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USE OF ATMOSPHERIC PRESSURE PLASMA TO IMPROVE THE ADHESIVE PROPERTIES OF GLASS AND POLYAMIDE 6 IN THE BONDING OF ADDITIONAL PARTS IN THE AUTOMOTIVE INDUSTRY

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In the search for alternatives to the commonly used methods of the pre-treatment of surfaces, plasma discharge applications are appearing more and more. In the case of the automotive industry, where the attention is focused on finding methods that are more environmentally friendly, more economically advantageous and process-friendly, plasma is a suitable option. In the case of gluing additional parts with polyurethane glue to the car glass, the use of plasma activation or cleaning of the joined materials improves the adhesion properties. Through this process, it is possible to achieve an increase in the force required to break the joint, as well as an increase in the proportion of the desired cohesive failure of the adhesive. A process including a point nozzle plasma used on the glass surface and a rotating plasma nozzle to activate the surface of the holder made of polyamide 6 with a glass fibre content of 30 % was found to be particularly suitable. The effect of plasma was also investigated using a surface tension test using test inks, observing the materials using an optical microscope, and the cleaning efficiency was analysed using infrared spectroscopy.

INTRODUCTION

Within the production of automotive glass, windows with attached additional parts are a group of products. These parts are usually made of plastic or metal [1, 2]. Polyurethane (PU) adhesives are most often used to join these different substrates [3]. The joint obtained must meet strict safety requirements, which requires the appropriately chosen pre-treatment of the surface of the bonded materials in order to achieve perfect adhesion between the adhesive and both substrates [4-10].

Glass has properties that are advantageous in terms of use in the automotive industry. This material has high hardness, high compressive strength and is chemically resistant [11, 12]. Its surface is made up of various oxides, among which compounds based on silicon and oxygen bonds predominate [13], which give the glass a polar character [14]. During the production and processing of glass in the automotive industry, glass is exposed to many environmental influences that can cause its pollution. The most common contaminants include dust, grease and other organic or inorganic pollution [15-20].

In general, plastics, metals and glass are considered difficult materials to bond [8]. In this work, attention was focused on additional plastic parts made of polyamide 6 with a glass fibre content of 30 %. This material is widely used for its advantageous properties, of which the mechanical ones are due to the glass fibre content [21]. The advantage of polyamide is its strength, availability and ductility [22]. Nevertheless, it is not completely perfect from the point of view of adhesion properties, since the polyamide surface has low surface energy and, thus, low wettability, due to the insufficient polar group content on the surface [23-27]. Low wettability then leads to a reduction in the adhesive strength, and, in the case of bonding with polyurethane, the bond formation is a challenge [28-32]. In order for the connection to be possible, it is necessary to use a cleaning process with the aim of ridding the surface of dirt and grease, but, at the same time, it is necessary to use an adhesion promoter coating, which enables the subsequent bonding to the adhesive [33]. The composition of these special mixtures is always adapted to the given substrate, i.e., it differs for glass and for plastic [8, 19, 20, 34-36].

Various substances are commonly used for cleaning the glass surface, especially various combinations including organic solvents, but also acids or bases can be used [37- 41]. Recently, the use of plasma as a pre-treatment of the surface of bonded materials has become very popular [42]. The use of plasma compared to conventional methods of cleaning using organic solvents and other chemicals is advantageous from the point of view of

the environment, but also due to the costs, since it is possible to use plasma using air and, thus, the treatment takes place under atmospheric pressure [43-47]. Also, costs are often key monitored process parameters in the automotive industry [32, 48, 49].

Plastics treated with a plasma flame acquire better surface properties, as impurities are removed from the surface by the action of ionised particles and free radicals. At the same time, polar functional groups based on hydroxyls, carbonyls and carboxyls are introduced to the surface of the low-energy plastic [50, 51]. Through this binding, the polarity of the surface increases and, thus, its surface energy and wettability and, therefore, the overall strength of the resulting adhesion is increased [28]. At the same time, the plasma acts to modify the surface structure, whereby the surface becomes more fragmented, or its surface area increases. [52]. Many publications focus on various polymers such as polypropylene, polyethylene, polyethylene terephthalate and others [53-55]. There are fewer articles dealing directly with the effect of plasma on polyamide parts as they usually deal with the issue of copolymers [22, 42].

The principle of plasma action on the glass surface is similar to that of polymers, and, here too, the basis for improving adhesion is to avoid the creation of a weak bonding interface [56]. The Si–O$^-$ groups present participate in the interaction of the glass with the adhesive, or other elements are bound to the oxygen, which endow the glass with its final surface properties that also affect the resulting adhesive properties [57, 58]. A number of works deal with the improvement of adhesion properties, but mainly focus on electronic components [59-61], possibly on dental applications, and minimally deal with the area of architecture and construction [62-65]. In the case of glass, polar groups, especially hydroxyl and carboxyl groups, are brought to the surface by plasma, which increases the wettability and adhesive properties without affecting the overall material [66, 67]. Due to the improvement of the adhesion, it is then possible to increase the force required to break the bond, thus achieving a higher joint quality [65].

EXPERIMENTAL

In all the presented experiments, float glass with dimensions of 40 × 40 cm was used as a basic substrate. Smaller pieces were cut from the glass sheets with a diamond cutter so that each additional part was glued to the glass separately and thus the results would not be distorted during the evaluation of the samples. The final dimensions of the glass sheets were 10 × 10 cm. Plastic holders made of polyamide 6 with 30 % of glass fibres simulated the real additional parts, which are glued to windows in the automotive industry. The dimensions of the holder are shown in the drawing below (Figure 1).

The quality of the surface of the glass and plastic holders was assessed by the surface tension value, which was determined using a set of test inks for both the glass and plastic holders. The set contained inks with surface tension values from 32 mN·m^{-1} to 44 mN·m^{-1}. According to experience and according to the general opinion of the supplier of test inks [68], a substrate surface tension of 38 mN·m^{-1} is considered suitable. This value was therefore the limit in this study as well, i.e., materials with a surface tension value equal to or higher than 38 mN·m^{-1} were considered suitable for the adhesive system.

The initial cleanliness of the glass surface was examined using a Keyence VHX-900F optical microscope. The possible impurities and the overall appearance of the glasses were examined.

A spectroscopic analysis was used to reveal, in more detail, the composition of the contamination present. A Nicolet iN10 FT-IR microspectrometer from Thermo Analytic was used in a reflective configuration using an MCT-A imaging detector. The spectra were measured in the spectral range 4000-675 cm^{-1} at a resolution of 4 cm^{-1} and with 64 spectrum accumulations. Omnic 9 and ImageJ 1.54d software were used for the evaluation.

In a standard manufacturing process, the surface of the bonded materials is cleaned, then an adhesion promoter is applied, and finally the parts are joined with a glue [7]. For the purposes of the experiment, the effect of plasma on the treated surfaces was compared with conventional pre-treatment and cleaning methods of materials. The standard glass cleaning method included the concentrated solvents isopropyl alcohol and heptane,

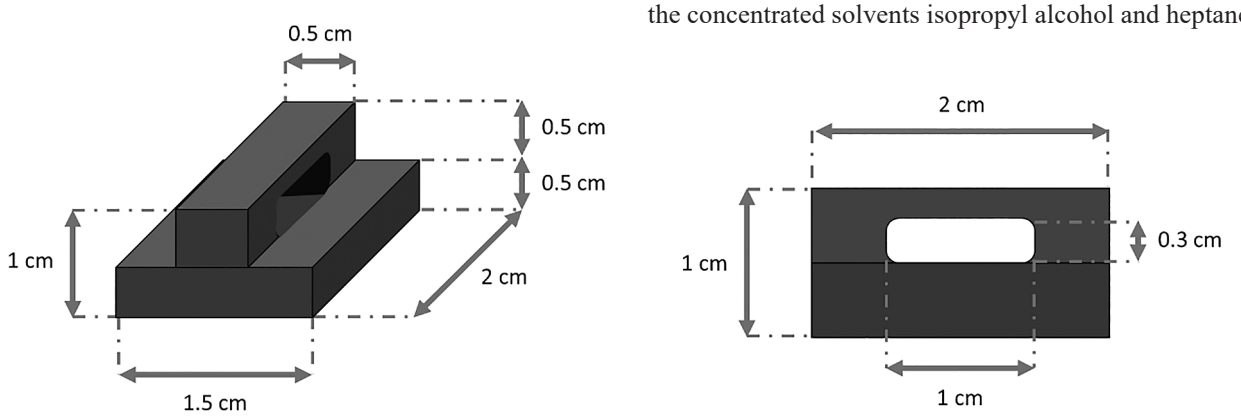


Figure 1. Dimensions of the holder made of polyamide 6 with the 30 % glass fibre content.

and a 2 % detergent solution made by mixing water with Jar Professional kitchen degreaser. These substances are usually applied to the surface of the glass using a wet paper towel, or using a bottle equipped with woollen or synthetic felt. In this case, the cleaners were applied using a cloth to allow for mechanical cleaning as well. The standard treatment and activation of the surface of the plastic holders was carried out using the activator of the Betaclean™ series from DOW®. This activator is based on isopropyl alcohol and also contains other components that improve the surface properties of the plastic.

Atmospheric pressure plasma was used for this experiment with two plasma nozzles – a rotary and a point one. The surface of the plastic holder was activated by the rotary nozzle. The point nozzle was mainly used to clean the surface of the glass from impurities. The basic parameters of the plasma used are an electrode voltage of 5-10 kV, a working frequency of 16-20 kHz, a discharge voltage of 2 kV and a plasma nozzle pressure of 1-3 bar. Dry air without oil was used as the gas.

Before applying the plasma treatment, the holders were placed next to each other in a plastic holder that ensured their correct position during this process. At the same time, time and energy were saved, as the plasma treatment took place for several pieces at once.

The setting of the distance of the plasma head from the surface of the treated material and the speed of movement of the device were chosen based on previous experience, i.e., according to the standard setting for similar applications. However, finding the most suitable setting was the goal of this experiment. For the treatment of plastic parts, three movement speeds and three distances of the nozzle from the surface were tested. The first combination was a speed of 18 $m \cdot min^{-1}$ and a distance of 10 mm. The second combination was a speed of 24 $m \cdot min^{-1}$ and a distance of 15 mm. The third combination was a speed of 12 $m \cdot min^{-1}$ and a distance of 20 mm. In the case of glass, the panels were inserted into the plasma treatment space separately, taking their dimensions into account. The speed was 15 $m \cdot min^{-1}$ and the distance 10 mm. The different distances of the plasma discharge from the treated surface have an effect on the resulting surface properties. The closer the plasma source is, the greater the amount of bound oxygen groups on the plastic surface [32]. In addition, precisely by adjusting the distance, it is possible to achieve various properties that are crucial for the resulting adhesion [69, 70].

A summary of the tested treatment configurations is shown in Table 1.

After using plasma or standard cleaning, the appropriate adhesion promoter of the Betaprime™ series was applied to the surface of the glass and the plastic part. A one-component polyurethane adhesive of the Betaseal™ brand from the same manufacturer was used to bond the substrates. The specification of this glue is shown in the Table 2.

Table 1. Designation of the group of samples and their characterisation according to the treatment of the glass surface, according to the treatment of the holder and the specification of the plasma used.

Sample	Glass treatment	Holder treatment	Plasma settings for holder treatment	
			Speed	Distance
A	cleaner	activator	N/A	N/A
B	plasma	activator	N/A	N/A
C	plasma	plasma	12 $m \cdot min^{-1}$	20 mm
D	plasma	plasma	18 $m \cdot min^{-1}$	10 mm
E	plasma	plasma	24 $m \cdot min^{-1}$	15 mm

Table 2. Selected properties of the polyurethane adhesive Betaseal™. (Source: MSDS from DOW®)

Property	Value (at 23 °C / 50 % RH)
Density	1.23 $g \cdot cm^{-3}$
Solid contents	> 98 %
Viscosity*	10 – 14 $g \cdot min^{-1}$
Processing temperature	10 – 40 °C
Tack-free time	approx. 30 min
Cure rate	> 4 mm in 48 h
Tensile strength**	8 $N \cdot mm^{-1}$
Elongation at break**	> 500 %
Lap shear resistance***	min. 4.5 $N \cdot mm^{-1}$ (7 days, height of layer 2 mm)
Shore A hardness****	47 – 57

** Extrusion, Ballan 4 mm nozzle, 4 bar*
*** DIN 53 504*
**** EN 1465*
***** DIN 53 505*

The adhesive was applied to the lower surface of the plastic holder using a cartridge application gun. The location and dimensions of the adhesive are shown in the illustration below (Figure 2).

The following illustration (Figure 3) shows the final configuration of the glued joint. After applying the adhesive, the holder was placed on the prepared glass surface and pressed so that the final height of the adhesive was 0.1 cm. To comply with this dimension, the holder was provided with four protrusions of the appropriate height on the bottom side, which defined the distance. The approximate dimensions of the glue after gluing the part to the glass are shown in the same picture.

After gluing the parts, a curing process followed under the defined conditions, i.e., at 25 °C and 45 % relative humidity (RH). This process took 96 hours to ensure the full curing of the adhesive providing the perfect bond strength. The setting was chosen based on the recommendations of the adhesive system manufacturer and also on the basis of experience from real practice [7, 71].

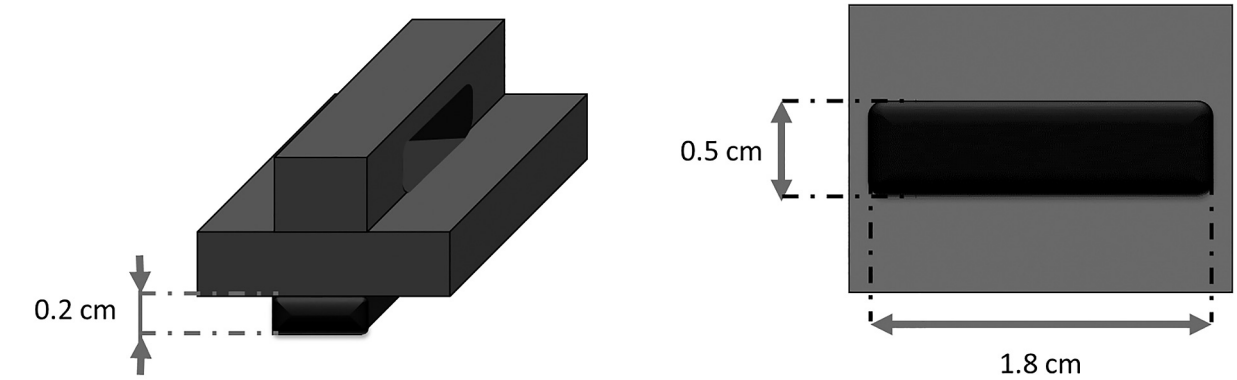


Figure 2. Dimensions of the polyurethane adhesive applied to the underside of the plastic holder.

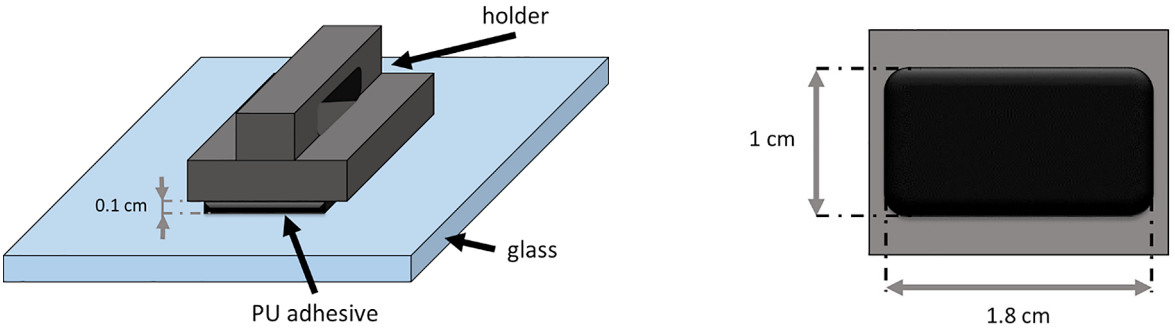


Figure 3. Illustrative drawing of the parts joined with the polyurethane glue and the final dimensions of the adhesive after gluing.

After curing, the samples were divided into a group that was evaluated immediately, i.e., the test took place under normal conditions. The second group of samples was subjected to a climatic test in which they were placed in a chamber for 7 days and exposed to a temperature of 70 °C. They were then moved to a –20 °C chamber for 2 hours. The final stage was at room temperature for 24 hours, when relaxation occurred. Subsequently, these samples were further evaluated in the same way as the samples from the first group.

The assessment of the bond strength was carried out using a tear-off test, in which the tested sample was attached to the moving part of the tear-off device. The movement of the machine was carried out perpendicular to the joint plane, at a defined speed according to the actual requirements and standards of the customers. An example of such a standard can be the standard DBL 7904 Adhesive bonds on components. The force values necessary to break the joint or material were measured and recorded using tear force meter software. At the same time, the way in which the connection was broken was also evaluated. The specific type of failure is defined in the DIN EN ISO 10365 standard, and, in this case, it may be a fracture of the material of the holder or glass, an adhesive failure between the adhesive, or between the adhesion promoter and the substrate, or the cohesion of the PU adhesive may fail.

An acceptable criterion is a tear-off force value of at least 200 N for these holder and adhesive dimensions. At the same time, it is desirable to achieve the cohesive failure of the joint in the glue, or cracking of the holder or glass. Conversely, adhesive failure between the substrate and the adhesive is assessed as unsatisfactory. These requirements are again inspired by real experiences with customer demands.

RESULTS AND DISCUSSION

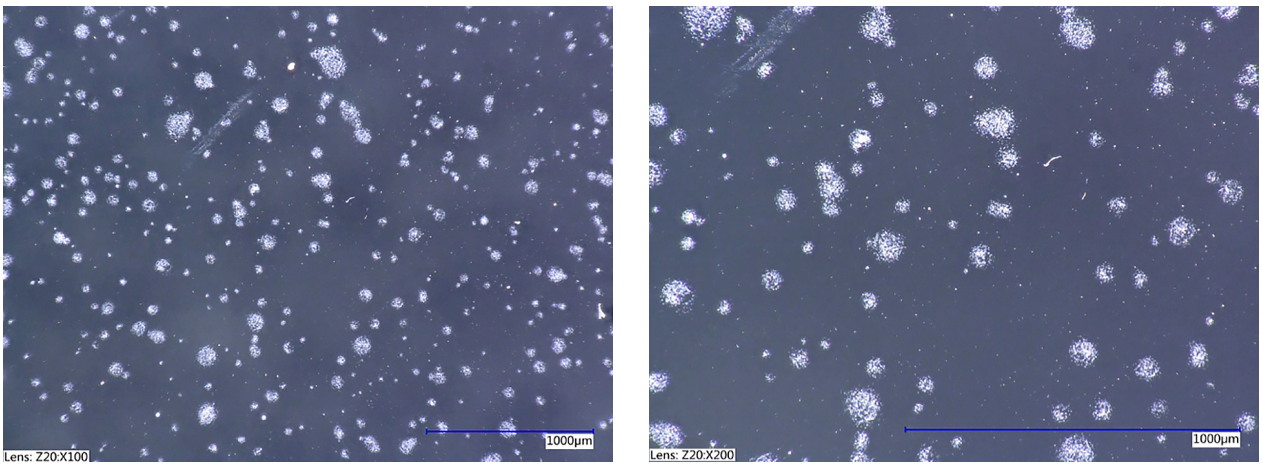
Initial assessment of the surface of bonded materials

Using a set of test inks, the surface tension of the glass was determined to be 36 $mN \cdot m^{-1}$, and the polyamide 6 plastic holders were 32 $mN \cdot m^{-1}$. Both of these values are below the set limit of 38 $mN \cdot m^{-1}$, so it is definitely necessary to pre-prepare the surface to achieve good adhesion.

When assessing the quality of the glass surface using an optical microscope, the presence of any contamination was detected on several glasses. Photographs were taken from several locations and are shown in the images of Figure 4. These contaminated samples were separated and served for further purposes of investigating the effectiveness of the cleaning.

Pre-treatment of the glass

The following Table 3 shows photos taken after applying the given method of cleaning the glass surface. This involved mechanical cleaning using a dry paper



a) b)

Figure 4. Photographs of the glass surface taken with an optical microscope to assess the initial cleanliness. A sample of glass sheets that had contamination on the surface.

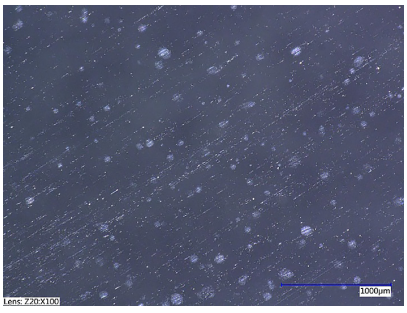
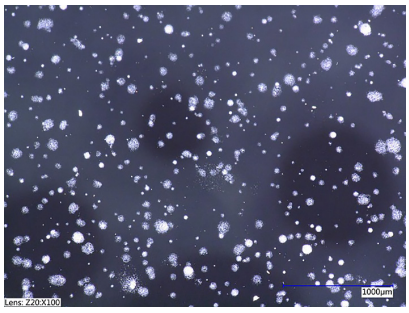
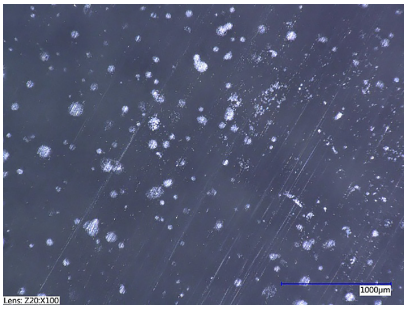
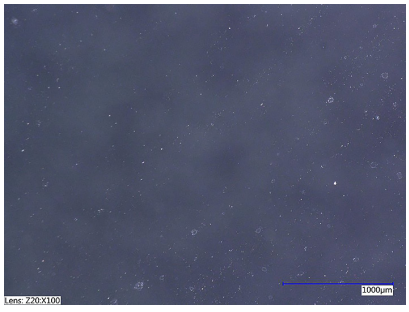
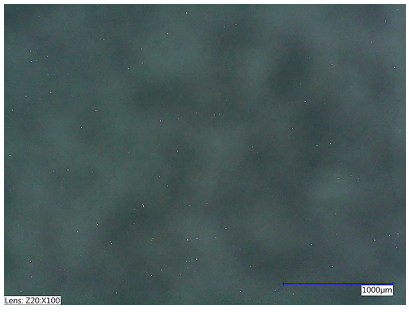
towel, mechanical cleaning with a towel soaked in a 2 % detergent solution, in heptane, or in isopropyl alcohol, and the last method was the use of plasma with the rotary nozzle and the point nozzle.

The significant removal of contamination was achieved with the treatment using heptane, isopropyl alcohol and plasma equipped with a point nozzle. The surface tension was determined for these samples, while, in the case of heptane and isopropyl alcohol, there was no significant improvement, on the contrary, a value exceeding 44 $mN \cdot m^{-1}$ was reached for plasma (Figure 5). Plasma applied with the point nozzle was assessed as the most effective pre-treatment method of the glass surface.

The increase in the surface tension and improvement in the wettability of glass by the use of plasma has already been confirmed in several studies [72, 73].

To identify the composition of the contamination, an infrared spectroscopy analysis was used, which was performed directly on the contaminated glass surface and then at the area of plasma treatment. Based on the

Table 3. Table with photos of the glass surfaces after using individual pre-treatment methods. The specific description is given above each image.

Mechanical cleaning with a dry paper towel	Mechanical cleaning with a towel soaked in heptane	Plasma cleaning with the rotary nozzle
		
Mechanical cleaning with a towel soaked in a 2 % detergent solution	Mechanical cleaning with a towel soaked in isopropyl alcohol	Plasma cleaning with the point nozzle
		

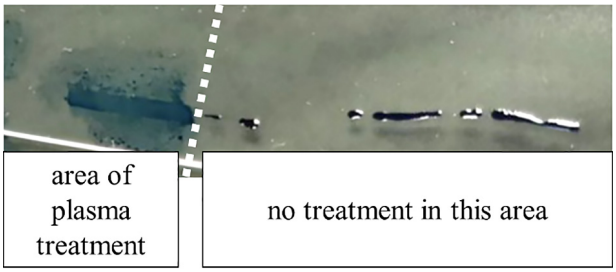


Figure 5. Photograph of a line created by a test ink with a value of 44 mN·m^{-1} to determine the surface tension of the glass in the area without any pre-treatment and in the area where the point nozzle plasma was used.

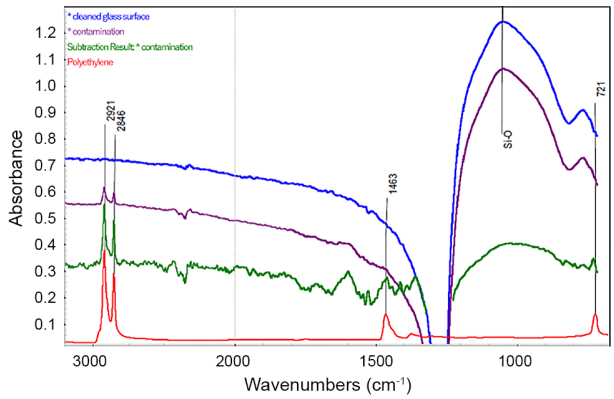


Figure 6. Typical measured reflection infrared spectra. In the area of contamination, bands of CH_2 bonds (polyethylene) are visible, while these bands are not visible on the cleaned surface.

difference, a spectrum corresponding to the spectrum of polyethylene was obtained (Figure 6). This is secondary contamination and, according to the available sources [74, 75], it is probably a mould release agent used in the injection of polymeric materials.

For further practical tests with the bonding of plastic holders, only the point nozzle plasma treated glasses were used, as the rotary nozzle proved to be ineffective for this application. Sheets treated with isopropyl alcohol as a cleaner were used as the comparative glass samples.

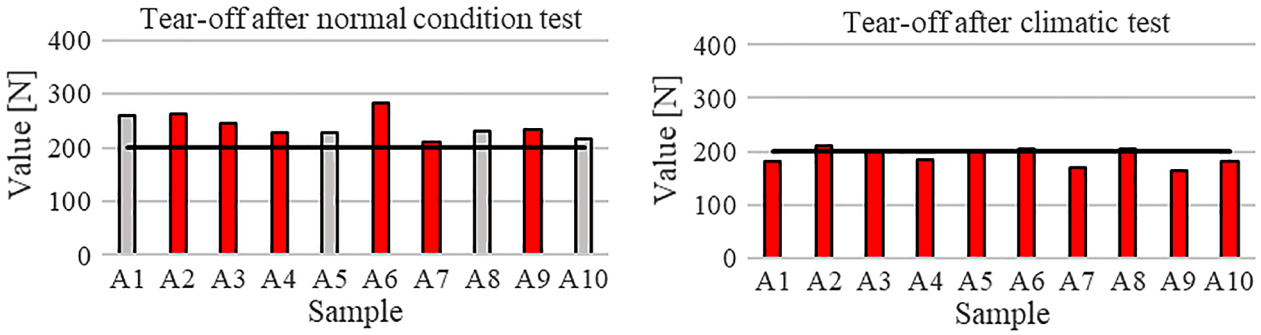
Bonding of polyamide 6 holders

For all the tested groups of samples, the surface tension was determined using test inks. The initial value was 32 mN·m^{-1}, with the use of plasma, a value of at least 42 mN·m^{-1} was achieved. It is therefore clear from this measurement that there has been a significant improvement in the coating properties. The increase in the mea-sured value is also in accordance with the available professional literature, in which the effects of plasma directly on polyamide 6 are investigated [22, 42].

Each group of samples marked A to E (according to Table 1) contained a total of 20 samples, half of which were used to evaluate the tear-off force under normal conditions and the other half were subjected to a climatic test followed by a tear-off. Each sample was evaluated from the point of view of the joint failure, with the mode of failure, i.e., adhesive or cohesive failure, the location of the failure and the force value in Newton units at

Table 4. A group of samples marked with the letter A and the results of the tear test performed under normal conditions and after the climatic test

	Normal conditions test									
Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
Cohesive failure (%)	100	80	50	70	–	40	70	–	50	–
Adhesive failure (%)	–	20	50	30	–	60	30	–	50	–
AF adhesive/holder	–	–	–	–	–		X	–	–	–
AF adhesive/glass	–	X	X	X	–	X	–		X	–
CF adhesive	X	–	–	–	–	–	–	X	–	–
Cracked holder	–	–	–	–	X	–	–	–	–	X
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	260	262	247	227	229	284	211	231	235	216
Overall rating	OK	NOK	NOK	NOK	OK	NOK	NOK	OK	NOK	OK
	Climatic test									
Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
Cohesive failure (%)	–	40	60	10	70	50	50	40	20	–
Adhesive failure (%)	100	60	40	90	30	50	50	60	80	100
AF adhesive/holder	–	–	–	–	X	–	X	X	–	–
AF adhesive/glass	X	X	X	X	–	X	–	–	X	X
CF adhesive	–	–	–	–	–	–	–	–	–	–
Cracked holder	–	–	–	–	–	–	–	–	–	–
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	181	211	200	184	199	206	168	205	164	180
Overall rating	NOK	NOK	NOK	NOK	NOK	NOK	NOK	NOK	NOK	NOK

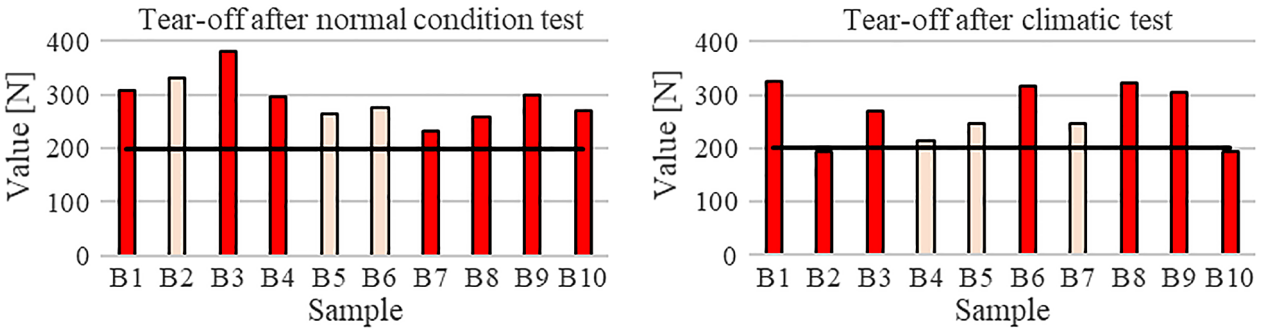


a) b)

Figure 7. Graphical representation of the tear strength values performed under normal conditions and after the climatic test for the group A specimens. Samples that failed the test either because of an insufficient strength value or due to the way the connection failed are marked in red.

Table 5. A group of samples marked with the letter B and the results of the tear test performed under normal conditions and after the climatic test.

	Normal conditions test									
Sample	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
Cohesive failure (%)	90	–	–	80	–	–	90	–	–	80
Adhesive failure (%)	10	–	100	20	–	–	10	100	100	20
AF adhesive/holder	X	–	X	X	–	–	X	X	X	X
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	–	–	–	–	–	–	–	–	–	–
Cracked holder	–	X	–	–	X	X	–	–	–	–
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	309	330	381	295	263	277	231	259	299	271
Overall rating	NOK	OK	NOK	NOK	OK	OK	NOK	NOK	NOK	NOK
	Climatic test									
Sample	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
Cohesive failure (%)	30	20	–	–	–	40	–	–	50	10
Adhesive failure (%)	70	80	100	–	–	60	–	100	50	90
AF adhesive/holder	X	X	X	–	–	X	–	X	X	X
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	–	–	–	–	–	–	–	–	–	–
Cracked holder	–	–	–	X	X	–	X	–	–	–
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	325	194	269	215	247	316	248	323	304	195
Overall rating	NOK	NOK	NOK	OK	OK	NOK	OK	NOK	NOK	NOK



a) b)

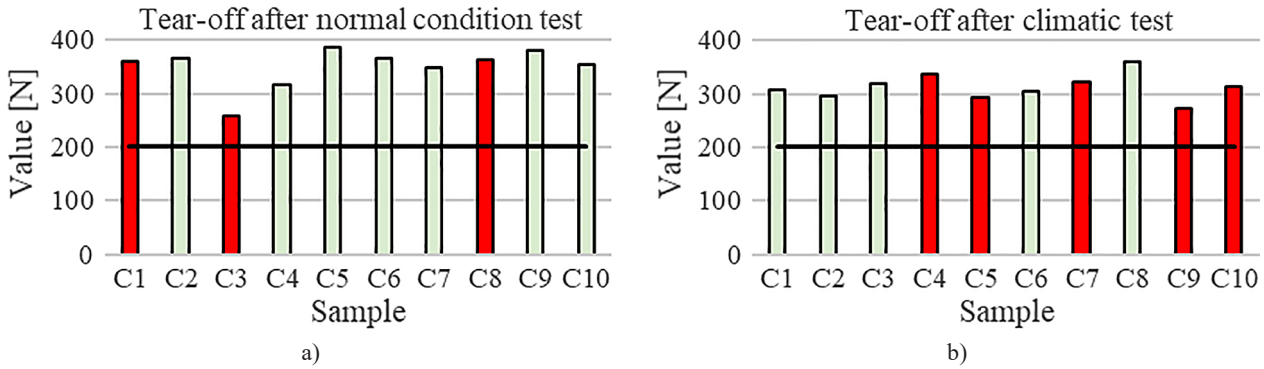
Figure 8. Graphical representation of the tear strength values performed under normal conditions and after the climatic test for the group B specimens. Samples that failed the test either because of an insufficient strength value or due to the way the connection failed are marked in red.

which it occurred. In the case of the adhesive failure, the location was recorded, whether the failure was between the adhesive (adhesion promoter) and the holder, or between the adhesive (adhesion promoter) and the glass. If the cohesion was broken, then the type of material was also recorded, i.e., if there was a cohesive failure of the adhesive, or if the holder or the glass cracked. The overall rating was based on these recorded values. For the resulting positive evaluation (marked as OK) it was necessary that there was a 100% cohesive failure of the adhesive, or that the holder or the glass cracked, and, at the same time, the force value had to be higher than the set limit of 200 N. In the opposite case, i.e., when the adhesive failure was present or when the measured value was less than 200 N, the overall evaluation of the sample was determined as unsatisfactory (marked as NOK). Below, each table (Table 4 to Table 8) is also a graphical representation of the measured values of the tear-off force (Figure 7 to Figure 11), the limit of 200 N is marked, and the columns of non-compliant samples are highlighted in red.

Based on the obtained results, the influence of the climatic test is evident, during which there was a visible deterioration in the results for all groups of samples (A-E), either from the point of view of the adhesive failure present, or just a reduced strength value compared to the standard test. Another finding is the fact that if the used glass is treated only with isopropyl alcohol (sample

Table 6. A group of samples marked with the letter C and the results of the tear test performed under normal conditions and after the climatic test.

Normal conditions test										
Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Cohesive failure (%)	20	100	50	–	100	100	100	30	100	100
Adhesive failure (%)	80	–	50	–	–	–	–	70	–	–
AF adhesive/holder	X	–	X	–	–	–	–	X	–	–
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	–	X	–	–	X	X	X	–	X	X
Cracked holder	–	–	–	–	X	X	–	–	–	–
Cracked glass	–	–	–	X	–	–	–	–	–	–
Value (N)	360	367	257	315	386	365	349	363	379	355
Overall rating	NOK	OK	NOK	OK	OK	OK	OK	NOK	OK	OK
Climatic test										
Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Cohesive failure (%)	100	100	100	90	50	–	60	100	80	80
Adhesive failure (%)	–	–	–	10	50	–	40	–	20	20
AF adhesive/holder	–	–	–	X	X	–	X	–	X	X
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	X	X	X	–	–	–	–	X	–	–
Cracked holder	–	–	–	–	–	X	–	–	–	–
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	308	295	318	336	293	304	321	360	274	312
Overall rating	OK	OK	OK	NOK	NOK	OK	NOK	OK	NOK	NOK



a) b)

Figure 9. Graphical representation of the tear strength values performed under normal conditions and after the climatic test for the group C specimens. Samples that failed the test either because of an insufficient strength value or due to the way the connection failed are marked in red.

group A), the resulting samples show a greater degree of adhesive failure just at the point between the glass and the adhesive.

Once the glass was pre-treated with plasma (specimen group B), an adhesive failure between the glass and the adhesive no longer occurred in any of the cases. However, the incidence of adhesive failure between the holder and the adhesive increased. So, it can be concluded that when using the activator on the holder and plasma on the glass, the weakest point of the connection became the surface of the holder.

When plasma was applied to both substrates to be joined, with plasma applied to the surface of the holder from a distance of 20 mm at a speed of 12 m·min^{-1} (specimen group C), the cohesive failure significantly prevailed over the adhesive failure. Compared to the samples of series A and B, an improvement was observed when tested under normal conditions, but also after the climatic test. Here, it is possible to confirm the positive effect of plasma on the surface of polyamide 6 with glass fibres. This result is in agreement with some similar investigations, where the effect of the plasma distance was investigated up to a value of 20 mm [69, 70].

A significant improvement in the results occurred in the case of a change in the process parameters of the applied plasma discharge (sample group D). When the speed was adjusted to 18 m/min and the distance was set to a lower value of 10 mm, no case of adhesive bond

Table 7. A group of samples marked with the letter D and the results of the tear test performed under normal conditions and after the climatic test.

Normal conditions test										
Sample	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10
Cohesive failure (%)	100	–	100	100	100	100	100	100	100	100
Adhesive failure (%)	–	–	–	–	–	–	–	–	–	–
AF adhesive/holder	–	–	–	–	–	–	–	–	–	–
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	X	–	X	X	X	X	X	X	X	X
Cracked holder	–	X	–	–	–	–	–	–	–	–
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	333	443	350	417	417	365	382	395	328	401
Overall rating	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK

Climatic test										
Sample	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10
Cohesive failure (%)	100	100	–	100	100	100	–	100	100	100
Adhesive failure (%)	–	–	–	–	–	–	–	–	–	–
AF adhesive/holder	–	–	–	–	–	–	–	–	–	–
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	X	X	–	X	X	X	–	X	X	X
Cracked holder	–	–	X	–	–	–	–	–	–	–
Cracked glass	–	–	–	–	–	–	X	–	–	–
Value (N)	325	354	270	370	334	371	349	389	400	427
Overall rating	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK

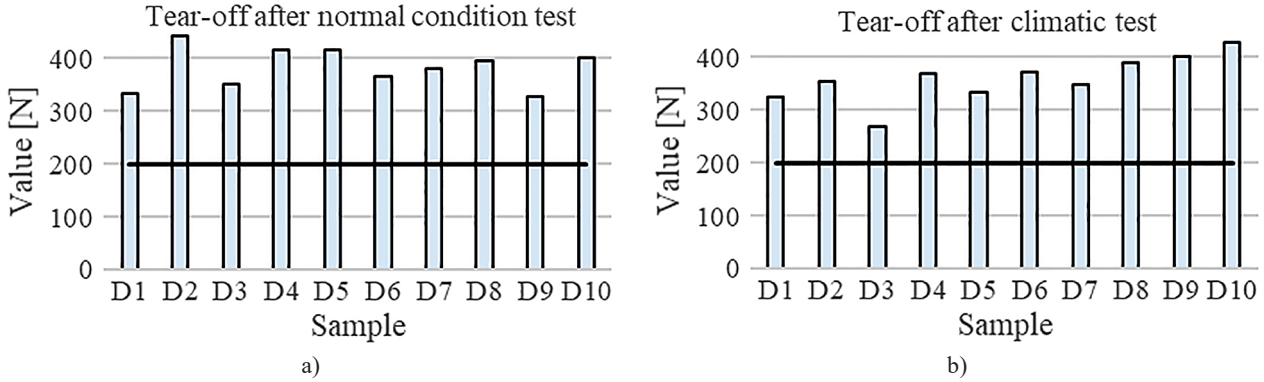


Figure 10. Graphical representation of the tear strength values performed under normal conditions and after the climatic test for the group D specimens.

failure was observed. The measured values also exceeded the specified limit, so all the samples were found to be satisfactory. Similar results were also achieved at a plasma speed acting on the surface of the holder with a value of 24 m·min^{-1} at a distance of 15 mm from the rotating nozzle to the substrate (sample group E).

In the summary graphical representation of the results (Figure 12), where the average values of the pull-off force for each group of samples under normal conditions and after climatic loading are given, the difference between the tested configurations is even more apparent. The highest average values were measured for sample groups marked with the letters D and E. This phenomenon of increasing values of the pull-off strength

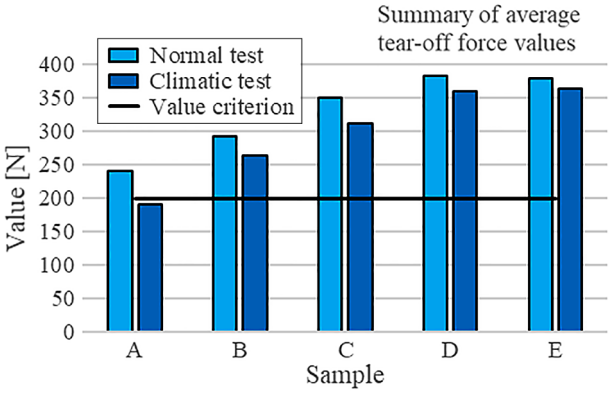


Figure 12. Summary of the average values of tear strength for the individual groups of samples marked A to E.

Table 8. A group of samples marked with the letter E and the results of the tear test performed under normal conditions and after the climatic test.

Normal conditions test										
Sample	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
Cohesive failure (%)	100	100	–	100	100	100	100	100	–	100
Adhesive failure (%)	–	–	–	–	–	–	–	–	–	–
AF adhesive/holder	–	–	–	–	–	–	–	–	–	–
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	X	X	–	X	X	X	X	X	–	X
Cracked holder	–	–	X	–	–	–	–	–	X	–
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	337	407	391	446	390	325	370	370	344	406
Overall rating	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK

Climatic test										
Sample	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
Cohesive failure (%)	100	100	100	100	100	100	–	–	100	–
Adhesive failure (%)	–	–	–	–	–	–	–	–	–	–
AF adhesive/holder	–	–	–	–	–	–	–	–	–	–
AF adhesive/glass	–	–	–	–	–	–	–	–	–	–
CF adhesive	X	X	X	X	X	X	–	–	X	–
Cracked holder	–	–	–	–	–	–	X	X	–	X
Cracked glass	–	–	–	–	–	–	–	–	–	–
Value (N)	349	331	376	377	387	412	336	409	286	373
Overall rating	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK

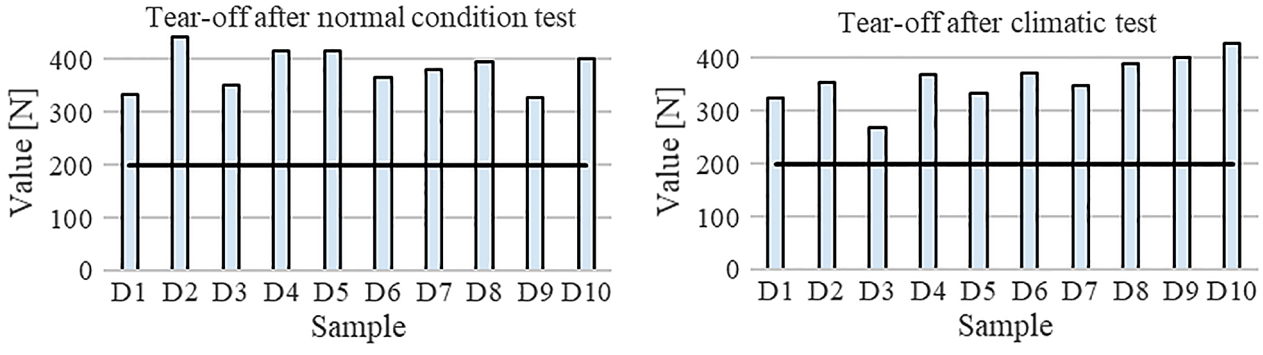


Figure 11. Graphical representation of the tear strength values performed under normal conditions and after the climatic test for the group E specimens.

and increasing the proportion of cohesive failure of the bond has also been observed by other researchers and has been described in several sources [22, 32, 76-78].

According to traceable sources, when polyamide 6 is treated with plasma, an increase in the surface area of the substrate is achieved, and hydroxyl groups are also bound to its surface, i.e., a bond is formed between the hydroxyl group and the carbon of the polymer. These functional groups can subsequently form a covalent bond with the isocyanates contained in the polyurethane [76-78]. The diagram of a possible reaction is shown in the figure (Figure 13).

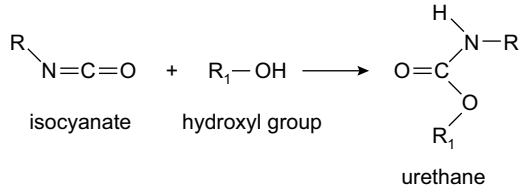


Figure 13. Schematic of a possible reaction between the functional hydroxyl group created by plasma treatment on the polyamide surface and the isocyanate group contained in the polyurethane adhesive [22].

CONCLUSIONS

During the present experiment with gluing parts made of polyamide 6 with a glass fibre content of 30 % to the surface of the glass substrate using polyurethane glue, a positive effect of the use of cold atmospheric plasma was demonstrated for both joined materials. The improvement in surface properties was demonstrated by the wettability test, with the glass improving from 36 $mN \cdot m^{-1}$ to more than 44 $mN \cdot m^{-1}$ and polyamide improving from 32 $mN \cdot m^{-1}$ to 42 $mN \cdot m^{-1}$. Similar conclusions are also confirmed in the available publications [72, 73].

In the case of glass, contamination was observed using an optical microscope, probably originating from the storage of glass in a place where a preparation for moulds called a release agent [74, 75] is used. Of the conventionally used methods, represented in this experiment by the substances, the 2 % detergent solution, heptane and isopropyl alcohol, the solvents isopropyl alcohol and heptane achieved the best results. It is important to note that the use of mechanical action on the contamination provided by the use of a paper towel in combination with these substances had a significant effect on the positive results. Plasma technologies were used in two configurations, namely plasma with a rotating nozzle and with a point nozzle. Contamination was not affected in any way by the action of the rotary nozzle, which is probably due to the fact that this type is mainly intended for the activation of plastic materials, not for cleaning. The stream of active components created by a burning plasma discharge is not as strong as in the case of a point nozzle, where the stream is more concentrated. The point nozzle was able to remove impurities from the surface perfectly, which was confirmed with the help of an optical microscope and the use of infrared spectroscopy. The analysis proved that it is contamination with polyethylene particles, which is used for the purpose of preventing the adhesion of the injected material to the surface of the mould [74, 75]. During the analysis, the point nozzle plasma cleaning site was also examined and the contamination was no longer detected, it can be stated that this plasma was effective in cleaning the glass surface.

Practical proof of the improvement in the overall adhesion properties was realised by gluing plastic parts made of polyamide 6 to the surface of the glass. Different combinations were chosen to observe the effects of different parameters (Table 1). The positive effect of the use of plasma on the surface of the plastic part and on the surface of the glass was confirmed. Thanks to this pre-treatment, an increase in the proportion of cohesive failure of the adhesive was achieved, which is a desirable phenomenon, as well as an increase in the values of the force required for tearing and breaking the bond. Both of these results were consistent with the available literature [22, 32, 76-78]. At the same time, the results from other articles were also confirmed, where a significant effect of the distance parameter of the plasma source from the treated surface was observed and confirmed [69, 70]. Overall, the best results from the point of view of tear strength and representation of cohesive failure of the adhesive were achieved for the samples that were composed of plasma-treated glass with a point nozzle and polyamide parts treated with a rotating nozzle plasma with a speed of 18 $m \cdot min^{-1}$ and a distance of 10 mm and with a combination of speed of 24 $m \cdot min^{-1}$ and a distance of 15 mm. Of these two configurations, the first mentioned case was slightly better from the point of view of tear-off force, i.e., point nozzle plasma acting from a distance of 10 mm moving at a speed of 18 $m \cdot min^{-1}$.

Overall, it can be concluded that plasma technologies have great potential and can be used as full-fledged substitutes for cleaners, while the benefit lies not only in the improvement of the adhesion properties, but also in the positive impact on the environment, work safety, treatment speed and having a favourable impact on the economic side of the process [32, 42-49].

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