terms of curing rate, the depth was converted to the percentage of cured material in the tested polyurethane block and a graphical representation (Fig. 6) was created.

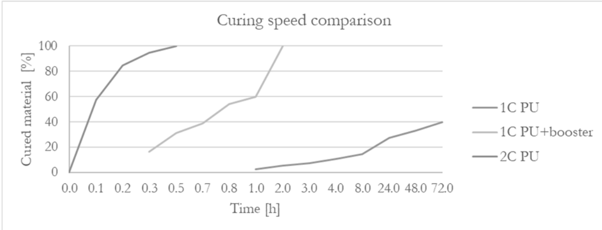

Fig. 6 *Comparison of the curing rate expressed as a percentage of the cured material in the tested blocks of polyurethane samples*

The two-component polyurethane adhesive cures to 100% after 30 minutes. In the case of a one-component adhesive with a booster addition of 3%, the time to complete curing was 2 hours. The slowest process was in the case of one-component polyurethane. This adhesive reached a solids value of 40% after 72 hours.

The results can be compared using the forces needed to break adhesion or cohesion during the pull off test. For the individual adhesives, the sample preparation conditions, ambient conditions and curing time were the same. The brackets (Fig. 2) used were also identical. The graphical representation of the force values was created (Fig. 7).

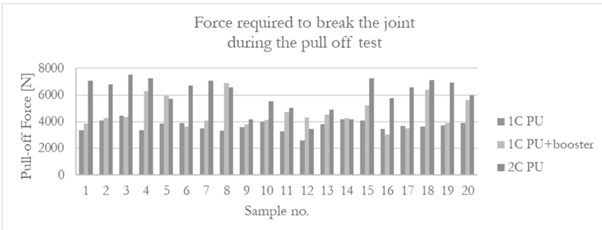

Fig. 7 *Comparison of the force required to break the joint during the pull off test of polyurethane samples whose joint area between the glass and the adhesive was 30.5 cm²*

The strength values were the highest for the two-component polyurethane, although the standard deviation was ± 1171 N in the sample. Polyurethane adhesive with a booster showed fluctuations in the measured values of force with a standard deviation of ± 1034 N. Lower values of force were similar to the one-component adhesive without booster, higher values, in some cases, were close to the values for two-component adhesive. The samples of standard moisture-cured polyurethane achieved the smallest variability of the resulting strength values. In this case, the standard deviation was ± 401 N.

The second possibility of evaluating the results was from the point of view of the nature of the joint failure according to standard DIN EN ISO 10365, i.e., whether it was an adhesive or cohesive failure. Based on the results, a pie chart was created (Fig. 8).

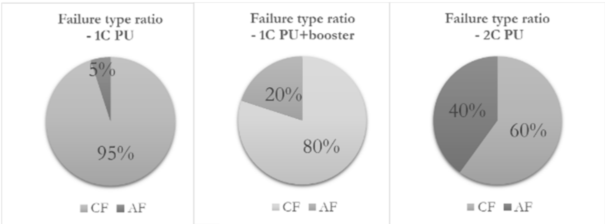

Fig. 8 *Comparison of the percentage representation of individual types of joint failure for each type of polyurethane*

These results can be summarized as 95% of the 1C polyurethane samples showed cohesion failure, only 5% had adhesive failure. In 1C polyurethane with a booster, cohesion was broken in 80% of the samples and 20% of the samples were evaluated as unsatisfactory due to the adhesive failure of the joint. Samples with a two-component adhesive achieved the worst results. There were 60% compliant samples and 40% non-compliant ones.

Although the lowest strength values were achieved for 1C polyurethane, according to the results of adhesion or cohesion failure, this type of adhesive appears to be the most suitable for the given application.

5.2 Evaluation of results with regard to real production

As Hipkin et al. [24] points out, improving existing processes and making them more efficient is a key factor in the automotive manufacturing industry. As stated in a study by Fabio de Felice [25], it is important to maintain consistent product quality while improving yield and reducing costs. In the case of gluing additional parts to glass, the key factor of production efficiency is the speed of curing of the adhesive. This quantity determines the storage time, which is very expensive. As the test results in this work show, 1C polyurethanes are very slow in terms of curing. According to studies by Sun et al [26] and Daniel-da-Silva et al. [27], this fact could be explained by the fact that the key is the rate at which moisture penetrates from the external environment towards the mass of the material, where it interacts with yet unreacted functional groups. The rate of diffusion of atmospheric moisture into the material and further through the mass of the material is a determining factor in the rate of the entire curing reaction. Acceleration is possible using a booster, as mentioned in the article [7] and in a study by Jennrich et al. [28]. When using an accelerator at a concentration of 3%, curing was complete after 120 minutes, whereas in case of 1C polyurethane without a booster, only 5% of the material volume was cured at the same time. In addition, an experiment with a sample of this 1C adhesive showed that the cure rate depends on humidity and temperature, which is confirmed by several sources, for example Sun et al [26], Daniel-da-Silva et al. [27] or Lepene et al. [29]. The curing process of 2C polyurethane adhesives is almost independent of ambient humidity, temperature, and layer thickness. Li et al. [30] states that 1C polyurethanes cure slower than 2C and are more dependent on ambient conditions, which is less advantageous for their use in industrial practice. This conclusion is consistent with the results of this experiment. 2C polyurethanes have the advantage of storage stability and as the Bockel et al. study [6] states, the reaction itself depends mainly on the degree of stoichiometric ratio between the reacting groups. This fast type of curing is very advantageous especially for fast production, where it is important to just pack and send the products without the need of long storage.

In addition to the reaction rate of the polyurethane used for gluing additional parts to the glass, the strength of the joint is also crucial in real production. When comparing the results using a standard polyurethane adhesive and fast-curing adhesives, it can be observed that the forces obtained were greater in case of a one-component polyurethane with a booster or a two-component polyurethane. However, fast-curing polyurethanes were more likely to cause adhesive bonding failure, which is undesirable. According to observations, the cause of the undesirable type of damage was the mechanical properties of the adhesive itself. The strength of these types of adhesives was greater, resp. standard 1C polyurethane was more elastic. On the contrary, fast-curing adhesives were more rigid. Thus, under stress, the bond to the substrate was disrupted rather than breaking cohesion. Different mechanical properties of 1C and 2C polyurethanes were observed, for example, in the work of Kläusler et al. [31]. To improve the mechanical properties, it would be possible to modify the adhesive with additives as described by Bockel et al. [6] or by Luedtke et al. [32]. As a result, the required bond strength would be maintained, but the failure according to DIN EN ISO 10365 could be more cohesive, inside the polyurethane mass.

6 Conclusions

Three adhesives were tested in the experiments. One-component adhesives in combination with a booster and two-component adhesives offer great potential to conventional moisture-cured 1C adhesives. In comparison with the variability of humidity, the temperature variability has been shown to have a greater effect on the shape of the curing curve of the 1C polyurethane adhesive. The shortest curing time was for 2C glue which was fully cured after 30 minutes. For 1C booster adhesive, this time was 2 hours. For standard moisture-cured adhesive, it takes more than 72 hours for perfect cure. The strength was tested using a pull off test, and the area of the adhesive bond between the glass and the adhesive was 30.5 cm². The average values of the pull off force were 3685 N for the samples with moisture-cured adhesive, 4638 N for the samples with 1C booster adhesive and 6083 N for the samples with 2C adhesive. 1C booster adhesives have the disadvantage of mixing glue and booster because the amount of accelerator added is in percent units, which can be difficult in terms of consistent quality. The most interesting for the investigated process is the use of 2C adhesives. Although in terms of the joint failure type according to DIN EN ISO 10365, it would be ideal to change the hardness of the adhesive to make it more elastic. Quality and fast production are key factors in the automotive industry, so the potential for financial savings associated with speeding up the process when using fast-curing adhesives is great.

Abbreviations

1C: One-component; 2C: Two-component; AF: Adhesive failure; CF: Cohesive failure; GF: Glass fibre; NCO-group: Cyanate group; PA66: Polyamide 6.6; RH: Relative humidity

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