DOI 10.14622/Advances_48_2022_03

Wetting and adhesion phenomena of surface-treated float glass

Sarah Patejdl, Ulrich Jung and Katharina Freieck

Bergische Universität Wuppertal, Gaußstraße 20, 42119 Wuppertal, Germany
E-mails: patejdl@uni-wuppertal.de; ujung@uni-wuppertal.de

Short abstract

Float glass is a commonly used substrate for automotive-, architecture-, decorating- and functional industries. The two-sidedness of float glass can form different adhesive forces depending on glass surface properties, like wettability. A significant example is the binding or bonding of organic UV radiation-curable fluid systems to the very smooth inorganic float glass surface which can result in insufficient adhesion. The main reason for this phenomenon is a well-known incompatibility of fluid/substrate combinations. Current research works on binding organic fluids to inorganic silica surfaces proved the reasonable use of silane-based self-assembling monolayers (SAMs), like hexamethyldisilazane (HMDS), to improve the adhesion. This work investigated the influence of cleaning methods with an alkaline solution of the float glass surface with an overall increasing wettability of air- and tin side and especially achieve a nearly equalised wettability behaviour. This hydrophilic behaviour is used to define an initial state for a following HMDS surface functionalising. The functionalisation methods lead to different hydrophobic wettability behaviours of the float glass surface, but do not lead to a strong improvement of adhesion, measured with the 90° peel test. This fact shows a significant missing link between wetting and adhesion properties of modified glass substrates.

Keywords: float glass, glass cleaning, contact angle, wetting, adhesion, peel test, HMDS, hydrophobic, hydrophilic, ultraviolet radiation curable coatings

1. Introduction and background

Combinations of mechanical, physical and chemical pre-treatments of surfaces are wildly used to modifier surfaces, e.g. polymers, metals or glass, to bind or bond coatings, inks and adhesives on surfaces or materials together to reach a defined adhesion behaviour depending on the application purpose. Theories of adhesion mechanisms are detailed described (da Silva, Öchsner and Adams, 2011). Especially the adhesive bind- and bonding of e.g. ultraviolet radiation curable coatings, inks, adhesives and metal oxide coating on float glass prefer only one side of the glass for application, but not even the same (Silvestru, et al., 2018; Saint-Gobain, 2018). The two-sidedness of float glass results from the Pilkington manufacturing process, which revolutionised the worldwide industrial production of flat glass (Pilkington, 1969; Persson, 1969) and is the predominant method for manufacturing soda-lime-silica (SLS) flat glass (Krohn, et al., 2005). By processing, the approx. 1 000 °C glass melt flows on a 232 °C molten tin bath (Haldimann, Luible and Overend, 2008) with building a smooth surface, roughness 1–2 nm (Silvestru, et al., 2018), and leads to the diffusion of tin ions up to 40 µm into the surface, with the highest tin concentration in the top of 100–200 nm (Goodman and Derby, 2011), depending on named process parameters (Tamglass Ltd Oy, 1997; Krohn, et al., 2005). This side, called the tin side, fluoresces milky white by using a tin detector ($\lambda \approx 254$ nm). The other side, called the air side, is surrounded by a protective gas atmosphere of N_2/H_2 to avoid the formation of tin oxide while the floating process (Zhang, Chen and Li, 2011; Fernández Oro, et al., 2008). In summary, the air- and tin side differ in their surface properties and wetting tests with water show after surface preparation methods in the majority still no levelling between the air- and tin sides (Lazauskas and Grigaliūnas, 2012). The influence of tin can only be removed by material removal (Neroth and Vollenschaar, 2011). Current research is concerned with self-assembling monolayer (SAM) pre-treatment of glass with organosilicon compounds as an adhesion promoter (Wang, et al., 2021), coupling agents or primer (Wypych, 2018), e.g. hexamethyldisilazane (HMDS) (Fiorillo, et al., 2017), to form a covalent network between surface and silane molecules (Herzer, Hoeppener and Schubert, 2010) to improve adhesion of inorganic- with organic materials. HMDS should give silica surfaces hydrophobic wetting properties and should serve as an adhesion promoter.

This research aims to equalise the two-sidedness of float glass with homogeneous hydrophilic wetting properties to define an initial state for HMDS-functionalisation of the float glass surface. The HMDS-functionalisation was practised in two different ways to get deviating wetting properties on float glass surfaces. Peel tests on the different modified glass surfaces, printed with UV varnishes, should allow the gaining of further insights into the adhesion behaviour of UV varnishes.

2. Materials and methods

2.1 Instruments

A contact angle measuring device (OCA 50, Dataphysics) is used to measure the static contact angle (sessile drop method) with test fluids according to DIN EN ISO 19403-7 (Deutsche Institut für Normung, 2020a) to get quantitative data about the wetting properties of the cleaned and functionalised float glass surface.

A flexo- and gravure pressure device (IGT, F1) is used for the application of UV varnishes with a 24 ml/cm^2 anilox roller in the flexographic procedure.

An adhesion tester (Kyowa, VPA-H100) is used to measure the adhesion of hardened UV varnishes on cleaned and functionalised float glass samples with the pull-off angle of 90° and defined pressure application of tape (type: 4204, width: 25 mm, tesa).

2.2 Materials

In Table 1 are all materials listed, which were used for this research work.

Table 1: Material used

Substrate	Float glass, clear, seamed edge
UV varnishes (radically hardening)	GSB-Wahl: PR9410, PR9415, PR9291 Weilburger: 360027 Hi-Tech Coatings: U8730, U888
Cleaning agents	Laboratory dishwasher cleaner (LDC), Neodisher Labo GK, Dr. Weigert Ethanol absolute 99.9 % (Chemsolute), CAS-no.: 64-17-5
Silylating agent	Hexamethyldisilazane, Carl Roth, CAS no.: 999-97-3
Contact angle (CA) test fluids	Water, Aqua Dest., Wittig Umweltchemie, CAS-no.:7732-18-5 Diiodomethane, 99 %, stab., Alfa Aesar, CAS-no.: 75-11-6 Benzyl alcohol, 99 %, Alfa Aesar, CAS-no.: 100-51-6 Glycerol, 99+ %, Alfa Aesar, CAS-no.: 56-81-5

2.3 Cleaning methods

Three cleaning methods were performed on float glass (batch of 34) and quantified by water contact angle (WCA) measurements. After cleaning, samples are stored dust-tight in sample boxes at room temperature for 24 h. In the first cleaning method (clear rinsing method = CRM) float glass is rinsed clear with distilled water in a mini-dishwashing machine (MD 37004, Medion) using programme P2 (wash: 50 °C, rinse: 65 °C, dry: 1h) to remove coarse organic/inorganic contaminants and to provide a basis for comparing the cleaning methods of their cleaning effect. The second method (room temperature method = RTM) involves cleaning the float glass in a ≈ 21.4 °C mildly alkaline cleaning bath with a concentration of 4 g/l laboratory dishwasher cleaner (LDC) in 4.3 l tap water for 1h, followed by rinsing with CRM. In the third cleaning method (enhanced method = EM), float glass is cleaned in a ≈60 °C cleaning bath with the same conditions as RTM. The product information sheet gives a pH value (20°C) of 10.8–11.9 by a concentration of 2–5 g/l LDC. For each cleaning method, 10 WCA on 10 samples (G1–G10) were measured, with the use of distilled water instead of tap water 10 WCA on 3 samples (G1–G3) on the front- and backside was measured.

2.4 Contact angle methodology

The contact angle measurement of lying drops is described in DIN EN ISO 19403-2:2020-4 (Deutsche Institut für Normung, 2020b) and recommends for evaluation of contact angles (CA) < 20° the circle fit (CF) method and >20° the ellipse fit method (EF), but not an evaluation time point for the determination of the fitting method and contact angle. The used test fluids show, because of their different disperse and polar components, a wide range of contact angles and spreading behaviours on different cleaned and functionalised float glass surfaces. To compare the contact angles, rules for evaluation of fitting method and evaluation time point of contact angle were defined as followed.

The placement of liquid drops (drop volume: 2 µl) on the cleaned and functionalised float glass surfaces was recorded by video (frame rate: 22.39 fps) and allows a defined assignment of CF- and EF-method. The data fit of the first complete and sharply contoured lying drop on the surface (t_1) is fitted with EF and decides first the final fit for evaluation. CA ≥ 20° receives the ellipse fit and CA < 20° receives the circle fit. The ellipse-fitted contact angle (CA) was evaluated after 10.0 s. (frame 224) to reach approximate a three-phase equilibrium. The circle fitted CA usually spreads so quickly, that the forwarded flat contact angle could not be detected by the Dataphysics software. Contact angle evaluation at time point 1.6 s (frame 35) after drop placement leads to stable detectable contact angles.

2.5 Surface energy methodology

The surface energy of room temperature-, enhanced cleaned and functionalised float glass surfaces were determined by using sessile drop data (Chapter 2.4) of test fluids water, diiodomethane, benzyl alcohol and glycerol (20 drops each on air- and tin side). The test fluid contact angles are abbreviated like followed:

- Water contact angle (WCA)
- Diiodomethane contact angle (DICA)
- Benzyl alcohol contact angle (BACA)
- Glycerol contact angle (GLCA)

For reference water [Ström, et al.], diiodomethane [Ström, et al.], benzyl alcohol [Rabel] and glycerol [Ström, et al.] was used and evaluated with Owens, Wendt, Rabel and Kaelble-method (OWRK). The references were chosen in accordance with DIN EN ISO 19403-7:2020-04.

2.6 Functionalisation methodology

EM-cleaned and one-week conditioned float glass are used to get hydrophobic behaviour of glass surfaces in two ways in batches of 8 float glass.

1. Hydrophobic method (HM1): Retention time of 1 h in HDMS at room temperature.
2. Hydrophobic method (HM2): Retention time of 1 h with 80 °C heated HDMS.

After functionalisation, the float glass is cleaned with a cleanroom cloth (Vipers PC 68) surrounded by a plastic squeegee with ≈3 ml ethanol with two repetitions and was stored for 1 h under vacuum in a desiccator with silica gel and is then clear rinsed (CRM). The hydrophobic wetting behaviour was determined with OCA 50 using two samples (G1, G2). On the front- and backside, 15 water-, diiodo-methane-, benzyl alcohol- and glycerol contact angles were applied and evaluated.

2.7 Peel test methodology

EM cleaned and functionalised (HM1/HM2) float glass was printed with 6 UV varnishes on air- and tin sides (five samples each) and hardened with a UV-belt dryer (Actiprint Mini/e 18-1, Technigraf, λ: 190 nm to 400 nm, speed: 3 m/min, 120 W/cm). Peel data (speed: 300 mm/min.) were evaluated with the mean value from peel length 40 to 100 mm. Approximately 15 min. elapsed between the tape application and the peel test. Measured peel forces ≤ 0.50N were counted as having no adhesion behaviour, because of delaminating and weak bounding adhesion forces.

2.8 Methodological overview

Figure 1 describes the methodological overview of practised tests on cleaned and functionalised float glass surfaces.

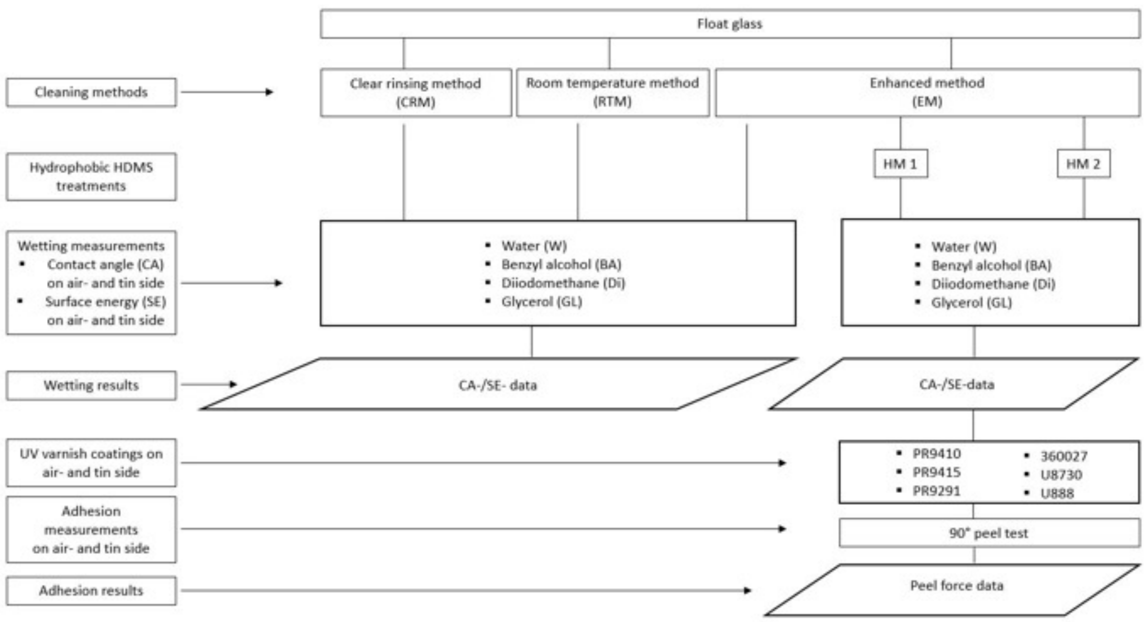


Figure 1: Methodological overview of practised tests on cleaned and functionalised float glass surfaces

3. Results and discussion

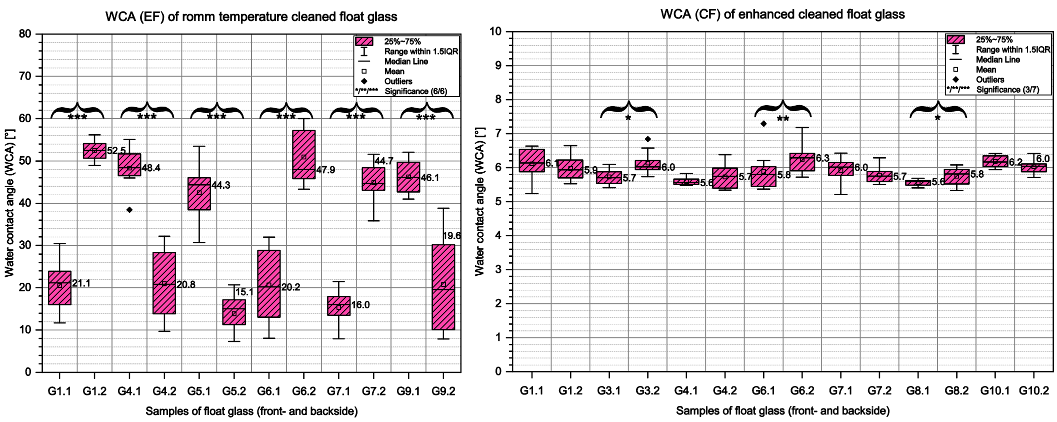
3.1 Contact angle measurements (cleaning methods)

Water contact angle results (G1–G10) of CRM-, RTM- and EM cleaned float glass were tested with software OriginPro2020 for normal distribution using Shapiro-Wilk-Test and afterwards normally distributed data pairs (air- vs. tin side contact angle of a sample) were tested on significance using the pair sample *t*-test.

Clear rinsed float glass shows 197 ellipses fitted WCA of 200 measured contact angles in a range of 12.9° to 45.4°. At time point $t_{1,}$ 9 (4.5 %) of 200 measured WCA have less than 20° and have to be circle fitted, but to compare the WCA-data they were additionally ellipse fitted with the Dataphysics software SCA 20. 3 out of 9 WCA measurements could not be ellipse fitted. Only 4 out of 8 normally distributed WCA data pairs show strong significance and did not allow reliable identification of the air- and tin side.

Room temperature cleaned float glass shows 181 ellipses fitted WCA of 200 measured contact angles in a range of 6.7° to 60.0° (Figure 2a). At time point t_1, 47 (23.5 %) of 200 measured WCA have less than 20° and have to be circle fitted. To compare the WCA data they were additionally ellipse fitted with the Dataphysics software. 19 out of 47 WCA measurements could not be ellipse fitted and reduced the number of evaluable data in measurement series G1 to G10. Contact angle series G2, G3, G8 and G10 were not evaluated, because due to too less ellipse fitted data (DF <7) and not normally distributed contact angle data. 6 out of 6 normally distributed contact angle data pairs enable clearly differentiable wetting effects from the front- to the backside of the float glass with $p \leq .001$ (Figure 2, Table 3).

Enhanced cleaned float glass shows WCA (CF) between 4.2° and 8.1° (Figure 2b); recognise the adjustment of the *y*-axis. The significance test shows by only 3 out of 7 normally distributed contact angle data pairs weak significant results (Table 4). Even if wetting differences between float glass sides are not visible, the tin detector shows still the existence of tin in the glass matrix. The enhanced method causes an equalising homogeneous interfacial layer on both sides of the float glass surface with hydrophilic wetting properties based on WCA data. The hydrophilic effect of glass storage in alkaline solution is well known (Schreithofer, Laskowski and Heiskanen, 2010) and the influence on the surface roughness of alkaline solutions, like NaOH, too (Hüppauff and Lengeler, 1994). EM cleaned float glass showed visible partial milky effects, looks like corrosion, and not like decreasing roughness in visible moderation. Additionally, the hydrophilic cleaning effect is slowly reversible and after 5 weeks verifiable with WCA.



a) b)

Figure 2: Ellipse fitted water contact angle on front- and backside of room temperature cleaned float glass (a) and enhanced cleaned float glass (b); the significance test for RTM shows clearly the reinforced two-sidedness of the float glass and the significance test for EM shows no differences between air- and tin side with homogenous hydrophilic surface properties

Subsequent investigations, by using distilled water in the cleaning procedure instead of tap water, and using a tin detector, confirm the results in tap water cleaned float glass (Table 2). In contrast to CRM, the air- and tin side of RTM cleaned float glass could be identified with the tin detector with a water contact angle range of 17.4° to 55.8° and 4.9° to 31.0°. Furthermore, the measured WCA-data shows on the "same" float glass sides different inhomogeneous CA-data. It is assumed that these different wetting effects can results in an unsaturated RTM cleaning effect or are caused by varying process parameters of the float glass manufacturing process. Organic- and inorganic contaminants were not visible on the cleaned float glass surface.

Table 2: WCA of float glass cleaning methods using distilled water

Cleaning methods		WCA Air side	WCA Tin side
CRM	min. – max. [°]	18.5 – 42.0	11.7 – 43.6
RTM	min. – max. [°]	17.4 – 55.8	6.3 – 31.0
EM	min. – max. [°]	4.0 – 6.4	– 6.9

Table 3: Significance results of room temperature cleaned (RTM) float glass

Samples RTM	*t*-statistics	Prob. > |*t*|	*p* ≤ .001	Mean	SD	SEM	Median
G1.1 DF (7) G1.2	−13.947	.000	***	20.518 52.451	6.210 2.432	2.195 0.860	21.141 52.487
G4.1 DF (7) G4.2	6.983	.000	***	48.320 20.983	4.992 8.486	1.765 3.000	48.389 20.826
G5.1 DF (8) G5.2	11.201	.000	***	42.456 13.863	6.723 4.668	2.241 1.556	44.344 15.053
G6.1 DF (8) G6.2	−12.170	.000	***	20.658 50.939	9.527 6.431	3.176 2.144	20.170 47.933
G7.1DF (8) G7.2	−15.425	.000	***	15.371 44.859	3.979 4.830	1.326 1.610	16.050 44.699
G9.1 DF (7) G9.2	5.771	.000	***	46.232 20.787	4.139 11.596	1.463 4.100	46.086 19.551

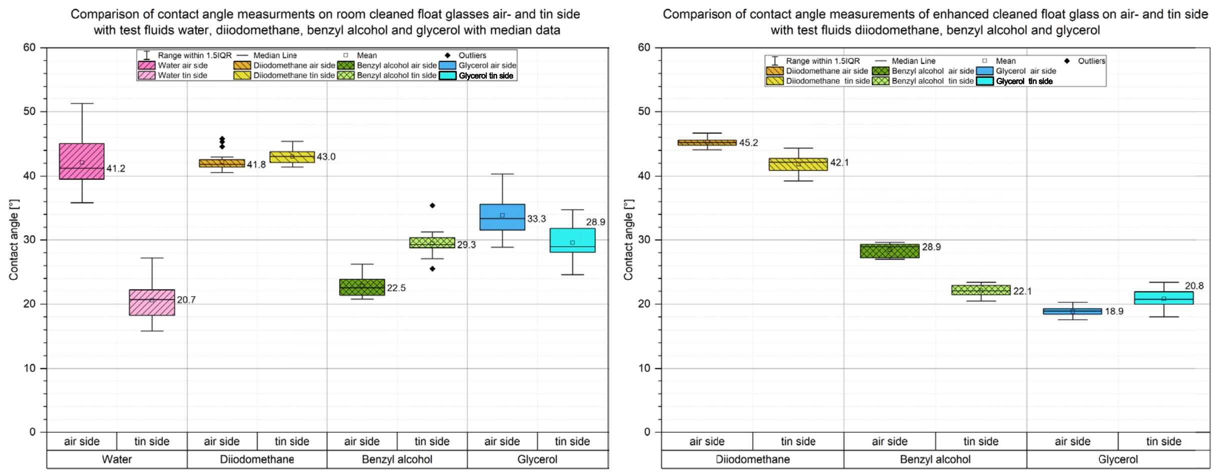
Table 4: Significance results of enhanced cleaned (EM) float glass

Samples EM, DF(9)	*t*-statistics	Prob. >|*t*|	*p* ≤ .05	*p* ≤ .01	*p* ≤ .001	Mean	SD	SEM	Median
G1.1 G1.2	0.941	.372	-	-	-	6.110 5.973	.435 .336	.138 .106	6.142 5.937
G3.1 G3.2	−2.599	.029	*	-	-	5.726 6.134	.235 .333	.074 .105	5.703 6.021
G4.1 G4.2	−0.993	.347	-	-	-	5.602 5.729	.127 .341	.040 .108	5.562 5.747
G6.1 G6.2	−3.733	.005	*	**	-	5.892 6.246	.571 .428	.180 .135	5.795 6.289
G7.1 G7.2	0.797	.446	-	-	-	6.925 5.784	.382 .241	.121 .076	6.013 5.750
G8.1 G8.2	−2.930	.017	*	-	-	5.560 5.748	.097 .260	.031 .082	5.590 5.818
G9.1 G9.2	1.761	.112	-	-	-	6.186 6.026	.174 .214	.055 .068	6.166 6.037

3.2 Surface energy measurement (cleaning methods)

Surface energy measurement of RTM- and EM cleaned float glass was carried out with test fluids water, diiodomethane, benzyl alcohol and glycerol (20 drops on each float glass side, one sample for each test fluid). The measured contact angles are shown in boxplots (Figure 3). Because of the strong spreading behaviour of water on enhanced cleaned float glass surface a WCA (EF) of 3° was assumed and used for surface energy evaluation. The wetting envelopes of air- and tin side are shown in Figures 4 to 7.

Water-, diiodomethane-, benzyl alcohol- and glycerol show clearly contact angle differences dependent on the float glass side for the room temperature- and enhanced cleaned float glass are shown in Figure 3. The contact angle range of used test fluids is listed in Table 5.



a) *b)*

Figure 3: Comparison of contact angle boxplots of test fluids water, diiodomethane, benzyl alcohol and glycerol on air- and tin side of room temperature cleaned (RTM) float glass (a) and of enhanced cleaned (EM) float glass (b); because of the hydrophilic behaviour with circle fitted contact angle water was not listed in the (b) figure, for comparison of RTM- and EM surface energies, for EM an ellipse fitted contact angle of 3.0° was assumed

Table 5: Contact angle range of RTM- and EM cleaned float glass with test fluids water, diiodomethane, benzyl alcohol and glycerol

Cleaning methods	Water		Diiodomethane		Benzyl alcohol		Glycerol	
	air	tin	air	tin	air	tin	air	tin
RTM min. – max. [°]	35.8 – 51.3	15.8 – 27.2	40.5 – 43.0	41.4 – 45.4	20.8 – 26.2	27.1 – 31.3	28.9 – 40.3	24.6 – 34.7
EM min. – max. [°]	3.0 – 3.0	3.0 – 3.0	44.1 – 46.7	39.3 – 44.4	27.0 – 29.6	20.5 – 23.4	17.6 – 20.3	18.0 – 23.4

The evaluated contact angles of the EM cleaned float glass sides show interestingly the opposite tendencies in comparison to the contact angles of the RTM cleaned float glass and describe clearly the different surface properties caused by cleaning methods, which differences results of the cleaning bath temperature. Furthermore, the WCA of EM cleaned float glass sides show a hydrophilic spreading behaviour with no detectable differences, but the test fluids diiodomethane, benzyl alcohol and glycerol show still the two-sidedness, which shows still the presence of surface wetting differences, resulting from the tin diffusion.

RTM cleaned float glass shows on the air side surface energy of 53.6 mN/m with the dispersive component of 27.7 mN/m and the polar component of 26.0 mN/m without outliers (Figure 4). The tin side shows higher surface energy of 61.7 mN/m with the dispersive component of 25.07 mN/m and the polar component of 36.6 mN/m without outliers (Figure 5). The wetting envelopes show additionally clearly the two-sidedness of room temperature cleaned float glass.

Surface energy measurement of EM cleaned float glass leads on the air side to surface energy of 51.8 mN/m with the dispersive component of 30.4 mN/m and the polar component of 21.5 mN/m (Figure 6). The tin side shows a little bit higher surface energy of 52.1 mN/m with the dispersive component of 32.3 mN/m and the polar component of 19.8 mN/m (Figure 7).

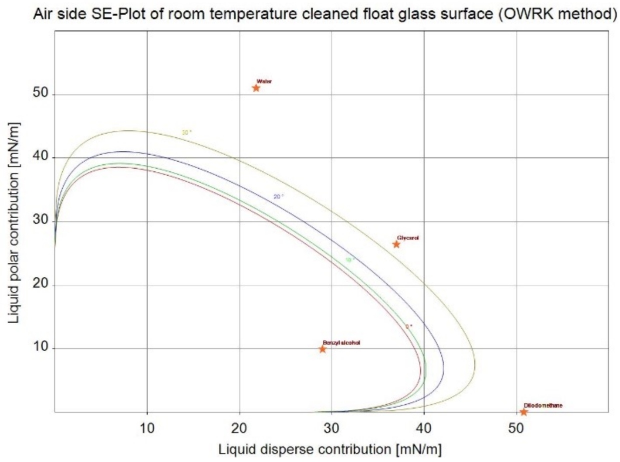


Figure 4: Wetting envelope, consisting of sessile drop measurement of test fluids water, diiodo-methane, benzyl alcohol and glycerol, on air side of RTM cleaned float glass; surface energy: 53.6 mN/m, disperse: 27.7 mN/m, polar: 26.0 mN/m, RQ: 0.8778, sChi: 11.71

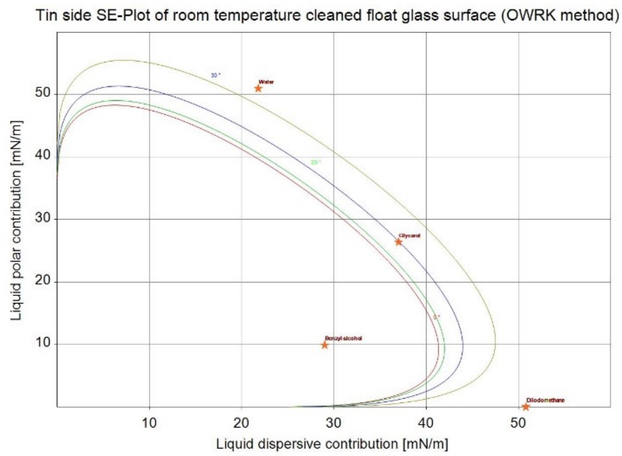


Figure 5: Wetting envelope, consisting of sessile drop measurement of test fluids water, diiodo-methane, benzyl alcohol and glycerol, on tin side of RTM cleaned float glass; surface energy: 61.7 mN/m, disperse: 25.1 mN/m, polar: 36.6 mN/m, RQ: 0.8623, sChi: 15.61

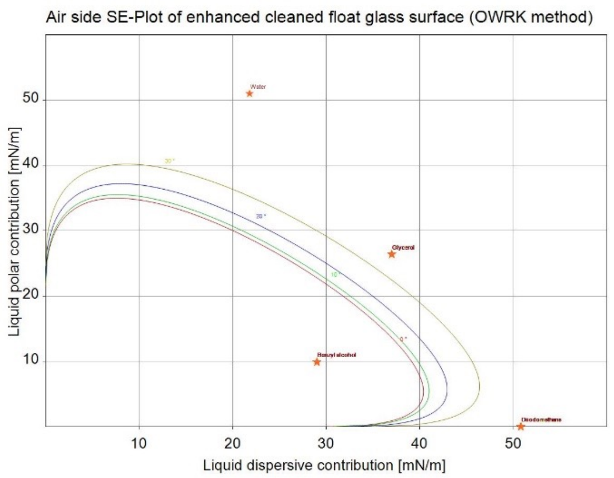


Figure 6: Wetting envelope, consisting of sessile drop measurement of test fluids water, diiodo-methane, benzyl alcohol and glycerol, on air side of EM cleaned float glass; surface energy: 51.8 mN/m, disperse: 30.4 mN/m, polar: 21.5 mN/m, RQ: 0.8478, sChi: 12.52

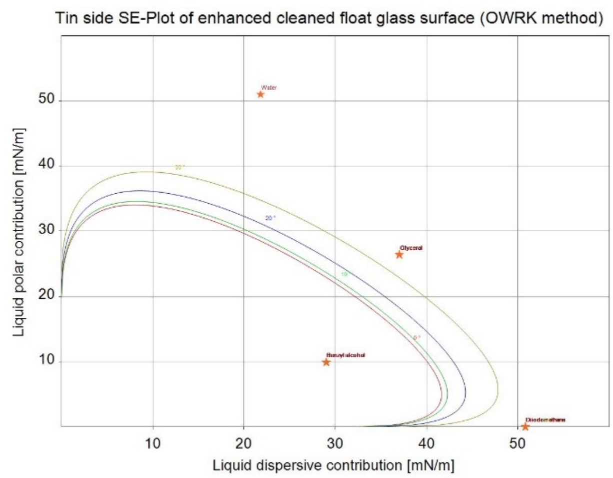


Figure 7: Wetting envelope, consisting of sessile drop measurement of test fluids water, diiodo-methane, benzyl alcohol and glycerol, on tin side of EM cleaned float glass; surface energy: 52.1 mN/m, disperse: 32.3 mN/m, polar: 19.8 mN/m, RQ: 0.8519, sChi: 11.62

3.3 Adhesion of hydrophilic surface (EM)

Following, peel forces on EM cleaned hydrophilic surfaces, air- and tin side, printed with UV varnishes (Table 1), were measured. Each combination, air- and tin side with UV varnishes, will be counted as one measurement series. In summary, 12 measurement series (❶…⓬) with 5 peel tests for each combination were analyzed (Table 6).

Table 6: Overview of peel forces from UV varnishes on enhanced cleaned float glass

Measurement series and their peel forces				
UV varnish	Measurement series	Air side peel force measurements	Measurement series	Tin side peel force measurements
PR9410	❶	0.50, -, -, -, -	❷	0.16, 0.12, 0.11, 0.08, -
PR9415	❸	3.22, -, -, -, -	❹	3.52, 3.96, 3.87, 4.01, -
PR9291	❺	0.01, 0.01, 6.85, 6.70, -	❻	4.06, -, -, -, -
360027	❼	3.60, 3.52, 3.53, -, -	❽	3.35, 3.48, 3.49, 3.49, 3.47
U8730	❾	4.96, 5.62, 5.39, 5.40, -	❿	4.57, 5.05, 0.50, 5.30, -
U888	⓫	5.38, 5.42, 5.97, 5.77, -	⓬	5.33, 5.23, 5.49, -

25 peel force measurements, red marked, out of 60, on hydrophilic surface show peel forces ≤ 0.50 N. Without peel forces ≤ 0.50 N, 5 out of 12 measurement series (❶, ❷, ❸, ❺, ❻) have less than 3/5 evaluable peel trials (grey-filled cells). The reached adhesion forces with ≥ 3/5 peel trials, blue marked, are between 3.35 N and 5.97 N (Table 7, Figure 8 to 13).

The evaluated mean value of min. and max. reached peel forces of each measurement series could be an indication of peel force differences between the air- and tin side (Table 7). A deviation of ± 0.3 N is set as the basis for assessing the adhesion force differences of the glass sides. Differences between the glass sides can be recognised by 4 out of 6 UV varnishes (blue-filled cells, Table 7).

In summary, the hydrophilic behaviour of the surface seems to be not only sufficient for the formation of adhesion of UV varnishes. Differences between air- and tin side of adhesion behaviour need more evaluable peel trials, but actually performed peel tests indicate first an influence of air- and tin side on the adhesion behaviour of UV varnishes.

Table 7: Peel forces and their trials on hardened UV varnishes on EM cleaned float glass surface

Cleaning method	UV varnish	PR9410		PR9415		PR9291		360027		U8730		U888	
		air	tin	air	tin	air	tin	air	tin	air	tin	air	tin
EM	min. [N]	-	-	3.22	3.52	6.70	4.06	3.52	3.35	4.96	4.57	5.38	5.23
	max. [N]	-	-	3.22	4.01	6.85	4.06	3.60	3.49	5.62	5.30	5.97	5.49
x̄ [min./max.]	[N]	0.00	0.00	3.22	3.77	6.78	4.06	3.56	3.42	5.29	4.94	5.68	5.36

Legend of peel trials	0/5	1/5	2/5	3/5	4/5	5/5

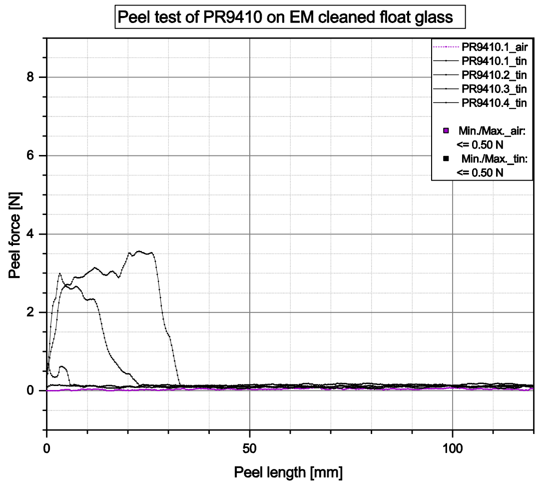


Figure 8: Peel test of PR9410 on EM cleaned float glass

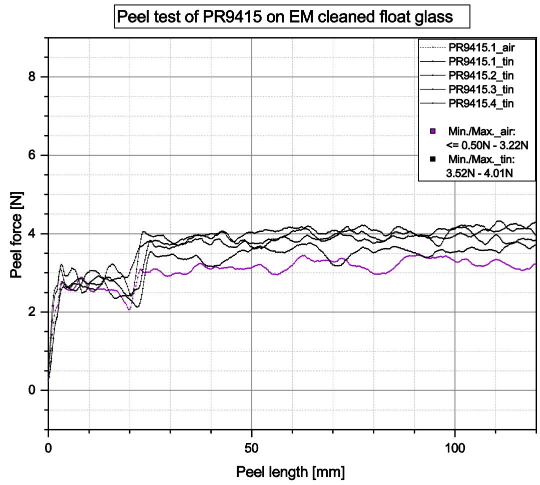


Figure 9: Peel test of PR9415 on EM cleaned float glass

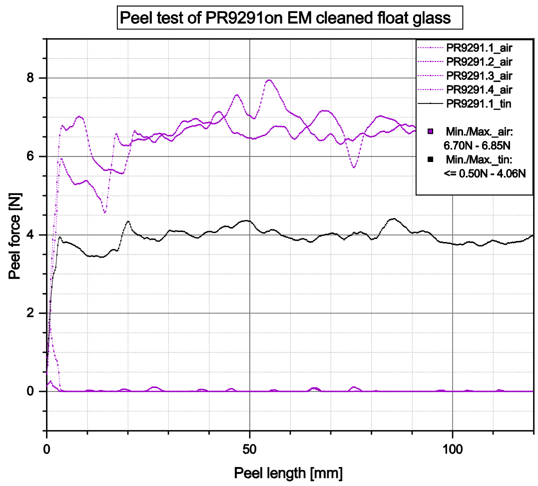


Figure 10: Peel test of PR9291 on EM cleaned float glass

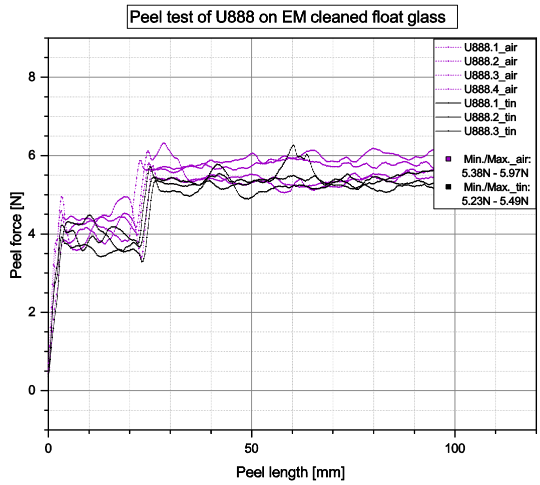


Figure 11: Peel test of 360027 on EM cleaned float glass

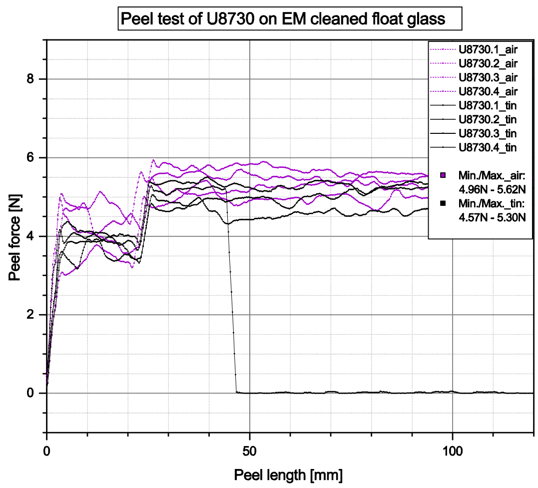


Figure 12: Peel test of U8730 on EM cleaned float glass

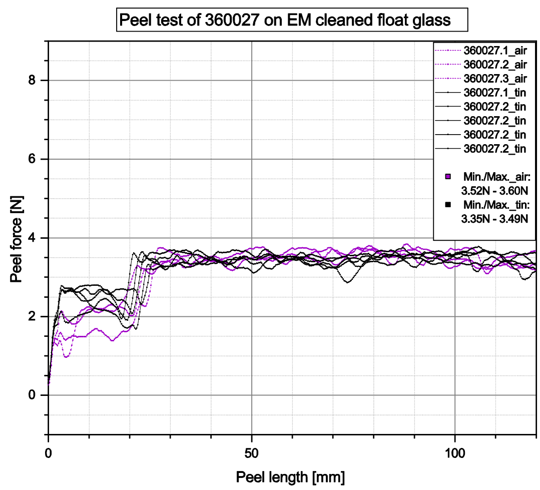


Figure 13: Peel test of U888 on EM cleaned float glass

3.3 Contact angle measurements on hydrophobic surfaces (HM1)

HM1 functionalising leads to a significant deviation of wetting behaviour in contrast to EM cleaned float glass, tested on samples G1 and G2. Figure 14 shows an example of the measured contact angles of sample G1 with test fluids water-, diiodomethane-, benzyl alcohol- and glycerol and their median data. The contact angle range of G1/G2 and their deviation are shown in Table 10 and the significances of functionalised samples in Table 8.

Benzyl alcohol and glycerol indicate a strong significant difference between the air- and tin side. Water and diiodomethane show no to only weak significance.

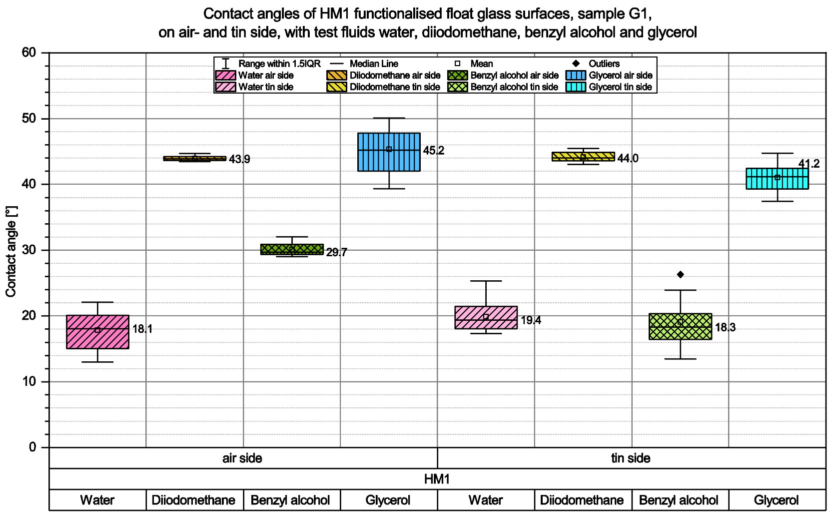


Figure 14: Comparison of contact angle boxplots of test fluids water, diiodomethane, benzyl alcohol and glycerol on air- and tin side of HM1 functionalised float glass (Sample G1)

Table 8: Significance results of WCA, DICA, BACA and GLCA of HM1 functionalised float glass

Samples G1, HM1, (DF 14)	*t*-statistics	Prob. > |*t*|	$p \leq .05$	$p \leq .01$	$p \leq .001$	Mean	SD	SEM	Median
HM1_WCA	−2.521	.024	*	-	-	17.871 19.871	2.848 2.275	.735 .587	18.070 19.375
HM1_DICA	−.719	.484	-	-	-	43.949 44.129	.350 .762	.090 .197	43.862 44.009
HM1_BACA	11.062	.000	*	**	***	30.101 19.094	.903 3.471	.233 .896	29.727 18.307
HM1_GLCA	4.012	.001	*	**	***	45.335 41.060	3.290 1.929	.850 .498	45.210 41.186

3.4 Contact angle measurements on hydrophobic surfaces (HM2)

HM2 functionalising leads to significant deviation of wetting behaviour, exemplarily of sample G1 with water-, diiodomethane-, benzyl alcohol- and glycerol-CA and median data (Figure 16), in contrast to HM1 (Figure 15). The contact angle range of G1/G2 and their deviation are shown in Table 10 and the significance of functionalised samples in Table 9.

Water and diiodomethane indicate a strong significant difference between the air- and tin side. Benzyl alcohol and glycerol show no to only weak significance.

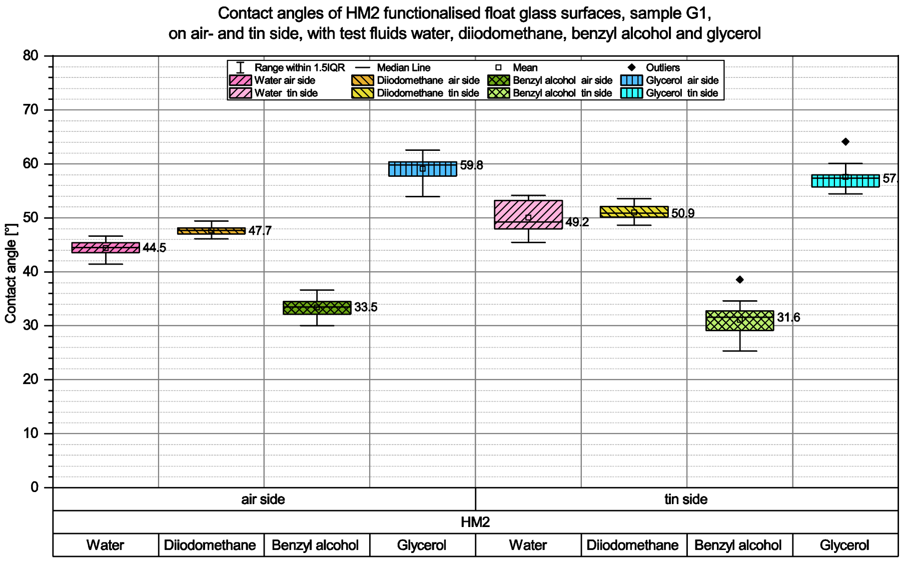


Figure 15: Comparison of contact angle boxplots of test fluids water, diiodomethane, benzyl alcohol and glycerol on air- and tin side of HM2 functionalised float glass (Sample G1)

Table 9: Significance results of WCA, DICA, BACA and GLCA of HM2 functionalised float glass

Samples G1, HM2, (DF 14)	*t*-statistics	Prob. > |*t*|	$p \leq .05$	$p \leq .01$	$p \leq .001$	Mean	SD	SEM	Median
HM2_WCA	−6.141	.000	*	**	***	44.373 50.036	1.338 2.799	.345 .723	44.488 49.240
HM2_DICA	−8.488	.000	*	**	***	47.667 50.969	.862 1.345	.223 .347	47.663 50.872
HM2_BACA	2.447	.028	*	-	-	33.376 31.089	1.860 3.303	.480 .853	33.507 31.609
HM2_GLCA	1.619	.128	-	-	-	59.105 57.573	2.381 2.429	.615 .627	59.819 57.341

Table 10: Contact angle range of samples G1/G2 of WCA, DICA, BACA and GLCA with functionalisation HM1/HM2 and mean values with deviation without outliers

Sample G1/G2	HM1		HM2	
	air side	tin side	air side	tin side
	min. – max.	min. – max.	min. – max.	min. – max.
Test fluids	[°]	[°]	[°]	[°]
Water	13.0 – 24.5	17.3 – 28.6	41.4 – 55.0	45.4 – 55.5
Deviation	18.8 ± 5.8	23.0 ± 5.7	48.2 ± 6.8	50.5 ± 5.1
Diiodomethane	43.3 – 45.5	42.5 – 45.5	45.7 – 49.5	47.2 – 53.5
Deviation	44.4 ± 1.1	44.0 ± 1.5	47.6 ± 1.9	50.4 ± 3.2
Benzyl alcohol	25.6 – 32.8	13.5 – 23.9	30.0 – 36.6	21.4 – 35.6
Deviation	29.2 ± 3.6	18.7 ± 5.2	33.3 ± 3.3	28.5 ± 7.1
Glycerol	32.4 – 50.1	31.1 – 44.7	49.0 – 62.6	50.5 – 65.5
Deviation	41.3 ± 8.9	37.9 ± 6.8	55.8 ± 6.8	58.0 ± 7.5

3.5 Surface energy measurement (functionalisation methods)

Surface energy measurements of HM1- and HM2 functionalised float glass surfaces were carried out with test fluids water, diiodomethane, benzyl alcohol and glycerol (20 drops on each float glass side, one sample for each test fluid). The wetting envelopes of air- and tin side are shown in Figures 16 to 19.

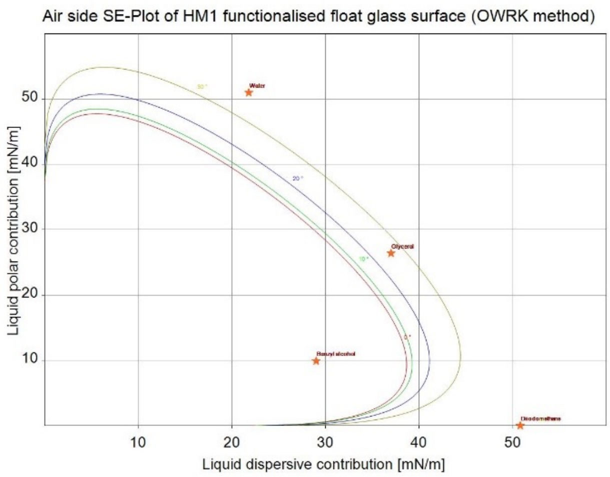


Figure 16: Wetting envelope of sample G1, consisting of sessile drop measurements of test fluids water, diiodomethane, benzyl alcohol and glycerol, on air side of HM1 cleaned float glass; surface energy: 59.6 mN/m, disperse: 22.3 mN/m, polar: 37.3 mN/m, RQ: 0.8056, sChi: 16.53

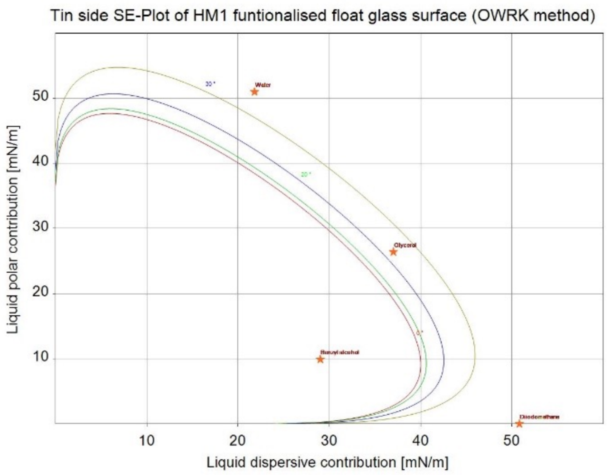


Figure 17: Wetting envelope of sample G1, consisting of sessile drop measurements of test fluids water, diiodomethane, benzyl alcohol and glycerol, on tin side of HM1 cleaned float glass; surface energy: 60.5 mN/m, disperse: 24.2 mN/m, polar: 36.3 mN/m, RQ: 0.8440, sChi: 14.50

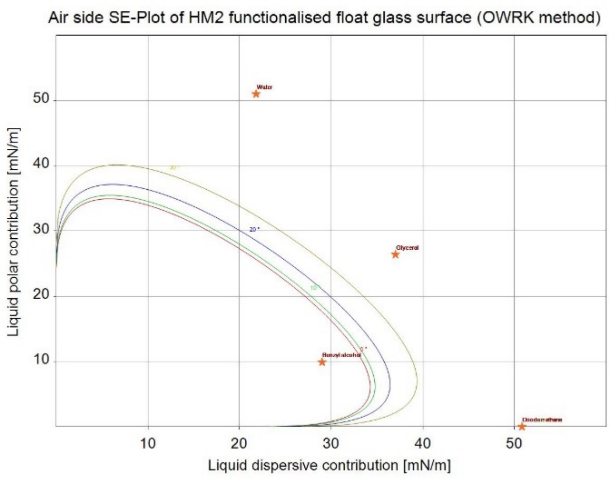


Figure 18: Wetting envelope of sample G1, consisting of sessile drop measurements of test fluids water, diiodomethane, benzyl alcohol and glycerol, on air side of HM2 cleaned float glass; surface energy: 47.5 mN/m, disperse: 23.2 mN/m, polar: 24.3 mN/m, RQ: 0.7524, sChi: 13.15

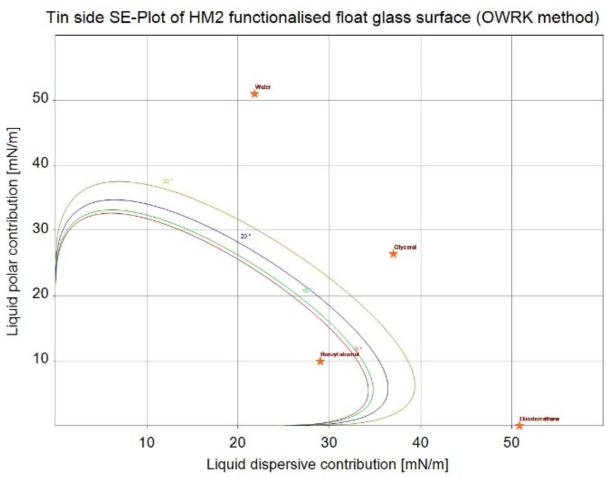


Figure 19: Wetting envelope of sample G1, consisting of sessile drop measurements of test fluids water, diiodomethane, benzyl alcohol and glycerol, on tin side of HM2 cleaned float glass; surface energy: 45.9 mN/m, disperse: 24.3 mN/m, polar: 21.6 mN/m, RQ: 0.8212, sChi: 10.54

HM1 functionalised float glass surface show on the air side surface energy of 59.6 mN/m with the dispersive component of 22.3 mN/m and the polar component of 27.3 mN/m without outliers (Figure 16). The tin side shows similar surface energy of 60.5 mN/m with the dispersive component of 24.2 mN/m and the polar component of 36.3 mN/m without outliers (Figure 17).

Surface energy measurement of HM2 functionalised float glass lead on the air side to surface energy of 47.5 mN/m with the dispersive component of 23.2 mN/m and the polar component of 24.3 mN/m (Figure 18). The tin side shows similar surface energy of 45.9 mN/m with the dispersive component of 24.3 mN/m and the polar component of 21.6 mN/m (Figure 19). The wetting envelopes and evaluated surface energies show not clearly the two-sidedness of HM1- and HM2 functionalised float glass, but the increasing hydrophobic wetting effect can be seen in smaller wetting envelopes of HM2 in comparison to HM1.

3.6 Adhesion on hydrophobic surfaces (HM1)

Following, peel forces on HM1 functionalised hydrophobic surfaces (air- and tin side) printed with UV varnishes were measured (Table 11). Each combination, air- and tin side with UV varnishes, will be counted as one measurement series. In summary, 12 measurement series with 5 peel tests for each combination were analyzed.

Table 11: Overview of peel forces from UV varnishes on HM1 functionalised float glass

Measurement series and their peel forces				
UV varnish	Measurement series	Air side peel force measurements	Measurement series	Tin side peel force measurements
PR9410	❶	4.89, 4.79, 3.85, 4.31, 3.66	❷	3.86, 4.27, 4.43, 4.36, -
PR9415	❸	3.69, 3.76, 3.72, 4.13, 3.90	❹	3.41, 3.53, 3.86, 3.68, 3.68
PR9291	❺	6.63, 6.79, 7.36, 6.92, 6.55	❻	6.76, 6.58, 6.96, 0.12, 0.12
360027	❼	3.90, 2.57, 2.79, -, -	❽	0.06, 1.74, 0.08, 2.26, 2.52
U8730	❾	4.57, 4.79, 5.31, 5.31, -	❿	4.92, 4.69, 5.33, 5.16, -
U888	⓫	5.68, 5.64, -, -, -,	⓬	4.58, 4.71, 5.02, -, -

14 peel force measurements, red marked, out of 60, on HM1 functionalised surface show peel forces ≤ 0.50 N (❻, ❼, ❽, ❾, ❿, ⓫, ⓬). Without peel forces ≤ 0.50 N, 1 (⓫) out of 12 measurement series have less than 3/5 evaluable peel trials (grey-filled cell) with clear adhesion results and forces between 1.74 N and 7.36 N (blue marked).

Peel force tendencies show the changing of peel force from EM cleaned- to HM1 functionalised float glass surfaces printed with UV varnishes (Table 12). UV varnish PR9410, PR9415 and PR9291 show strong increasing adhesion forces in comparison to EM cleaned float glass surface. The other UV varnishes show similar to decreasing adhesion forces. UV varnish 360027 and U888 tend to show differences between air- and tin side (blue-filled cells).

Table 12: Peel forces and their trials on hardened UV varnishes on HM1 functionalised float glass

Method	UV varnish	PR9410		PR9415		PR9291		360027		U8730		U888	
		air	tin	air	tin	air	tin	air	tin	air	tin	air	tin
HM1	min. [N]	3.66	3.86	3.69	3.41	6.63	6.58	2.57	1.74	4.57	4.69	5.64	4.58
	max. [N]	4.89	4.43	4.13	3.86	7.36	6.96	3.90	2.52	5.31	5.33	5.68	5.02
x̄ [min./max.]	[N]	4.28	4.15	3.91	3.64	7.00	6.77	3.24	2.13	4.94	5.01	5.66	4.80
Peel force tendency: EM to HM1		⇧	⇧	⇧	▬	⇧	⇧	⇩	⇩	⇩	▬	▬	⇩

Legend of peel trials and peel force tendencies	0/5	1/5	2/5	3/5	4/5	5/5
	⇧		Increasing peel force			
	⇩		Decreasing peel force			
	▬		Similar peel force			

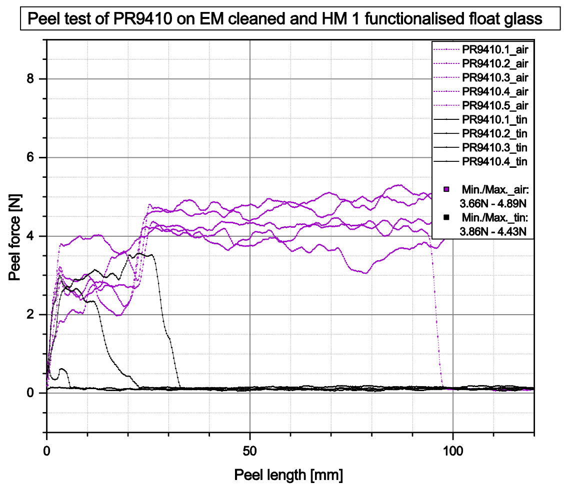


Figure 20: Peel test of PR9410 on EM cleaned and HM1 functionalised float glass

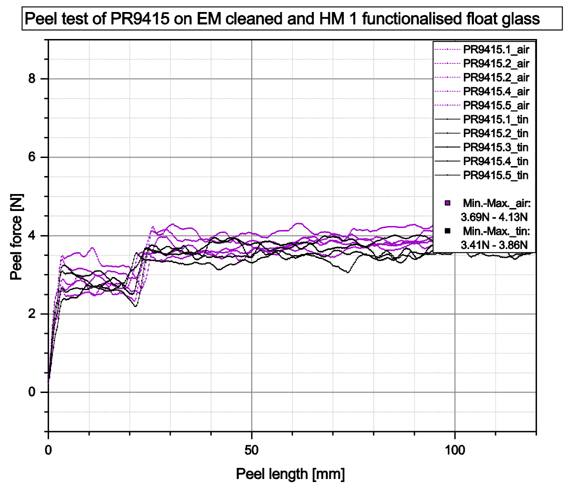


Figure 21: Peel test of PR9415 on EM cleaned and HM1 functionalised float glass float glass printed with PR9415

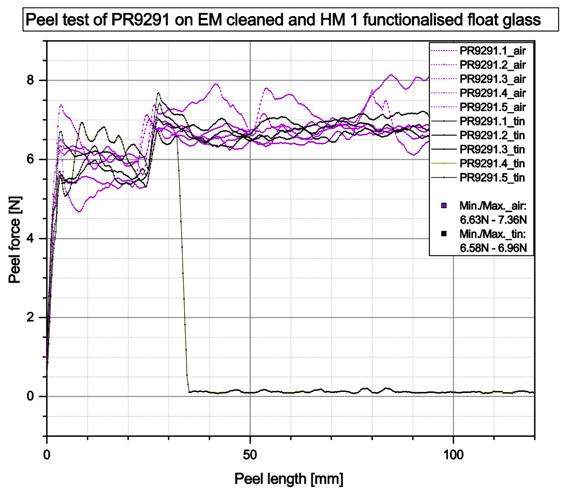


Figure 22: Peel test of PR9291 on EM cleaned and HM1 functionalised float glass

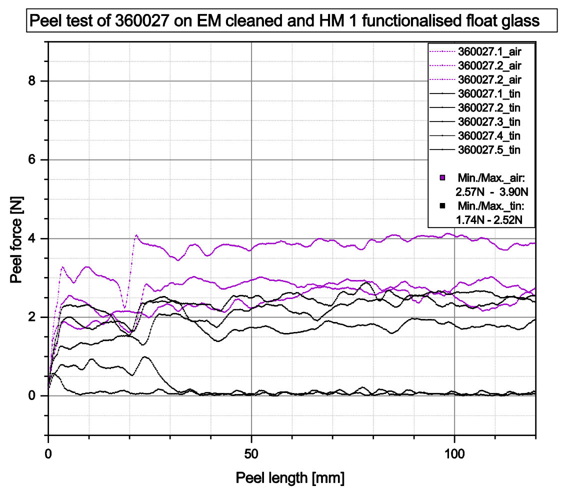


Figure 23: Peel test of 360027 on EM cleaned and HM1 functionalised float glass float glass printed with PR9415

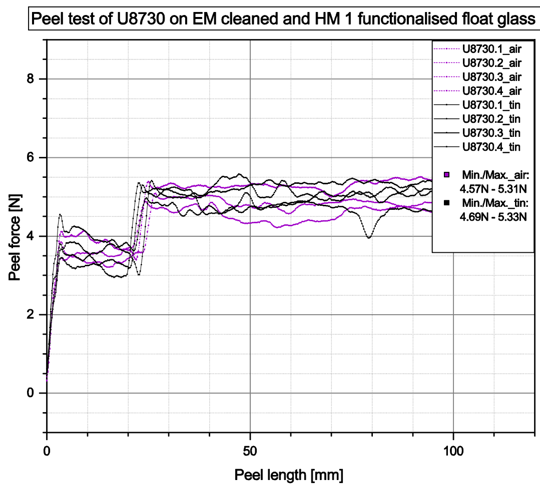


Figure 24: Peel test of U8730 on EM cleaned and HM1 functionalised float glass float glass printed with PR9415

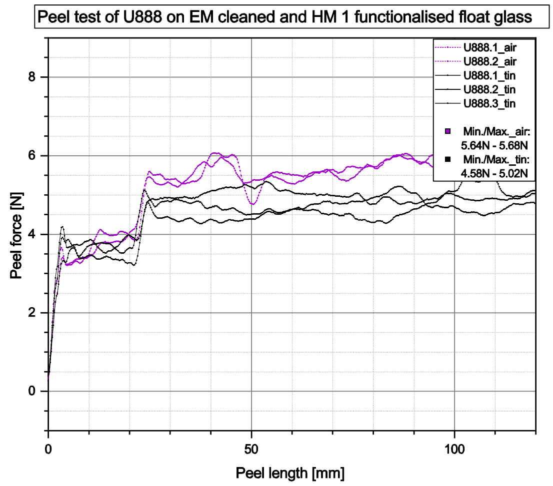


Figure 25: Peel test of U888 on EM cleaned and HM1 functionalised float glass float glass printed with PR9415

3.7 Adhesion on hydrophobic surfaces (HM2)

Following, peel forces on HM2 functionalised hydrophobic surfaces (air- and tin side) printed with UV varnishes were measured (Table 13). Each combination, air- and tin side, printed with UV varnishes will be counted as one measurement series. In summary, 12 measurement series with 5 peel tests for each combination were analyzed.

Table 13: Overview of peel forces from UV varnishes on HM2 functionalised float glass

Measurement series and their peel forces				
UV varnish	Measurement series	Air side peel force measurements	Measurement series	Tin side peel force measurements
PR9410	❶	4.08, 0.12, 4.35, 4.09, 3.83	❷	4.00, 3.23, 3.88, 3.96, 4.03
PR9415	❸	2.88, 3.10, 3.02, 3.12, -	❹	2.57, 2.75, 2.63, -, -
PR9291	❺	6.66, 6.75, 6.23, -, -	❻	5.69, -, -, -, -
360027	❼	3.31, 3.10, 2.66, 3.19, 3.53	❽	2.36, 2.84, 2.99, 3.12, 3.30
U8730	❾	5.32, 5.17, 4.93, -, -	❿	4.99, 5.09, 5.06, -, -
U888	⓫	4.82, 0.05, 5.37, -, -	⓬	4.44, 4.50, 5.11, 5.07, -

18 peel force measurements, red marked, out of 60, on HM2 functionalised float glass surface show peel forces ≤ 0.50 N (❶, ❸, ❹, ❺, ❻, ❾, ❿, ⓫, ⓬). Without peel forces ≤ 0.50 N, 2 out of 12 (❻, ⓫) measurement series (Figure 14) have less than 3/5 evaluable peel trials (grey marked cells) with clear adhesion results and forces between 2.36 N and 6.75 N (blue marked).

In the majority, the measured adhesion forces slightly decrease with increasing WCA in comparison to HM1. 4 of 6 UV varnishes show adhesion differences between air- and tin side.

Table 14: Peel forces and their trials on hardened UV varnishes on HM2 functionalised surface.

Method	UV varnish	PR9410		PR9415		PR9291		360027		U8730		U888	
		air	tin	air	tin	air	tin	air	tin	air	tin	air	tin
HM2	min. [N]	3.83	3.23	2.88	2.57	6.23	5.69	2.66	2.36	4.93	4.99	4.82	4.44
	max. [N]	4.35	4.03	3.12	2.75	6.75	5.69	3.53	3.30	5.32	5.09	5.37	5.11
x̄ [min./max.]	[N]	4.09	3.63	3.00	2.66	6.49	5.69	3.09	2.83	5.13	5.04	5.10	4.78
Peel force tendency: HM1 to HM2		▬	⇩	⇩	⇩	⇩	⇩	▬	⇧	⇧	▬		▬

Legend of peel trials and peel force tendencies	0/5	1/5	2/5	3/5	4/5	5/5
	⇧		Increasing peel force			
	⇩		Decreasing peel force			
	▬		Similar peel force			

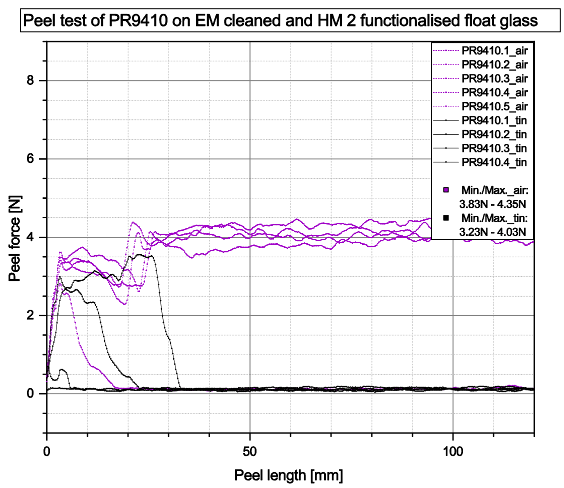


Figure 26: Peel test of PR9410 on EM cleaned and HM2 functionalised float glass

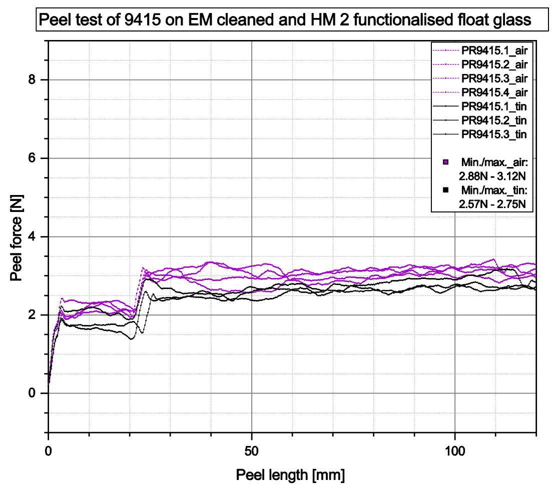


Figure 27: Peel test of PR9415 on EM cleaned and HM2 functionalised float glass

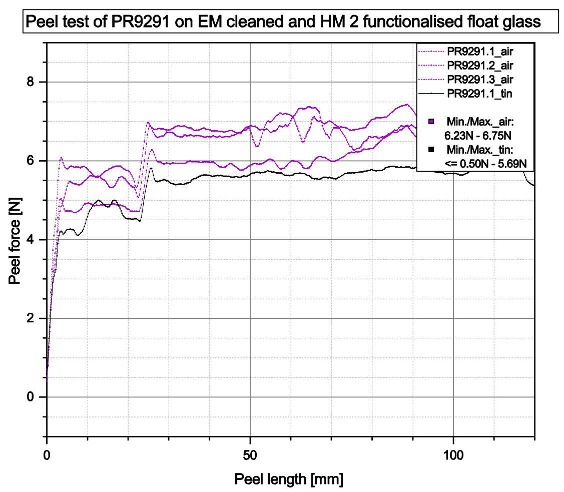


Figure 28: Peel test of PR9291 on EM cleaned and HM2 functionalised float glass

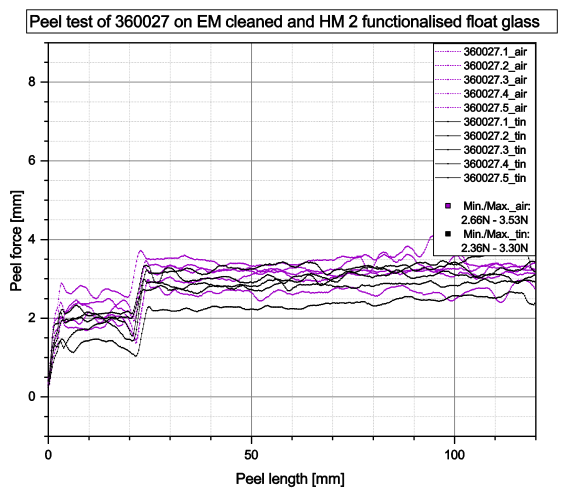


Figure 29: Peel test of 360027 on EM cleaned and HM2 functionalised float glass

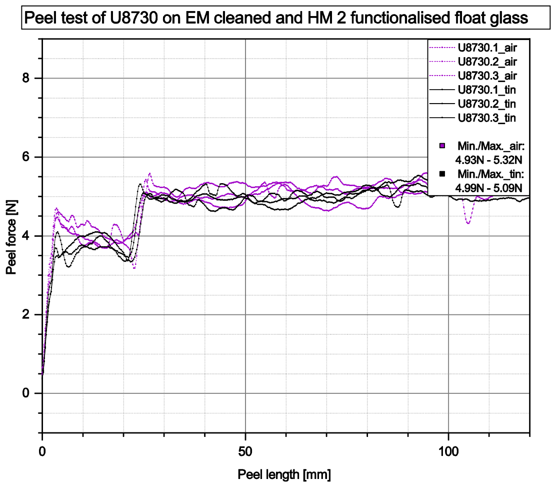


Figure 30: Peel test of U8730 on EM cleaned and HM2 functionalised float glass

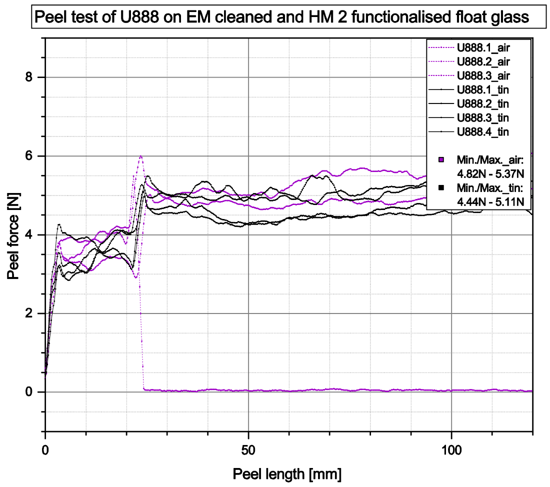


Figure 31: Peel test of U888 on EM cleaned and HM2 functionalised float glass

4. Conclusion

4.1 Wetting results

The wetting properties of float glass can be influenced by cleaning methods RTM and EM by using a mildly alkaline cleaning bath with different adjustments of temperature. RTM reinforces significant the two-sidedness of the float glass with WCA (air/tin): 17.4° to 55.8°/6.3° to 31.0°. The enhanced cleaning method, in contrast, equalises the two-sidedness with WCA (air/tin): 4.0° to 6.9° and gives the float glass surface a very hydrophilic and homogeneous wetting behaviour.

RTM cleaned float glass shows on the air side surface energy of 53.6 mN/m and on the tin side 61.7 mN/m. The two-sidedness is clearly differential in water contact angle and surface energy. In contrast to RTM, EM cleaned float glass shows on the air side surface energy of 51.8 mN/m and on the tin side 52.1 mN/m. The surface energy of the air- and tin side are relatively similar, but contact angle measurement with test fluids diiodomethane, benzyl alcohol and glycerol show still the expected influence of tin doping.

In summary, the EM cleaned float glass cares for a very homogenous and hydrophilic float glass surface, that was used as preliminary cleaning method and initial state for a following HMDS surface functionalising, to reach a homogeneity hydrophobic wetting behaviour with used functionalisation methods HM1 and HM2. Furthermore, the surfactant-free laboratory dishwasher cleaner is a harmless, easy to handle and cost-effective alternative in comparison to the mainly used Piranha cleaning.

The functionalisation of float glass surface with HM1 and HM2 cares for two clearly differentiable hydrophobic wetting behaviour in contrast to EM. Contact angles of test fluids water, diiodomethane, benzyl alcohol and glycerol were measured and evaluated. The homogeneity of contact angles decreased, in contrast to EM, but is comparable with the research of Wang, et al. (2021) and Prístavok (2006) and confirms the implementation of the functionalisation methods. The results were listed in Table 10. Significance test of normally distributed contact angle data pairs of HM1 functionalised float glass surface shows a strong significance difference between air- and tin side by using test fluids benzyl alcohol and glycerol. In contrast to HM1, HM2 shows a strong significance between air- and tin side, and so sensibility to the two-sidedness of the float glass, with test fluids water and diiodomethane.

HM1 functionalised float glass show on the air side surface energy of 59.6 mN/m and on the tin side 60.5 mN/m. HM2 functionalised float glass show on the air side surface energy of 47.5 mN/m and on the tin side 45.9 mN/m**.** The evaluated polar components decreased with increasing functionalisation (HM1 to HM2) and changed the sensibility of the test fluids in relation to the functionalisation method.

4.2 Adhesion results

The adhesion results of used UV varnishes on EM cleaned, HM1- and HM2 functionalised float glass surfaces are characterised by incomplete peel force measurement series. The adhesion measurement failures were not attributable to a specific UV varnish, so might be, the reason for failure could be a too-low contact pressure of the defined applied tape to the hardened UV varnishes surface and/or a too-short duration time of the tape on the hardened UV varnishes between application and peel force testing and/or an adhesive inhomogeneity of the used tape. Next investigations should include more peel trails and an optimisation of the tape application to reduce this source of deviation.

The evaluation of the peel tests with ≥3/5 trials and without peel forces ≤ 0.50 N show for applicated UV varnishes on EM cleaned float glass surface peel forces between 3.35 N and 5.97 N, for applicated UV varnishes on HM1 functionalised float glass surfaces between 1.74 N and 7.36 N and for HM2 functionalised float glass surfaces peel forces between 2.36 N and 6.75 N. The peel force overview (Table 15) gives an impression of the peel force deviation depending of the applied 6 UV varnishes from the air- to tin side and between the 3 different surface modifications.

Table 15: Overview of measured peel forces on, printed with UV varnishes, EM cleaned and HM1- and HM2 functionalised float glass with marked peel force tendencies in relation to the surface modifications

Peel forces	PR9410		PR9415		PR9291		360027		U8730		U888	
	air	tin	air	tin	air	tin	air	tin	air	tin	air	tin
EM x̄ [min./max]	0.00	0.00	3.22	3.77	6.78	4.06	3.56	3.42	5.29	4.94	5.68	5.36
HM1 x̄ [min./max]	⇧ 4.28	⇧ 4.15	⇧ 3.91	▬ 3.64	⇧ 7.00	⇧ 6.77	⇩ 3.24	⇩ 2.13	⇩ 4.94	▬ 5.01	▬ 5.66	⇩ 4.80
HM2 x̄ [min./max]	▬ 4.09	⇩ 3.63	⇩ 3.00	⇩ 2.66	⇩ 6.49	⇩ 5.69	▬ 3.09	⇧ 2.83	⇧ 5.13	▬ 5.04	⇩ 5.10	▬ 4.78

Legend of peel force tendencies		
	⇧	Increasing adhesion
	⇩	Decreasing adhesion
	▬	Similar adhesion

Hydrophilic wetting properties seem not to be only sufficient for the formation of "good" adhesion of UV varnishes, although good wetting of a surface is considered a prerequisite for good adhesion between applied fluid and substrate. The "good" adhesion behaviour is not clear defined, because it depends on the application purpose. The pre- tested solvent based 2K screen printing ink ZGM with hardener SVC/H, especially for glass printing, is used in this report as reference for the evaluation of the determined adhesion forces. The screen printing ink showed an average adhesion force of 4.40 N on EM cleaned float glass surface. In comparison, the applied and hardened UV varnishes show adhesion values between 0.00 N and 6.78 N and show of the in-/compatibility of UV varnishes to the very hydrophilic float glass surface.

The peel force investigations show with increasing water contact angle, EM to HM1, by 5 measurement series an unexpected slight increase of peel force, e.g. the UV varnish PR9410, 3 measurement series show similar peel force and 4 measurement series show a decreasing peel force. So, a higher water contact angle in a range of 13.0° to 28.5° can improve the adhesion behaviour in comparison to EM cleaned and printed float glass samples (WCA ≈ 3°). The authors suspect an increasing formation of covalent bonds on the float glass surface which result to higher peel forces. The other UV varnishes show no interaction with the HMDS functionalisation (HM1).

The influence of the two-sidedness of the float glass is better detectable on EM cleaned float glass as on HM1 functionalised float glass. Further investigations with customised UV formulations and extended peel trials will provide information about these phenomena.

The peel force investigations show with increasing water contact angle, HM1 to HM2, by only 2 measurement series an increasing peel force (U8730 and U888), 4 measurement series show similar peel force and 6 measurement series show a decreasing peel force. So, a higher water contact angle in a range of 41.4° to 55.5° can reduce the adhesion properties in comparison to HM1 functionalised and printed float glass samples. The increase in temperature results in decreasing wetting behaviour, but in the majority not to increasing peel forces.

The two-sidedness of the float glass is better detectable on HM2 functionalised float glass as on HM1 functionalised float glass. Further investigations with known UV formulations and more peel trials can provide information about these phenomenas. The lowest influence of the air- and tin sides seems to be on the HM1 functionalised float glass surfaces.

The printing industry preferred the printing on the air side of the float glass. By viewing the measured peel forces in Table 15, it seems like, the tin side has lower peel forces as on the air side, if a deviation of ± 0.3 N is assumed. Exceptions occurred with UV varnish PR9415 (EM) and U8730 (HM1). It might be one of the reasons why in printing industry application often prefer the air side of the float glass.

The research of adhesion behaviour in comparison of wetting properties on modified float glass show this interdependancy as a worthwhile goal although there are used mature and stable industrial applications. Peel results showed different peel forces depending on glass cleaning/-functionalisation/-side and applied UV varnishes with different reactive diluents, binding agents and photoinitiators. Future investigations of peel tests with known UV formulations and different silanes are meaningful to allow gaining further insights into the adhesion of UV varnishes and different wetting states on functionalised float glass surfaces.

References

Deutsche Institut für Normung, 2020a. *EN ISO 19403-7:2020: Paints and varnishes - Wettability - Part 7: Measurement of the contact angle on a tilt stage (roll-off angle).* Berlin: DIN.

Deutsche Institut für Normung, 2020b. *DIN EN ISO 19403-2:2020-04: Beschichtungsstoffe - Benetzbarkeit - Teil 2: Bestimmung der freien Oberflächenenergie fester Oberflächen durch Messung des Kontaktwinkels (ISO 19403-2:2017)*. Berlin: DIN.

Fernández Oro, J.M., Argüelles Díaz, K.M., Santolaria Morros, C., Cobo Hedilla, A. F. and Lemaille, M., 2008. Multiphase modelling of pouring glass over the spout lip of an industrial float in the flat glass forming process. *International Journal for Numerical Methods in Fluids,* 58(10), pp. 1147–1177. https://doi.org/10.1002/fld.1793.

Fiorillo, M.R., Liguori, R., Diletto, C., Bezzeccheri, E., Tassini, P., Maglione, M., Maddalena, P., Minarini, C. and Rubino, A., 2017. Analysis of HMDS self-assembled monolayer effect on trap density in PC70BM n-type thin film transistors through admittance studies. *Materials Today: Proceedings,* 4(4), pp. 5053–5059. https://doi.org/10.1016/J.MATPR.2017.04.113.

Goodman, O. and Derby, B., 2011. The mechanical properties of float glass surfaces measured by nanoindentation and acoustic microscopy. *Acta Materialia,* 59(4), pp. 1790–1799. https://doi.org/10.1016/j.actamat.2010.11.045.

Haldimann, M., Luible, A. and Overend, M., 2008. *Structural use of glass*. Zürich: International Association for Bridge and Structural Engineering (IABSE). https://doi.org/10.2749/sed010.

Herzer, N., Hoeppener, S. and Schubert, U.S., 2010. Fabrication of patterned silane based self-assembled monolayers by photolithography and surface reactions on silicon-oxide substrates. *Chemical communications,* 46(31), pp. 5634–5652. https://doi.org/10.1039/C0CC00674B.

Hüppauff, M. and Lengeler, B., 1994. Surface analysis of floatglass by means of x-ray absorption, reflection, and fluorescence analysis. *Journal of Applied Physics,* 75(2), pp. 785–791. https://doi.org/10.1063/1.356430.

Krohn, M.H., Hellmann, J.R., Mahieu, B. and Pantano, C.G., 2005. Effect of tin-oxide on the physical properties of soda-lime-silica glass. *Journal of Non-Crystalline Solids,* 351(6-7), pp. 455–465. https://doi.org/10.1016/j.jnoncrysol.2005.01.050.

Lazauskas, A. and Grigaliūnas, V., 2012. Float glass surface preparation methods for improved chromium film adhesive bonding. *Materials Science,* 18(2), pp 181–186. http://dx.doi.org/10.5755/j01.ms.18.2.1924.

Neroth, G. and Vollenschaar, D. eds., 2011. *Wendehorst Baustoffkunde: Grundlagen – Baustoffe – Oberflächenschutz*. 27th ed. Wiesbaden: Vieweg + Teubner (Praxis).

Persson, R., 1969. *Flat glass technology*. Boston, MA: Springer US.

Pilkington, L.A.B., 1969. Review lecture: the float glass process. *Proceedings of the Royal Society A,* 314(1516), pp. 1–25. https://doi.org/10.1098/rspa.1969.0212.

Prístavok, R., 2006. *Analyse und Modellierung der Haftungsmechanismen bei der Beschichtung und Verklebung von Papierwerkstoffen*. Dr.-Ing. Dissertation. Technischen Universität Bergakademie Freiberg.

Saint-Gobain, 2018. *CSP_Broschuere_TIMELESS_A4_01115_CSP_04_2018_001_RZ*. [pdf] Available at: <https://climaplus-securit.com/xde-content/uploads/2018/04/CSP-Brosch%C3%BCre-TIMELESS-A4-01115-CSP-04-2018-001-RZ.pdf> [Accessed 2018].

Schreithofer, N., Laskowski, J.S. and Heiskanen, K., 2010. Changes of methylated silica surfaces on ageing. *Adsorption,* 16(4–5), pp. 271–277. https://doi.org/10.1007/s10450-010-9226-1.

da Silva, L.F.M., Öchsner, A. and Adams, R.D. eds., 2011. *Handbook of adhesion technology.* Berlin, Heidelberg, Cham: Springer.

Silvestru, V.A., Drass, M., Englhardt, O. and Schneider, J., 2018. Performance of a structural acrylic adhesive for linear glass-metal connections under shear and tensile loading. *International Journal of Adhesion and Adhesives*, 85, pp. 322–336. https://doi.org/10.1016/j.ijadhadh.2018.07.006.

Tamglass Ltd Oy, 1997. Glass processing days. In: *The Fifth International Conference on Architectural and Automotive Glass [now and in the future]*. Tampere, Finland, 13–15 September 1997. Tampere: Tamglass Engineering Oy.

Wang, Y., Hansen, C.J., Wu, C.-C., Robinette, E.J. and Peterson, A.M., 2021. Effect of surface wettability on the interfacial adhesion of a thermosetting elastomer on glass. *RSC Advances,* 11(49), pp. 31142–31151. https://doi.org/10.1039/D1RA05667K.

Wypych, G., 2018. *Handbook of adhesion promoters*. Toronto, Ontario: ChemTec Publishing.

Zhang, Q., Chen, Z. and Li, Z., 2011. Simulation of tin penetration in the float glass process (float glass tin penetration). *Applied Thermal Engineering* 31 (6–7), pp. 1272–1278. https://doi.org/10.1016/j.applthermaleng.2010.12.030.