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Improved glass bonding with plasma treatment

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Abstract

Bonding of automotive glass is generally performed with 1C PUR adhesive on a primed ceramic frit or naked glass surface. The aim of this research was to replace the chemistry of the primer with an atmospheric pressure plasma treatment (APPT) with compressed air for cleaning and activation directly before bonding. Characterization of the glass surface was performed with surface energy through contact angle, XPS, TOF-SIMS and adhesive peel bead test. The results show that APPT treatment can clean the surface, improve the wetting, improve the bonding but reduce the number of non bridging oxygen for the adhesive to bond to. The highest measured spot temperature of the glass during APPT was measured up to 270 °C, but the temperature was depending on process parameters. A reduction in non bridging oxygen was also seen during heating of the reference glass at 100 °C. A further reaction was seen when measured after a 550 °C heating. A modified APPT treatment with deionized water as precursor was used. The results show that the APPT with water does not lower the level of non bridging oxygen and the bonding was further improved.

Keywords: APPT, Plasma jet, Plasma treatment, Adhesive bonding, Glass bonding

Introduction

In the automotive industry float glass of soda lime glass is used for different types of automotive glass. The name float glass comes from the manufacturing process were molten glass is floated out and formed on a bath usually of molten tin. This result in a very flat and parallel glass. In this process the surrounding atmosphere is carefully controlled with a N_2/H_2 mix that prevents oxidation of the tin bath. From the process the glass sides will be exposed to different chemistry. One side will be affected from tin "tin side" and the other from the atmosphere "fire side". The difference in chemistry does also affect the chemistry of the glass surfaces that will differ from each other as well as the bulk [1–4].

On automotive glass a pigmented glass enamel "ceramic frit" is sometimes applied to the perimeter of the windshield glass. It is fused permanently to the glass surface in a high temperature process. The ceramic frit is used both for cosmetic and protective purposes where it is used to protect the adhesive against harmful UV rays responsible for degradation. The ceramic frit is nowadays typically a zinc- or bismuth-based paint rather than a lead-based paint.

The function of the windows in a modern car is different from the one when the windows solely were used for protection against wind and rain. Today, they play a multifunctional role also acting as a stability component in the vehicle. Since the glass and body in white have a difference in coefficient of thermal expansion and the windows are wide there is a need of a flexible adhesives. Therefore, glass bonding in automotive manufacturing is often performed with a 1C PUR adhesive. The adhesives are flexible moisture curing adhesives that consists of binder, plasticizer, filler, carbon black, additives and catalysts. Some contain silane as adhesion promoter and they are applied in thick triangular beads. When bonded they are compressed to a thickness of approximately 6 mm. The bonding is performed on either the ceramic frit surface or the naked tin or fire side of the glass. To improve the bonding between the glass and adhesive a primer with long open time is applied at the glass manufacturer. The glass is then transferred to the automotive manufacturer with a risk of contamination during transport and handling [5].

Adhesive bonding on glass is performed through an interaction with the non bridging oxygen (NBO) e.g. (–Si–O–H) groups present on the surface, [1, 6, 7]. But bonding with urethanes functional groups (–N=C=O) on a glass surface is a slow process that can be improved with alkoxysilanes. The silanes acts as a coupling agent and can be mixed in the primer, the adhesive or be applied otherwise. Bonding will then be performed between silane and non bridging oxygen [6].

Plasma treatment to improve bonding can be used in order to clean [2, 3], activate [1, 5] or deposit layers [8] on a surface. A variation in effect can be seen with process and process parameters [9]. The aim of this research was from the Swedish automotive industry to investigate the possibility of replacing the chemistry of the primer from a health and environmental perspective with an APPT treatment for a rapid and local treatment to ensure cleaning and activation performed directly before bonding and through that achieve an environmentally and quality ally improved process. This study differs from other with an industrial like robotized local plasma treatment with air as process gas, water as precursor and no need of primer or activator on automotive float glass during bonding with 1C moisture curing PUR adhesives.

Experimental

Materials

Transparent sodium silicate glass, manufactured in a float glass process on liquid tin and with local prints of ceramic frit was evaluated. Three different surfaces of the glasses were studied, the tin side that during the manufacturing process was in contact with the tin bath, the fire side that was exposed to the atmosphere and a ceramic frit surface printed on the fire side. Three different automotive glasses were studied in the first part of the project and the results were then verified on a demonstrator. The first two glasses were a reference glass and a similar from another batch manufactured in Europe of Belgian sand. The third glass was a similar glass but manufactured in China from local sand. In the final part a demonstrator glass was used, a European windscreen similar to the reference. The glasses were provided by Sekurit Saint Gobain (Herzogenrath, Germany). All sides of glass were initially evaluated, but the tin and ceramic side where the most difficult to bond to and are therefore the focus here.

A heating study was performed where reference glasses were heated at 100 °C or 550 °C in argon atmosphere. This was performed to determine the effect on non bridging versus bridging oxygen (NBO-BO) ratio. It was performed with TOF-SIMS and similar fragments with and without H was studied (e.g. SiO_3H/SiO_3 and Si_2O_5H/Si_2O_5) and their levels compared.

Adhesive bonding was performed with the 1C PUR moisture curing adhesive with silanes called Sikaflex 260N from SIKA Automotive (Romanshorn, Switzerland). Beads were dosed in a triangular shape and compressed to a height of 6 mm. The curing was performed in 23 °C and 50%RH for 14 days. The adhesive bonding was evaluated through a peel test where the adhesive bead was pulled in a 90° from the surface during regularly cross cutting down to the glass, see Fig. 1, commonly used in the automotive industry. The bonding strength was evaluated through measuring the failure mode where a full cohesive failure is to be preferred [5].

APPT treatment

An APPT device Dragon MAW from Tigres GmbH (Marschacht, Germany) was used for cleaning and activation. The device was a 2000 W APPT, with 4 bar, 50 l/min compressed air and placed on a robot. Two different nozzles were used a blowing free and a plasma curtain. The plasma curtain is a ceramic nozzle with a narrow and deep slot in which the plasma is led, see Fig. 2, for a wider and smoother treatment. Blowing free parameters used was 7 mm height between nozzle and surface, 4 mm distance between rows and a treatment speed of between 50 and 400 mm/s. The choice of process parameters was performed based on a tape peel test described in [1]. Parameters used for the

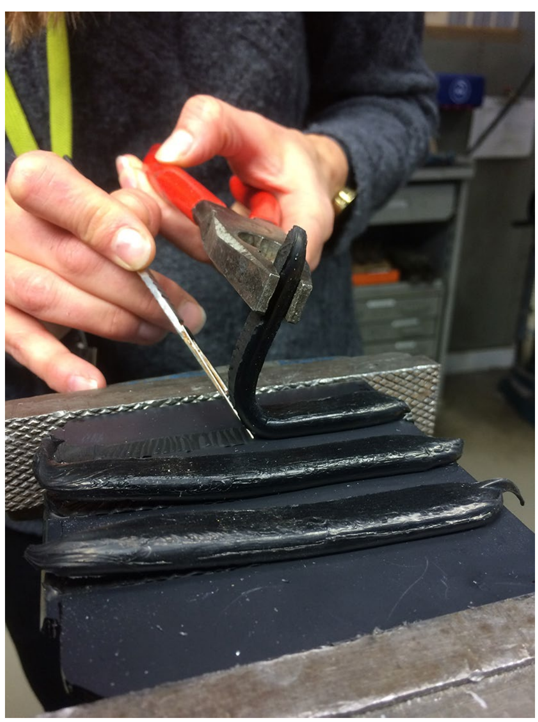

Fig. 1 Peel test during cross cutting

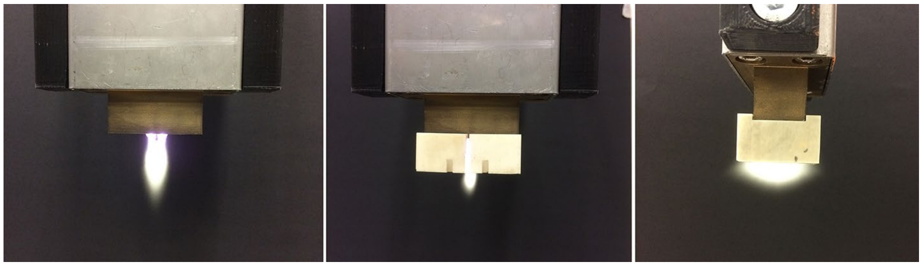

Fig. 2 Left in picture a blowing free plasma, middle and right the curtain nozzle

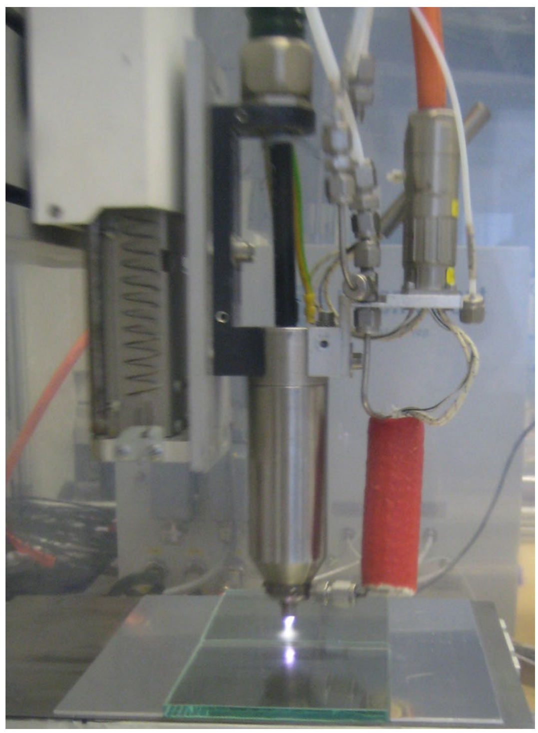

Fig. 3 Plasma treatment with water as precursor

curtain nozzle was 4 mm height between nozzle and surface, 10 mm distance between rows and a treatment speed of 10–100 mm/s.

An APPT device, Plasma Plus with FG5001 generator, from Plasma Treat GmbH (Steinhagen, Germany) was used together with precursors, see Fig. 3. Compressed air was used in a flow of 300 l/h. Deionized water was used as precursor. The height between nozzle and surface was 6 mm, the distance between rows 3 mm and the treatment speed 100 mm/s. Adhesive bonding was performed within 20 min after plasma treatment.

Contact angle measurements and surface energy determination

The contact angle was measured before and after plasma treatment to determine the effect on wettability, see Fig. 4. The contact angles were measured by a Mobile Surface

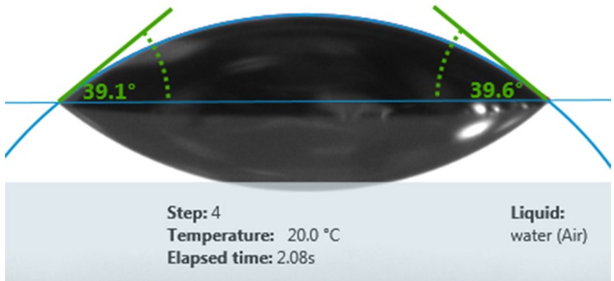

Fig. 4 Contact angle

Analyzer—MSA from Krüss (Hamburg, Germany). Two liquids were used, deionized water and diiodomethane. The droplet size was set to 1 µl and the contact angles were measured 5 s after dosing. The surface energy was calculated by the instrument with the Owens–Wendt–Rabel–Kaelble formula.

XPS chemical composition analysis

The instrument used was a Physical Electronics Quantum 2000 scanning XPS, from Physical Electronics GmbH (Ismaning, Germany) with the system control software COMPASS version 6.3 and an AlKa monochromatized X-ray source (1486.6 eV). The normal take-off angle is 45°. The pressure was $< 10^{-8}$ mbar during the analysis. A 0.4×0.4 mm area was used for the analysis.

Argon ions were used for surface cleaning (sputtering). Low energy electrons were used to neutralize electrostatic charges accumulated on the sample surface.

The surface concentrations were calculated with MultiPak version 6.1A software using a "Shirley background" subtraction routine to calculate the peak areas. The atomic concentrations were calculated using tabulated sensitivity factors for the different elemental transitions. To determine the ratio of non bridging oxygen versus bridging oxygen (NBO/BO) with XPS a chemical state composition of oxygen peak was performed through spectral deconvolution and synthetic curve fitting. OH is believed to show up in an O1s XPS spectrum at lower binding energies as part the concentration of Non–bridging oxygen (NBO) as opposed to bridging oxygen (BO), e.g. Si–O–Si or Si–O–Na

TOF-SIMS

TOF-SIMS analyses were conducted in the static regime using a TOF-SIMS IV instrument (IONTOF GmbH, Münster, Germany) with 25 keV Bi3+ primary ions and low energy electron flooding for charge compensation. Positive and negative spectra were acquired with the instrument optimized for high mass resolution (bunched mode, $m/\Delta m = 5000$), but only results for negative ions are presented here. The glass samples analyzed were 1×1 cm. Plasma treatment was performed in the morning and the analysis of the samples in the afternoon of the very same day.

Thermal heating

A Testo 881 (Testo, Lenzkirch, Germany) thermal imaging camera with a temperature resolution of under 50mK and detector type 160×120 pixels was used to measure the highest spot on the glass substrate during plasma treatment. The camera was mounted on a tripod with a fixed position and angle to the glass during the evaluation.

Results and discussion

APPT for activation without precursor

In the early phase of the study three different glass and glass sides were studied with without APPT treatment. The fire side (side in atmosphere) showed an even and high surface energy when comparing the glasses and value between 67 and 71 mN/m. The tin side (side in contact with tin bath) was in general lower and varied more between 51 and 68 mN/m and the ceramic frit side gave the lowest wetting with a surface energy of 39–51 mN/m, see Fig. 5.

The evaluation was repeated after APPT and the wetting was improved. The wetting with water was so high that the contact angle of water was not measurable, well below 10°, an effect also seen in [3]. The water droplet was flowing out over such a large area and with such a flat angle that they were not detectable with the MSA instrument.

Besides the increase in wetting the cleaning effect with APPT was studied. An elementary analysis with XPS for characterizing the outermost atomic layers on the glass surface was performed. The results, shown in atomic percentage (at %), for detected levels of C, O and Si can be seen in Table 1. Other elements (Na1s, Mg1s, Ca2p and Sn3dS) was also detected but are not presented in details. The analysis show that there is a high amount of carbon on the glasses before treatment. The untreated tin glass has 56.1 at% carbon on the surface and the untreated fire side 45.3 at%. This is likely connected organic contamination on the surface, since the carbon content was reduced to 2.2% and 2.0% with a light XPS argon sputter of the surfaces. Plasma treatment does also seem to have a cleaning effect and reduce the level of carbon in the surface to 10.6 and 9.1 at%.

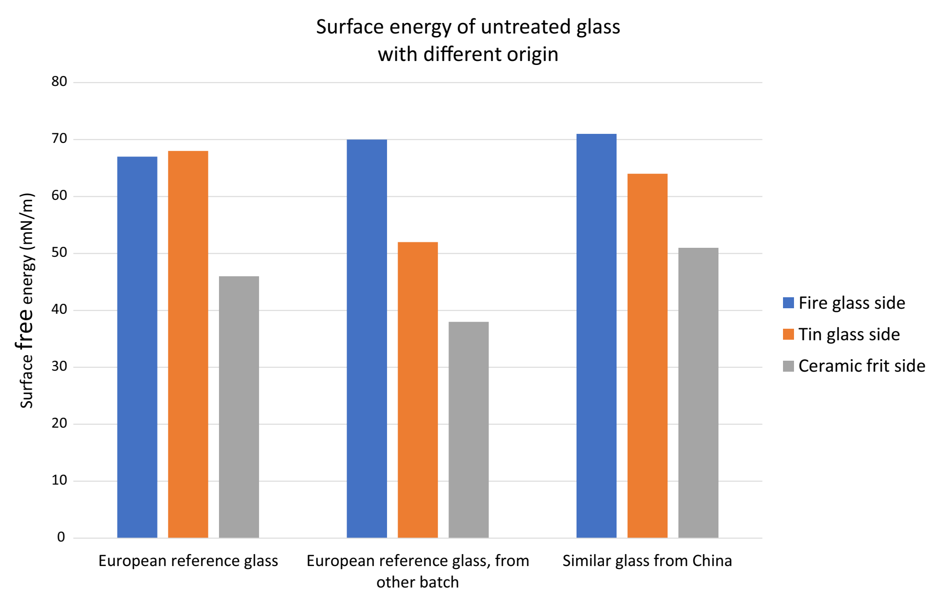

Fig. 5 Surface energy of three different glasses on the three different glass surfaces

Table 1 C, O and Si elementary composition evaluated with XPS, shown in at% of the glass

Glass side	Elementary composition on glass surfaces with different pretreatment in atomic percentage (at%) of C, O and Si		
	C1s	O1s	Si2p
Tin side, untreated surface	56.1	27.5	8.3
Tin side, untreated surface after light sputter	2.2	61.0	23.2
Tin side, plasma treated surface	10.6	55.8	18.1
Fire side, untreated surface	45.3	34.5	12.4
Fire side, untreated surface after light sputter	2.0	62.7	24.8
Fire side, plasma treated surface	9.1	59.1	20.4

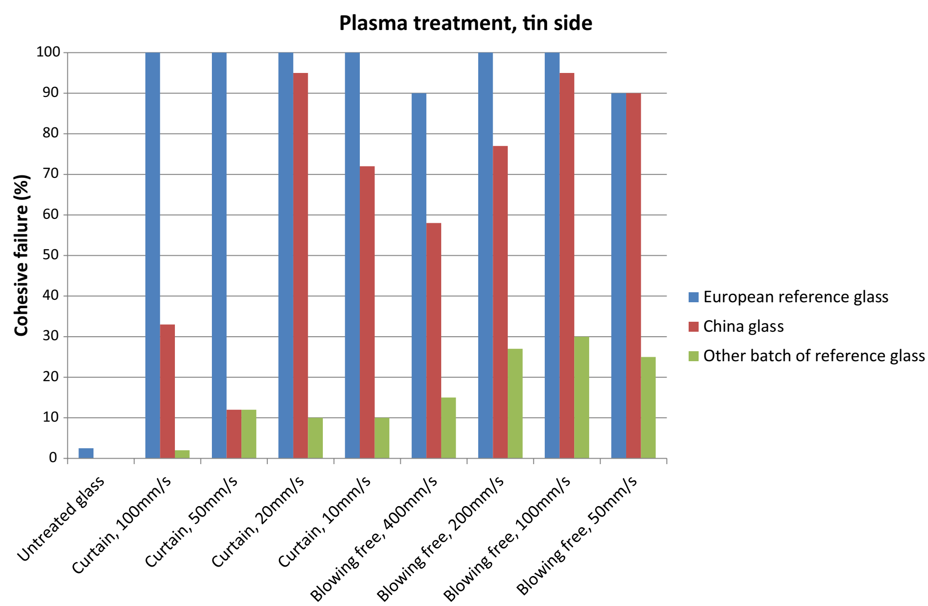

Fig. 6 Cohesive failure during evaluation of bonding

The effect of plasma treatment studied with adhesive peel test showed an improvement in cohesive failure. The bonding was performed on the tin side of three glasses and studied after different process parameters and nozzles. The reference glass showed only 2% cohesive failure before plasma treatment, but a fully cohesive failure with the curtain nozzle and two of the parameters with blowing free and a near fully cohesive failure of 90% with the other two blowing free parameters, see Fig. 6. The glass from China had no cohesive failure before plasma treatment but received up to 95% cohesive failure with one parameter each of different nozzle. The other batch did also have no cohesive failure without plasma treatment but did improve the bonding as much as the others but to an increase of 30% cohesive failure. The cause of variation between the glasses after plasma treatment is interesting to investigate further but was not possible to do within the presented work.

The improvement in wetting, cleaning and bonding was followed up by studying the level of non bridging oxygen on the glass surface. It was measured through studying the ratio of non bridging oxygen to bridging oxygen with TOF-SIMS (ratio NBO-BO). This was performed through evaluating SiO_3H/SiO_3 and Si_2O_5H/Si_2O_5, see Fig. 7. The reference surface, as is, showed a higher level of non bridging oxygen in the surface compared to the plasma treatment. This was also seen in [1, 6, 7]. Heat treatment of glass did also show a reduction in non bridging oxygen [8, 10]. This was seen when studying glass heated to 100 °C and 550 °C, where the higher temperature resulted in a stronger decrease.

The APPT process was therefore studied with a thermal camera during treatment of glass. The temperature rise in the surface was in the study affected by both treatment speed and type of nozzle, see Figs. 8 and 9. A slower treatment speed resulted in a higher measured spot temperature.

For the APPT with a blowing free nozzle did 400 mm/s on the tin side correspond to 98 °C and 50 mm/s on the fire and ceramic frit side corresponded to 193 °C.

For APPT with curtain nozzle the heating varies from 114 °C for 100 mm/s treatment on tin side to 271 °C for 10 mm/s on the tin side.

When comparing the non bridging oxygen level in Fig. 7 with the used parameter (20 mm/s curtain nozzle) a connection can be seen with the heating effect of plasma and the regular heat treatment in the span between 100 and 550 °C.

APPT for activation with water as precursor

APPT was seen to improve the adhesive bonding although the level of non bridging oxygen was reduced. In order to remain the level an APPT with deionized water as precursor was used. This part was not initially planned and was performed late in the study. It is therefore not very extensive. Like in the previously performed APPT the wetting was very good. The surface energy was not measurable with the MSA due to a wide droplet and flat contact angle with deionized water.

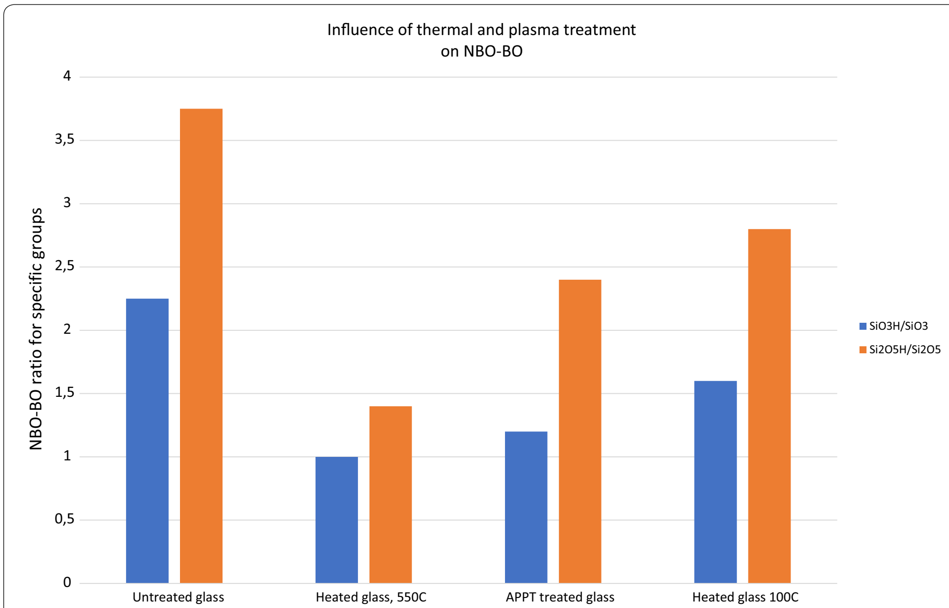

Fig. 7 Silanol contribution in the surface

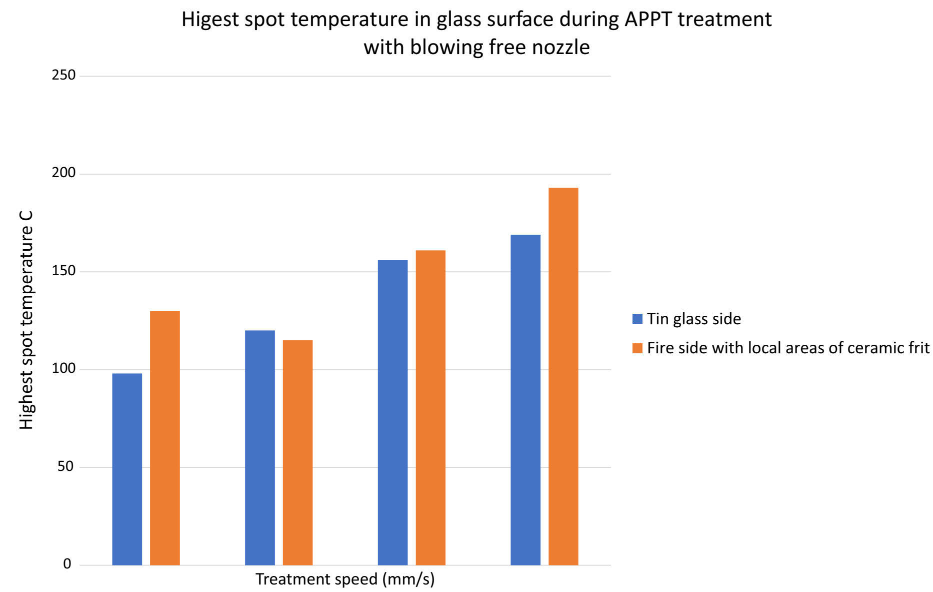

Fig. 8 Highest measured glass spot temperature during APPT blowing free

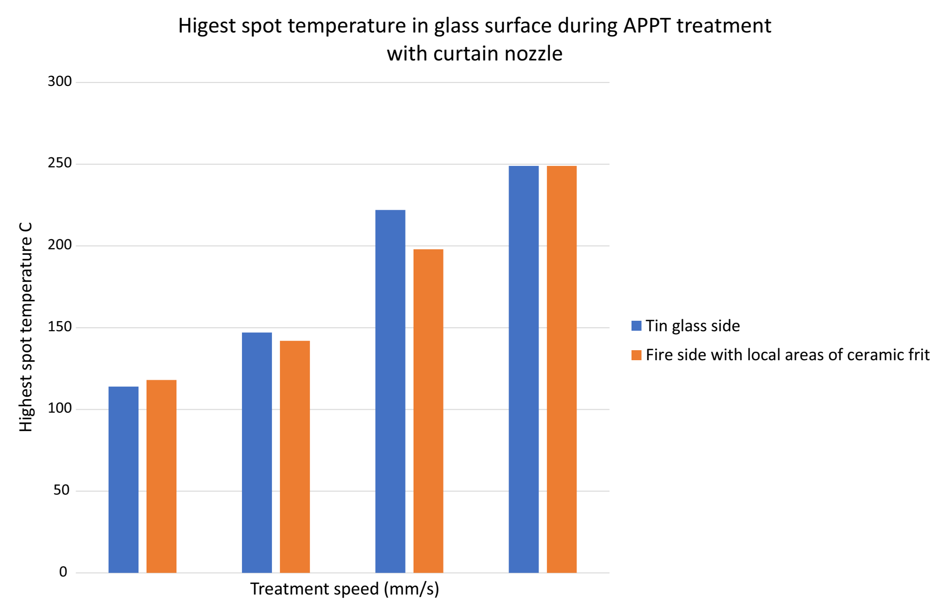

Fig. 9 Highest measured glass spot temperature during APPT with curtain nozzle

A comparison with XPS of non bridging oxygen on the windscreen demonstrator surface showed like in the first part of the study that plasma with compressed air is lowering the non bridging oxygen versus bridging oxygen (ratio NBO/BO) see Fig. 10. The APPT with deionized water as precursor did not show a reduction in non bridging oxygen but rather a slight improvement.

The improvement in non bridging oxygen level was followed up in a bonding study. On ceramic frit side the bonding was poor with a 19% cohesive failure before APPT

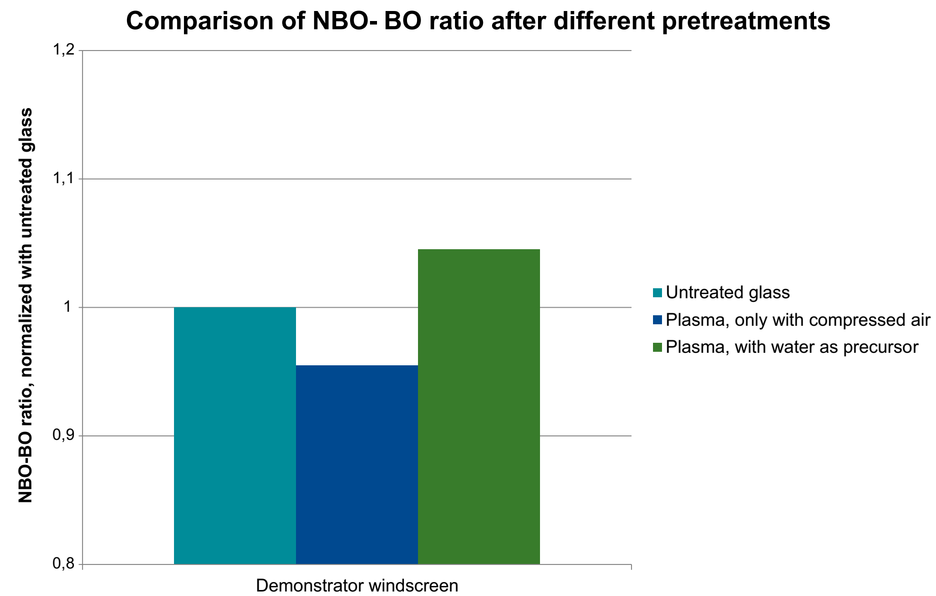

Fig. 10 Silanol content comparison with different APPT

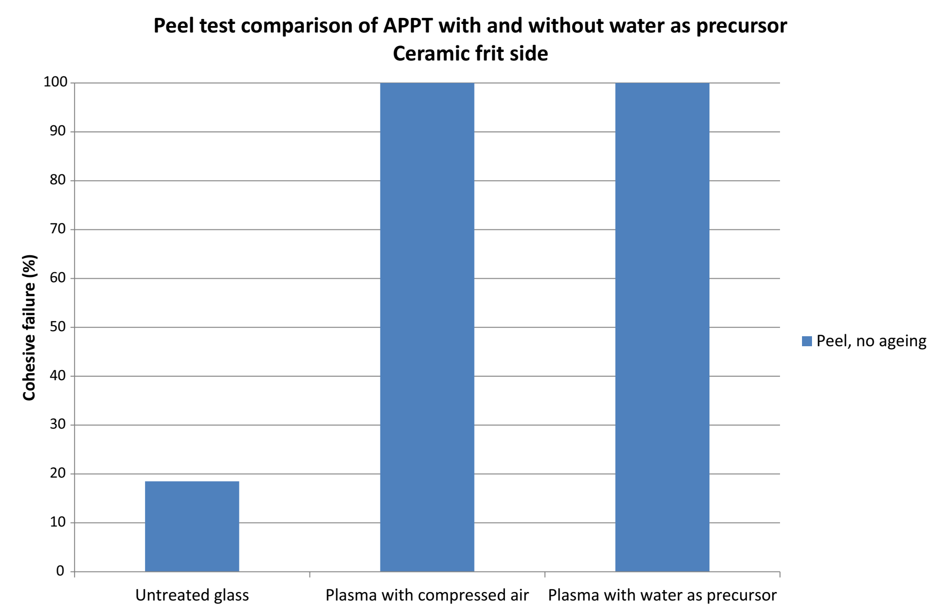

Fig. 11 Peel test after APPT with precursor on ceramic frit side

treatment, see Fig. 11. The treatment with both APPT with just air improved the bonding to a fully cohesive failure, which is the best result that can be measured. A fully cohesive failure was also seen with APPT with deionized water as precursor. The limitation in the method can therefore not determine whether the bonding strength was improved with the precursor or not, but a fully good results was seen. On the tin side the untreated glass received a 40% cohesive failure before APPT treatment.

This was not increased with the APPT treatment without precursor, see Fig. 12. The treatment with APPT with deionized water as precursor showed a 90% cohesive failure. The results from Figs. 11 and 12 does therefore show that APPT with just air can improve the bonding strength, but when just air is not enough the results can be improved even more with water as precursor in the APPT.

Conclusion

The results show that there is a chemical variation between the glass sides initially, seen with XPS and surface free energy. A contamination layer of untreated glasses was seen through a high carbon level. The contamination was reduced through argon sputtering as well as APPT treatment.

OH-groups in NBO influences the surface properties in wettability and reactivity. APPT treatment has the potential to improve both the wetting and bonding. But the level of NBO on the surface, that the silanes in the adhesive can react with, was although lowered compared with the untreated surface. This is likely connected to the heating effect of the glass surface during the APPT plasma where the level of OH after APPT almost corresponds to a heating effect of about 200 °C. The increase although found in bonding strength is likely connected to the cleaning and increase in surface free energy from APPT.

To overcome the reduction in NBO an APPT with deionized water as precursor was developed. The result showed a high level of wetting, cleaning and no reduction in NBO level and that where APPT with just air is not enough to receive a good bonding APPT with water as precursor can improve the result.

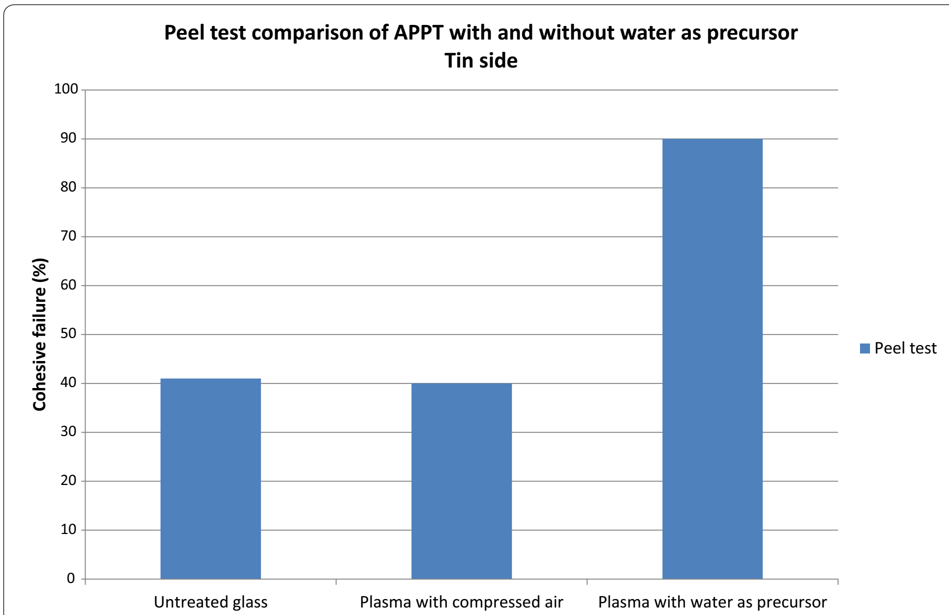

Fig. 12 Peel test after APPT with precursor on tin side

Abbreviations
1C: one component; PUR: polyurethane; APPT: atmospheric pressure plasma torch; XPS: X-ray photoelectron spectroscopy; NBO: non bridging oxygen; BO: bridging oxygen; TOF-SIMS: Time-of-Flight Secondary Ion Mass Spectrometry; MSA: Mobile Surface Analyzer; SFE: surface free energy.

Authors' contributions
ÅL (First and corresponding author) was responsible for completing the article as well as the adhesive bonding, plasma treatment and measuring of the surface energy. PS was responsible for heat treatment and TOF-SIMS analysis. LM was responsible for XPS analysis. All authors read and approved the final manuscript.

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Competing interests
The authors declare that they have no competing interests.

Availability of data and materials
All relevant data are presented in the manuscript, if needed additional information may be made available upon request.

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