Glass lap joints with UV-cured adhesives: Use of a perfluoropolyether methacrylic resin in the presence of an acrylic silane coupling agent

Original
Glass lap joints with UV-cured adhesives: Use of a perfluoropolyether methacrylic resin in the presence of an acrylic silane coupling agent / Dalle Vacche, S.; Forzano, S.; Vitale, A.; Corrado, M.; Bongiovanni, R.. - In: INTERNATIONAL JOURNAL OF ADHESION AND ADHESIVES. - ISSN 0143-7496. - ELETTRONICO. - 92:(2019), pp. 16-22. [10.1016/j.ijadhadh.2019.04.003]

Availability:
This version is available at: 11583/2737753 since: 2019-06-27T12:07:10Z

Publisher:
Elsevier Ltd

Published
DOI:10.1016/j.ijadhadh.2019.04.003

Author's postprint version (refereed)

International Journal of Adhesion and Adhesives, Volume 92, July 2019, Pages 16-22

Editorial version at: https://doi.org/10.1016/j.ijadhadh.2019.04.003

Glass lap joints with UV-cured adhesives: use of a perfluoropolyether methacrylic resin in the presence of an acrylic silane coupling agent.

Sara Dalle Vacche[a,*], Stefano Forzano[a,1], Alessandra Vitale[a,b], Mauro Corrado[c], Roberta Bongiovanni[a,b]

[a]Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy

[b]INSTM−Politecnico di Torino Research Unit, 50121 Firenze, Italy

[c]Department of Structural, Geotechnical and Building Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

e-mail: sara.dallevacche@polito.it, stefanoforzano@live.it; alessandra.vitale@polito.it, mauro.corrado@polito.it; roberta.bongiovanni@polito.it

[*] corresponding author: Sara Dalle Vacche, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.

Tel: +39 011 0904565 e-mail: sara.dallevacche@polito.it

Abstract

In this work the adhesion to glass of a UV-curable resin with a high fluorine content, namely a methacrylic resin based on perfluoropolyether (PFPE) chains, was studied. In particular, focus was on how the presence of a silane coupling agent, with an acrylate functional group, used either for functionalizing the glass substrates or as an additive to the resin formulations, influenced such adhesion. The adhesive bond strength in shear of lap joints and their resistance to a humid

---

[1] Current address: 2Gamma s.r.l., corso Inghilterra 15, 12084 Mondovì (CN), Italy.

environment and water were assessed. The silane was found to enhance the adhesive strength of the PFPE resin joints, and the silanization of glass proved to be more efficient than the addition of the additive into the formulations. The results were compared to those obtained with a fluorine free acrylic resin. Although the adhesion strength of the PFPE resin was lower compared to that of the fluorine free resin, it showed a better resistance to water as the hydrophobicity of the PFPE chains hindered the transport of water molecules at the resin/glass interface.

Keywords

fluorinated adhesive, glass, cure / hardening by radiation, lap-shear, (meth)acrylate functional silane

1. Introduction

The glass bonding adhesives market is experiencing a steady growth, driven by applications in the construction, furniture, automotive and transportation, and electronics field [1]. Indeed, due to the inherent brittleness of glass, it is convenient to use adhesives for bonding, rather than bolted joints; adhesives are also crucial in the production of transparent laminated glasses, e.g for windshields. Among the many classes of adhesives, photocurable adhesives are particularly interesting [2,3]: in fact, their processing is environmentally friendly, as it is solvent-free, is solely induced by light without heating the substrate and shows a spatial resolution (i.e., the reaction can take place only within the joint by selectively irradiating the area of interest). The light induced curing processes can be employed either to prepare thermoset adhesives starting from low molecular weight resins or to crosslink thermoplastic adhesives after application on the adherends: one can obtain structural adhesives as well as pressure-sensitive adhesives (PSAs) or hot-melts [4,5].

Among the many sources of radiation available, UV light is still the most common [6]: the UV-cured adhesives market will be worth $1.2 billion by 2021, at a compound annual growth rate of 9.15% from now on, glass bonding being one of the key drivers [7]. Glass bonding needs polymeric adhesives with excellent thermal and chemical resistance, which is generally a challenge. For instance, in medical and electronics applications, silicone-based adhesives are very common, although they are not oleophobic and can suffer from swelling in some classes of solvents. As an alternative, fluorinated adhesives, which are also available in the form of UV-processable systems [8–10], can be used. Fluoropolymers are well known for being resistant to temperature and harsh environments; they exhibit insolubility in most solvents, in particular water. It is well known that silicones and fluoropolymers are hydrophobic and they have inherent low adhesion due to their low surface tension [11]; nevertheless, their adhesion can be improved by either modifying the glass surface or introducing coupling agents in the formulation. Plasma treatments are widely used for surface modification. For instance, an atmospheric plasma torch treatment has been found to enhance the adhesion strength of a polyurethane joint on glass, although it was not as effective with epoxy, silicone or cyanoacrylate adhesives [12,13]. The use of primers, such as silane coupling agents is widespread [14,15]. In the case of UV-curable adhesives, the use of silanes that have a functional group able to co-react with the resin under irradiation is of particular interest [16,17]: in this way the silane forms covalent bonds both with glass through silanol condensation and with the polymer through the co-reactive group, and acts as a bridge, linking the cured polymer and the glass surface. Silanes can be used for functionalizing the glass surface before applying the adhesive, or as an additive to the adhesive formulation. As the glass silanization procedure consists of several steps, the second method is preferable from a processing point of view, although it may be less efficient [18].

In this work we examine the adhesion to glass of a UV-curable system with a high fluorine content, guaranteeing chemical and thermal resistance. In particular we have chosen a methacrylic resin based on perfluoropolyether (PFPE) chains: they are preferred to perfluoroalkylic structures which give concerns for their impact on the environment and on human health due to their biopersistence [19]. This resin has a good thermal stability, as its degradation starts at high temperatures, being the T_2 (i.e., temperature at which the sample loses 2% of its weight) and the T_{50} (i.e., temperature at which the sample loses 50% of its weight) above 175 °C and 310 °C, respectively, as measured by thermogravimetric analysis in air in a previous work [25]. In this work, we tested the adhesive bond strength of lap joints in shear and examined their resistance to a humid environment and water; in particular, we investigated the effect on adhesion of silanes with an acrylate functional group, either functionalizing the glass substrates with them or adding them to the resin formulations. Moreover, we compared the results with those obtained for a fluorine free resin.

2. Materials and methods

2.1 Materials

A bifunctional urethane methacrylate-PFPE macromer containing more than 80% PFPE, with a molecular weight of ca. 2000 g mol^{-1} (Fluorolink® MD700, F, by Solvay Specialty Polymers, Bollate Milano, Italy) was used as oligomer; tricyclodecanediol diacrylate (Ebecryl® 130, E, by Allnex Belgium SA, Drogenbos, Belgium) was chosen for comparison. The photoinitiator added to all formulations was 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur® 1173, D, by BASF, Germany). 3-(acryloyloxy) propyltrimethoxysilane, 94%, was supplied by Alfa Aesar (Thermo Fisher (Kandel) GmbH, Karlsruhe, Germany) and will be referred to as silane (S) in what follows. The chemical structures of the above listed chemicals are reported in Figure 1, and the adhesive formulations used in this work are summarized in Table 1. Thermo Scientific™ British Standard Slides made from extra-white soda-lime glass, (Thermo Fisher Scientific Inc., Waltham, USA) were used as substrates.

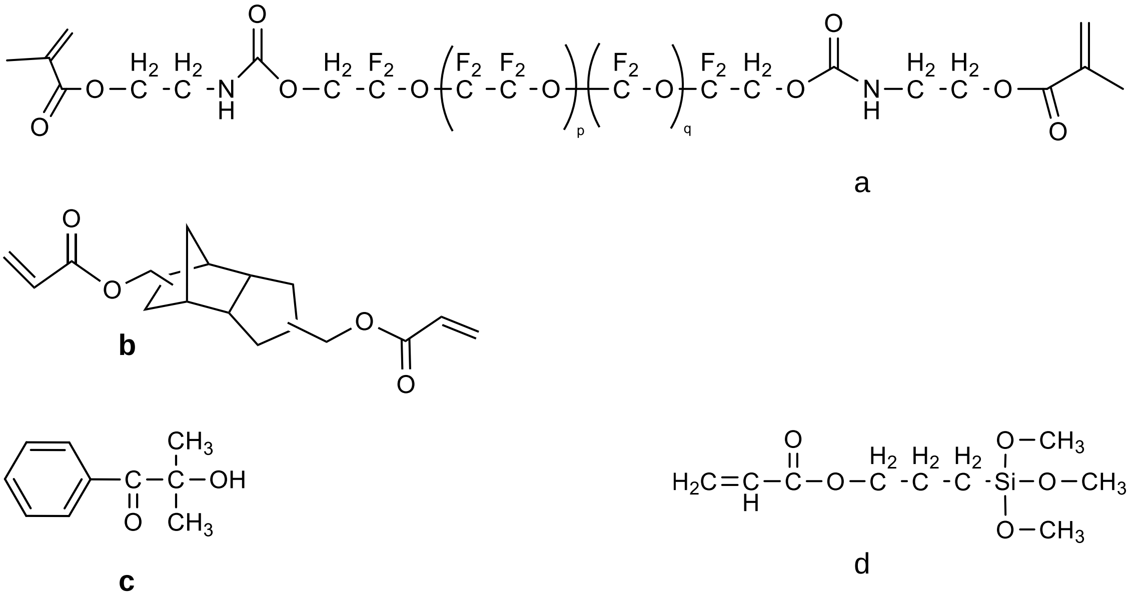

Figure 1 – Chemical structures of (A) Fluorolink® MD 700 oligomer;(B) Ebecryl® 130 oligomer; (C) Darocur® 1173 photoinitiator; (D) 3-(acryloyloxy) propyltrimethoxysilane coupling agent (silane)

Table 1 - Adhesive formulations used in this work: composition in phr

Formulation code	Fluorolink® MD700 (F)	Ebecryl® 130 (E)	Darocur® 1173 (D)	Silane (S)
FD	100		3	
FDS	100		3	2
ED		100	3	
EDS		100	3	2

2.2 Silanization of glass slides

Part of the glass slides were surface modified by immersion in solutions of the silane in ethanol or water. The silanization procedures were adapted from the literature [20–22], and the effectiveness of the silanization was checked by contact angle measurements as described in section 2.3. When the ethanol solutions were used, the concentration of silane was 0.2 or 1 vol%, the glass slides were left immersed for 2 h, while the solution was kept at 70 °C and stirred with a magnetic mixer; the slides were then washed for 15 min in fresh ethanol in an ultrasound bath in order to remove non-bound silane. When the water solution was used, the concentration of silane was 0.2 vol%, the silanization was performed at room temperature (RT) by immersing the glass slides for 5 min; then the slides were rinsed with deionized water. After rinsing, all the silanized slides, obtained both by ethanol-based and water-based reaction solutions, were placed in an oven at 100 °C for 30 min to promote silanol condensation.

2.3 Preparation of test specimens

With formulations FD and ED, resin specimens with a rectangular cross-section were prepared in an open aluminum mold. The cross-section dimensions were 7.75 mm x 1.05 mm for the FD resin, and 7.75 mm x 1.20 mm for the ED resin. These specimens were used for tensile testing.

Coatings with 50 μm thickness were prepared with all formulations on glass slides, either standard or surface modified with the silane, using a wire bar coater. These specimens were used for contact angle measurements, for checking the transparency of the polymeric layers under visible light, and to assess resistance of the coatings to water.

Single lap joint specimens with a squared overlapping area of 26 mm x 26 mm were prepared by curing a 50-100 μm thick layer of adhesive formulation between two glass slides. These samples were used to check the resistance of the joints to water.

The specimens for the single lap-shear test were prepared using standard or surface modified glass slides, with the procedure sketched in Figure 2. Polytetrafluoroethylene (PTFE) masks (0.1 mm thick) were used to obtain a circular bonded area with a 6 mm or 4 mm diameter, adapting the procedure described by Swentek and Wood [23]: a circular hole was punched on a rectangular portion of PTFE foil, slightly larger than the overlapped area of the two slides; a syringe was used to place a controlled amount of resin formulation in the circular area, and a second glass slide was placed on top, as shown in Figure 2. Glass spacers were used to ensure the alignment of the specimens, both during assembly and in the electromechanical universal testing machine. After photocuring of the adhesive, the PTFE mask was removed by tearing it apart with the help of four pre-made perpendicular cuts. Rubber spacers were then glued to prevent the rupture of the glass slides while tightening the electromechanical universal testing machine clamps and avoid slippage during the test.

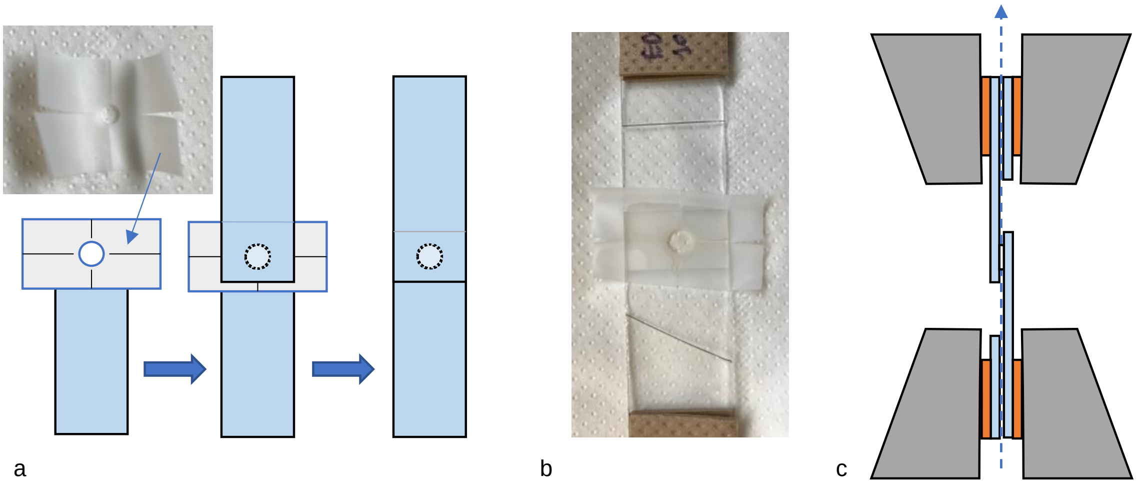

Figure 2 - (a) Scheme of the preparation of the lap-shear specimens and photo of the PTFE mask; (b) photo of a cured specimen before removal of the mask, showing also the glass and rubber spacers; (c) scheme of the lap-shear specimen mounted in the tensile test set-up

For curing all specimens, a 5000-EC UV flood lamp system (Dymax Corporation, Torrington, CT, USA) with medium intensity mercury bulb was used. The intensity was tuned by changing the distance between the specimen and the light source, and measured by means of a UV Power Puck II radiometer (EIT, LLC., Leesburg, USA). The curing conditions for the thick casted samples and the coatings were 100 mW cm^{-2} for 2 min under N_2 flow; FD and FDS coatings were additionally kept under N_2 flow for 30 s prior to curing (these conditions ensured absence of tackiness). The lap joints and the lap-shear specimens were cured in air, with 100 mW cm^{-2} intensity for 3 min (1.5 min per side).

2.3 Characterization methods

Static contact angle measurements were performed at room temperature by means of a Krüss DSA100 instrument (KRÜSS GmbH, Hamburg, Germany), equipped with video camera and image analysis software, with the sessile drop technique. For glass slides water was used as liquid, while for the coatings two liquids were used: water and hexadecane. Five drops per sample and per liquid were analyzed. The contact angle values were then used to estimate the dispersive and polar components, γ_s^D and γ_s^P, of the surface energy, γ_s, of the cured polymers by means of the FTA32 Software (First Ten Ångstroms). The geometric mean method [24] was used:

$$(1+\cos\theta_i)\cdot\gamma_i = 2\cdot\left[(\gamma_i^D\cdot\gamma_s^D)^{1/2}\cdot(\gamma_i^P\cdot\gamma_s^P)^{1/2}\right] \qquad i = w, h \tag{1}$$

$$\gamma_s = \gamma_s^D + \gamma_s^P \tag{2}$$

where γ_s, γ_s^D and γ_s^P, indicate the surface energy of the solid surface (polymer), and its dispersive and polar components, respectively; γ_i, $\gamma_i^D$and γ_i^P indicate the surface energy, and the respective dispersive and polar components, of the test liquids, for which the values embedded in the FTA32 Software database were used; θ_i is the contact angle measured for the liquid i on the solid surface; the subscript i indicates either water ($i = w$) or hexadecane ($i = h$). Water contact angle was also measured for lap-shear specimens, after mechanical tests, on the site of detachment of the joint, immediately and after rinsing with ethanol. In this case, due to the small area of interest, only one drop of liquid per sample could be used.

Fourier-transform infrared (FT-IR) spectroscopy analysis was performed with the Attenuated Total Reflectance (ATR) method by means of a Nicolet iS 50 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, US), equipped with a diamond probe, in the 4000 – 600 cm^{-1} range, with 32 scans per spectrum and a resolution of 4 cm^{-1}. The degree of cure was evaluated from the decrease of the intensity of the peak at 1635 cm^{-1}, or of the double peak at 1635 cm^{-1} and 1618 cm^{-1}, assigned to the C=C bond stretch in the methacrylate group and in the acrylate group, respectively; the C=O stretch peak at 1725 cm^{-1} was used as an internal reference, as described elsewhere [25,26].

The insoluble (gel) fraction of the cured adhesives was assessed by measuring the weight of cured films, detached from the glass substrate, before and after immersion in dichloromethane or acetone for 24 h, and evaporation of the residual solvent at RT for 24h followed by drying at 60 °C for 24 h.

The transparency of the cured polymers, coated on glass slides, was evaluated by means of a Jenway 6850 UV/Vis spectrophotometer (Cole-Parmer, Stone, UK) in the 300-800 nm range, using a bare glass slide as a reference.

Resistance to water was tested by immersion of coatings and single lap joint specimens in demineralized water at RT for 14 days, followed by immersion in demineralized water at 60 °C for 4h. The samples were visually inspected daily for evidence of detachment, with a protocol inspired to that described in the ASTM D820 standard [27].

An Instron 3366 electromechanical universal testing machine (ITW Test and Measurement Italia S.r.l. Instron CEAST Division, Pianezza (TO), Italy) equipped with a 10 kN load cell, was used to perform the tensile tests on the resin specimens and the lap-shear tests (see section 2.2). Six specimens were tested for each adhesive formulation, with a 5 mm min^{-1} cross-head speed. For the tensile tests on resin specimens, the tensile strength (σ_{max}) was taken as the maximum stress value, and the elongation at break (ε_{max}) was taken at the rupture of the specimen. For the lap-shear specimens, the glass spacers glued to the specimen compensated the offset of the lap-shear design, and the rubber spacers prevented the rupture of the glass while tightening the clamps (Figure 2c). The shear adhesive strength τ_{max} was calculated from the maximum load F_{max} and the bonded area A, which was obtained from the diameter of the PTFE mask's circular hole, i.e. 28.3 mm^2 or 12.6 mm^2.

3. Results and discussion

3.1 Surface treatment of glass and properties of the adhesive formulations

In view of preparing and characterizing adhesive joints for glass surfaces, the surface properties of the glass substrates and of the adhesives, as well as the bulk properties of the adhesives, were assessed. In order to obtain better adhesion, the use of a silane containing an acrylic functional group that can co-react with the photocurable adhesive formulation was explored. The silane was used either to functionalize the glass surface, or as an additive in the resin formulation.

For the functionalization of the glass substrate the concentration of silane and the type of solvent were changed with the aim of assessing different and more environmentally friendly process conditions in view of a commercial application. The static contact angle of water, θ_w, measured on the standard glass slides was lower than 10°. Independently on the functionalization reaction conditions, the surface modification increased the θ_w, to a higher extent with increasing concentration of the silane in the ethanol solution. The contact angle obtained with the 0.2 vol% solution of silane in ethanol, i.e 56.6° ± 3.0° was sensibly lower than the value of 70° reported by Arkles et al. [28] for a similar silane (methacryloxypropyltrimethoxysilane), possibly indicating incomplete coverage of the surface. A contact angle of 69.4° ± 3.1° was obtained with the 1 vol% silane solution in ethanol indicating that a denser layer of silane was deposed on the surface. When functionalization was carried out in water, a θ_w of 67.6° ± 4.1° was obtained with 0.2 vol% of silane, indicating that silanization in water was more effective than in ethanol due to a faster hydrolysis of the silane.

The curing of the fluorinated resin FD and of the resin ED used as a comparison was assessed by measuring the gel content of the polymers after irradiation and by monitoring the conversion of the reactive groups (i.e. the C=C double bond of the (meth)acrylic group) by ATR FT-IR spectroscopy (see Table 2). For the cured FD coating the peak characteristic of the C=C bond was no more detectable after irradiation as previously reported [26], while for the ED formulation the double peak nearly disappeared, as shown in Figure 3, indicating a high conversion. Figure 3 also shows that there is not a significant difference between the two sides of the coatings (i.e., glass side and air side), thus confirming the homogeneity of the curing process along the film thickness. The gel content of the cured FD and ED resins was higher than 96% both in dichloromethane and in acetone. The results obtained with both techniques confirm that a full cure was reached.

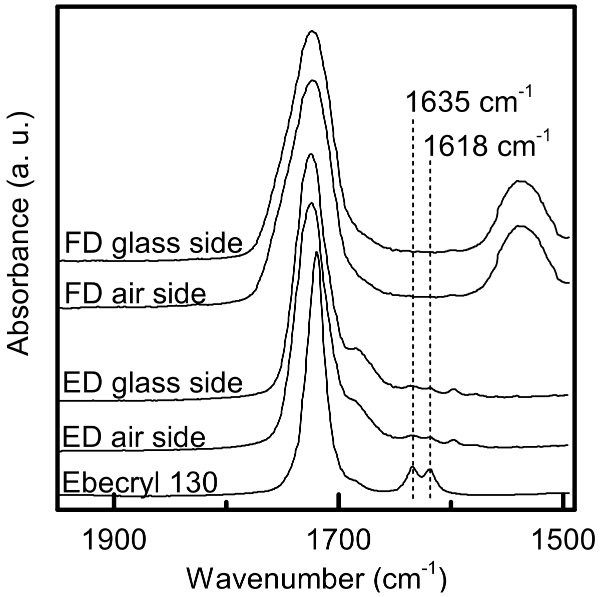

Figure 3 – FT-IR spectra of cured coatings, taken both on the air and glass sides, between 1900 and 1500 cm^{-1}; the vertical lines shows the position of the C=C bond stretch signals. The spectrum of the uncured Ebecryl® 130 is also given as a reference.

Table 2 – Gel fraction (%gel) and tensile properties of cured ED and FD resins

	Conversion, FT-IR (%)	%gel, dichloromethane (%)	%gel, acetone (%)	σ_{max} (MPa)	ε_{max} (%)
FD	100	97.5	96.5	2.5 ± 0.1	7.3 ± 0.5
ED	93.4 ± 2.9	98.1	99.5	32.8 ± 6.5	2.8 ± 0.7

The UV-vis measurements confirmed that all the joints did not affect the transparency of glass in the visible light range (380 – 750 nm), where transmission was close to 100%, as shown in Figure 4

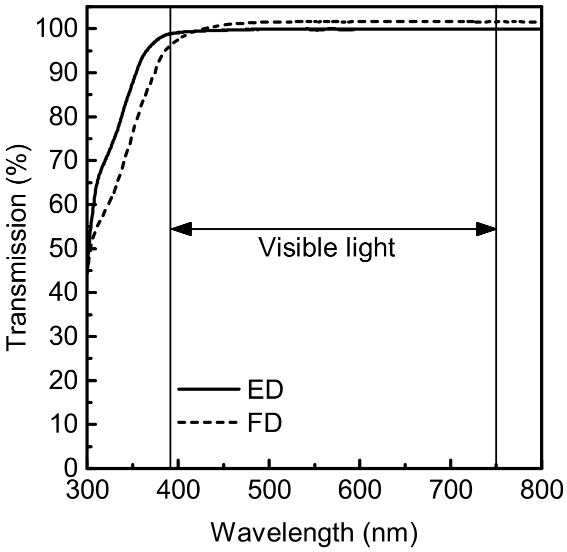

Figure 4 – UV-vis spectra of ED and FD, showing that both resins are transparent in the visible light range

The tensile properties of the cured FD and ED resins are reported in Table 2 and the corresponding stress-strain curves in Figure 5. Both resins showed a brittle rupture under the experimental conditions applied. As expected the tensile strength of the FD resin was one order of magnitude lower than that of the ED resin, as it has a much lower T_g. Indeed, the photocured PFPE resin, measured by dynamic mechanical analysis in a previous work [25], has two glass transition temperatures, a first one related to the fluorinated part of the chain, at - 68 °C, and a second one related to the non-fluorinated part of the chain at 47 °C, while according to the data published by the manufacturer the photocured ED resin, due to its rigid cycloaliphatic structure, has a T_g of 157 °C, also measured by dynamic mechanical analysis [29].

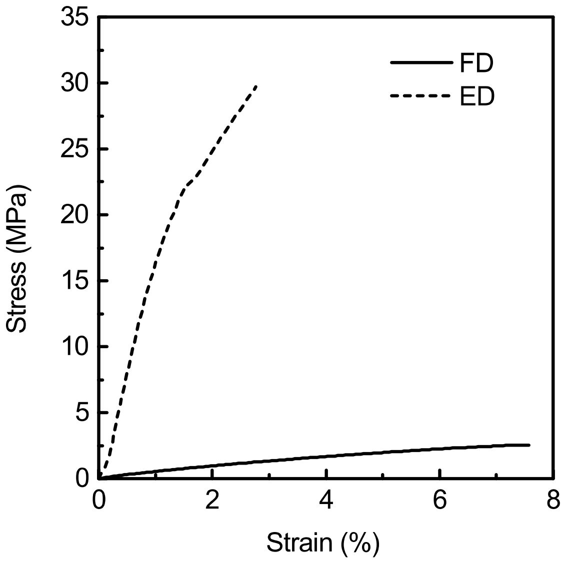

Figure 5 – Representative stress-strain curves for photocured FD and ED resins

The static contact angles of water and of hexadecane, on the photocured films, taken on the side exposed to air during irradiation (air side), were measured and are reported in Table 3, together with the calculated surface energies. The θ_w and θ_h values found for the FD coating confirmed the hydrophobic and oleophobic character of perfluoropolyethers, which assures a low surface energy γ (which can be as low as polytetrafluoroethylene), mainly due to the very low polar component, as also found in other works [26,30]. For the ED coating, values were in the expected range for a cycloaliphatic acrylate, below the hydrophobicity threshold. The addition of silane to both formulations was taken equal to 2 phr, which is in the range typically used for this method of application [31], and sufficiently low to avoid changes in the properties of the adhesives. The presence of the silane did not significantly affect the surface properties of the photocured films. Only in the case of EDS, the hexadecane contact angle slightly increased (compared to that of ED), hence decreasing the total surface energy and its dispersive component, although to a very small extent.

Table 3 – Contact angles of water and hexadecane on the coatings, with the respective calculated surface energies.

	θ_w (°)	θ_h (°)	γ_s (mN m^{-1})	γ_s^D (mN m^{-1})	γ_s^P (mN m^{-1})
FD	102.9 ± 2.6	52.7 ± 3.1	19.2	17.7	1.5
ED	67.6 ± 4.1	43.0 ± 2.4	37.2	20.6	16.6
FDS	102.8 ± 1.3	52.8 ± 2.0	19.2	17.7	1.5
EDS	68.6 ± 0.8	49.0 ± 1.9	35.8	18.9	16.9

The adhesion of films coated onto the glass substrates was checked by immersing the samples in water for 14 days at RT, and then for 4 hours in water at 60°C; the results (time to failure of the coating) are reported in Table 4. The adhesion of the FD and ED resins on standard glass slides was taken as reference to assess the efficacy of the silane treatments in improving adhesion. The better resistance of the FD coating (7 days at RT) compared to the ED coating (1 day at RT) is ascribed to the hydrophobicity of the PFPE based film, which hindered the transport of water to the film/glass interface. The addition of silane in the formulations improved the adhesion properties: the EDS coating detached from standard glass after 14 days at RT, while the FDS coating survived the entire immersion test, i.e. 14 days in water at RT plus 4 hours in water at 60 °C, confirming the superior water resistance properties of the PFPE based resin with respect to the cicloaliphatic one. When silanized glass was used, all the joints survived the entire immersion test.

Table 4 – Results of the immersion test for coatings and single lap joints: 14 days in water at room temperature (RT) plus 4 hours in water at 60 °C. The time elapsed until detachment of the coating or failure of the joint is reported;" No" indicates that no detachment/ failure happened during the test.

Coating/adhesive formulation	Glass type	Failure of the coating
FD	Standard	7 days RT
FDS	Standard	No
FD	Silanized (1 vol% in ethanol)	No
FD	Silanized (0.2 vol% in ethanol)	No
FD	Silanized (0.2 vol% in water)	No
ED	Standard	1 day RT
EDS	Standard	14 days RT
ED	Silanized (1 vol% in ethanol)	No
ED	Silanized (0.2 vol% in ethanol)	No
ED	Silanized (0.2 vol% in water)	No

3.2 Properties of the joints

The resistance of single lap joints to water was tested by immersing them in water (as for the cured coatings): the results are reported in Table 5. As for the ED photocured coating, the ED joint on standard glass failed after 1 day. The EDS joint on standard glass and the ED joints on silanized glass passed the immersion test; as in the joints the resin surface exposed to water was smaller than for the free coatings, the increase of adhesion due to the presence of silane in the EDS formulation was sufficient for preventing the failure. Quite unexpectedly, the FD joint between standard glass slides withstood the entire immersion test; the combination of the hydrophobicity of the film and the smaller surface exposed is likely to prevent water from reaching the adhesive/glass interface, thus preserving the integrity of the joint. The FDS joint on standard glass and the FD joints on silanized glass confirmed the behavior exhibited by the coatings, with no joint failure in the immersion test.

The results of lap shear tests are reported in Table 5: τ_{max} is listed together with data regarding the inspection of the joints after failure, according to the classification given in ASTM D5573 [32]. Unless stated otherwise, the joints failed leaving the entire polymer disk on one glass slide (i.e., on a single side of the joint). Upon visual inspection, all joints seemed to have undergone adhesive failure. To gain further information on the rupture mode, the water contact angle on the glass surface where the joint detached from the substrate was measured; in some cases, as will be detailed in what follows, these measurements suggested that rupture had, at least partially, happened in the adhesive near the adhesive/glass interface.

Table 5 – Shear adhesion strength of joints. When joints failed while mounting in the clamps, or rupture happened in the glass substrate, the number of such failures out of the total number of tested specimens is given in the columns BBT (broken before testing) and SB (stock-break failure), respectively. The values of θ_w*, measured on the glass slide at the site of detachment, immediately* (θ_w) *and after rinsing with ethanol (*$\theta_{w,\text{rinsed}}$*), are also reported. The bonded area had a diameter of 6 mm, except for the measurements indicated with (*) for which the diameter was 4 mm.*

Adhesive formulation	Glass type	τ_{max} (MPa)	BBT	SB	θ_w (°)	$\theta_{w,rinsed}$ (°)	Failure of the joint in water
ED	Standard	10.7 ± 2.7	-	-	15	< 10	1 day RT
EDS	Standard	12.8 ± 4.1	-	-	18	< 10	No
ED	Silanized (1% e.)	16.9 ± 1.6	-	2/6	63	63	No
ED	Silanized (0.2% e.)	> 18.5 ± 1.4	-	6/6	-	-	No
		25.4 ± 2.8 (*)	-	-	61	-	
ED	Silanized (0.2% w.)	-	-	2/2	-	-	No
		30.3 ± 3.7 (*)	-	-	59	-	
FD	Standard	-	6/6	-	30	30	No
FDS	Standard	2.9 ± 0.9	-	-	54	50	No
FD	Silanized (1% e.)	6.0 ± 1.1	-	-	84	82	No
FD	Silanized (0.2% e.)	5.8 ± 1.0	-	-	75	> 70	No
FD	Silanized (0.2% w.)	7.2 ± 1.8	-	-	76	-	No

For ED on standard glass, the measured τ_{max} (ca. 11 MPa) was in the same range of that measured for commercial structural or dental UV-curable adhesives [18,33]. Only for one specimen (over a total of six) the polymer disk was split between the two glass slides; adhesive failure was confirmed by a very low contact angle on the detachment site, similar to that measured on standard glass slides. For EDS, a slight increase of the average τ_{max} (ca. 13 MPa) was observed, still with a very low contact angle on the detachment site confirming adhesive rupture; the high standard deviation of τ_{max} , though, would make a more in-depth discussion too speculative. The use of silane to functionalize the glass substrates increased the adhesion to a larger extent. For ED joints, when the adherend was modified in 1 vol% silane solution in ethanol, two out of the six specimens showed breaking of the glass substrate prior to the failure of the joint, and τ_{max} was about 17 MPa; the contact angle of about 63° confirmed that silane remained attached to the glass, although the presence of a thin layer of ED resin could not be excluded. For the ED joints on glass modified with 0.2 vol% silane both in ethanol and water, the glass always broke before failure of the joint; therefore the τ_{max} of the joint can be supposed to be higher than the measured average stress at rupture (18.5 MPa). The test was repeated reducing the diameter of the adhesive area to 4 mm. In this case there was no rupture of the glass substrate, and τ_{max} of about 25 MPa (ethanol) and 30 MPa (water) were achieved. The lower adhesion strength obtained with the glass silanized in the more concentrated alcoholic solution could be attributed to the deposition of silane in polymer form, with the possibility of rupture within the silane layer itself; in the case of the less concentrated solutions, the silane molecules most likely formed a monolayer, resulting in a stronger link between the resin and the glass, even when not fully covering the glass surface.

For FD on standard glass all but one of the specimens separated while mounting in the clamps, and the one which did not, failed already with an applied force of 2 N, corresponding to a τ_{max} of 0.07 MPa. The FDS joints on the other hand had a τ_{max} close to 3 MPa, showing therefore a significant increase of adhesion thanks to the silane added into the formulation. With both FD and FDS on standard glass, a somewhat higher water contact angle at the detachment site was observed with respect to that initially measured for standard glass, which persisted after rinsing the surface with ethanol; small traces of the fluorinated resin therefore must have remained attached to the glass. The τ_{max} of the FD joints on silanized glass was double (i.e. 6 – 7 MPa) than that of FDS on standard glass, confirming the higher efficiency of glass silanization with respect to addition of silane in the formulation, as seen for ED. These values of τ_{max} were close to those obtained for a similar PFPE UV curable acrylate adhesive on perfluoropolyether polyurethanes, for which covalent bonds between the adhesive and the substrate were created by abstraction of hydrogen from OH groups and allylic insaturations [10]. For the FD joints on glass silanized in the 1 vol% solution in ethanol, for almost all specimens parts of the polymer disk were found attached on both glass slides. This happened for two out of six and one out of six specimens for FD on glass silanized in the 0.2 vol% solutions, in ethanol and in water, respectively; the θ_w at the site of detachment was higher than initially measured for the corresponding silanized glass, suggesting that resin residues remained attached to the glass. This may indicate that, due to the low tensile strength of the FD cured resin, the failure happened in the polymer close to the interface with silane, and not within the silane layer or at the silane/polymer bond.

Finally, for some of the tested specimens, after the lap-shear test, the polymer disks were removed from the glass substrate, in order to take FT-IR spectra on the two sides (spectra not shown here); no differences were found between the two sides of a same disk, confirming that there was no preferential detachment on one side due to conversion or composition gradients within the adhesive layer.

4. Conclusions

A highly fluorinated UV-curable resin, characterized by perfluoropolyether chains, was successfully used as adhesive for glass bonding as the polymer formed is highly chemically resistant. The curing of the resin was efficient due to the high reactivity of the resin; as also reported in previous work, the polymer formed was transparent and the glass joints were transparent too. Due to the high fluorine content, adhesion was obtained by using an acrylated silane: being able to form covalent bonds both with the glass substrate and with the methacrylic adhesive formulation, it was found to enhance the adhesive strength of the joints even when used in very low amount. The direct silanization of glass proved to be more efficient than the addition into the formulations, at least at the concentration chosen in this work (i.e., 2 phr). The adhesion strength of the PFPE photocured resin, measured as the τ_{max} of the glass joints, compared to a fluorine free resin, was lower. However, it showed a better resistance to water thanks to its hydrophobicity hindering the transport of water molecules at the resin/glass interface.

Acknowledgements

Funding: This work was supported by Politecnico di Torino and Compagnia di San Paolo within the programme “Create a network around your research idea”.

References

[1] Glass Bonding Adhesives Market Size | Industry Report, 2014-2025. https://www.grandviewresearch.com/industry-analysis/glass-bonding-adhesives-market (accessed April 5, 2018).

[2] Vitale A, Trusiano G, Bongiovanni R. UV-Curing of Adhesives: A Critical Review. Rev Adhes Adhes 2017;5:105–61. doi:10.7569/RAA.2017.097305.

[3] Mittal KL, Etzler FM. Adhesion in Pharmaceutical, Biomedical, and Dental Fields. Wiley; 2017.

[4] Woods JG. Radiation-Curable Adhesives. Radiation Curing, Springer, Boston, MA; 1992, p. 333–98. doi:10.1007/978-1-4899-0712-7_9.

[5] Roffey CG. Radiation-curable adhesives. Photogeneration of Reactive Species for UV Curing, Wiley, New York, NY; 1997, p. 631–41.

[6] Pizzi A. Principles of Polymer Networking and Gel Theory in Thermosetting Adhesive Formulations. In: Pizzi A, Mittal KL, editors. Handbook of Adhesive Technology, Revised and Expanded, Taylor & Francis Group; 2003, p. 181–92.

[7] UV Adhesives Market by Resin Type (Acrylic, Cyanoacrylate, Epoxy, Silicone, Polyurethane), Application (Medical, Electronics, Glass Bonding, Packaging, Transportation, Industrial Assembly) and Region - Global Forecast to 2021 - Research and Markets ltd; https://www.researchandmarkets.com/reports/3926486/uv-adhesives-market-by-resin-type-acrylic accessed 06/06/2018.

[8] Wang Y, Long J, Bai Y, Zhang C, Cheng B, Shao L, et al. Preparation and characterization of fluorinated acrylic pressure sensitive adhesives for low surface energy substrates. Journal of Fluorine Chemistry 2015;180:103–9. doi:10.1016/j.jfluchem.2015.09.007.

[9] Murata N, Nakamura K. UV-Curable Adhesives For Optical Communications. The Journal of Adhesion 1991;35:251–67. doi:10.1080/00218469108041012.

[10] Vitale A, Priola A, Tonelli C, Bongiovanni R. Improvement of adhesion between a UV curable fluorinated resin and fluorinated elastomers: Effect of chemical modification onto the mechanical

properties of the joints. International Journal of Adhesion and Adhesives 2014;48:303–9. doi:10.1016/j.ijadhadh.2013.09.033.

[11] Vitale A, Bongiovanni R, Ameduri B. Fluorinated Oligomers and Polymers in Photopolymerization. Chem Rev 2015;115:8835–66. doi:10.1021/acs.chemrev.5b00120.

[12] Abenojar J, Colera I, Martínez MA, Velasco F. Study by XPS of an Atmospheric Plasma-Torch Treated Glass: Influence on Adhesion. Journal of Adhesion Science and Technology 2010;24:1841–54. doi:10.1163/016942410X507614.

[13] Abenojar J, Martínez MA, Encinas N, Velasco F. Modification of glass surfaces adhesion properties by atmospheric pressure plasma torch. International Journal of Adhesion and Adhesives 2013;44:1–8. doi:10.1016/j.ijadhadh.2013.02.002.

[14] Walker P. Organosilanes as adhesion promoters. Journal of Adhesion Science and Technology 1991;5:279–305. doi:10.1163/156856191X00369.

[15] Walker P. Silane and Other Adhesion Promoters in Adhesive Technology. In: Pizzi A, Mittal KL, editors. Handbook of Adhesive Technology, Revised and Expanded, Taylor & Francis Group; 2003, p. 205–22.

[16] Zhang K, Li T, Zhang T, Wang C, Wang C, Wu M. Adhesion improvement of UV-curable ink using silane coupling agent onto glass substrate. Journal of Adhesion Science and Technology 2013;27:1499–510. doi:10.1080/01694243.2012.746159.

[17] Chiang TH, Hsieh T-E. The effect of organo-functional silanes on the adhesion of epoxide resins to ITO glass. Journal of Adhesion Science and Technology 2005;19:1–18. doi:10.1163/1568561053066927.

[18] Yoshihara K, Nagaoka N, Sonoda A, Maruo Y, Makita Y, Okihara T, et al. Effectiveness and stability of silane coupling agent incorporated in ‘universal’ adhesives. Dental Materials 2016;32:1218–25. doi:10.1016/j.dental.2016.07.002.

[19] Zaggia A, Ameduri B. Recent advances on synthesis of potentially non-bioaccumulable fluorinated surfactants. Current Opinion in Colloid & Interface Science 2012;17:188–95. doi:10.1016/j.cocis.2012.04.001.

[20] Iijima M, Sato N, Wuled Lenggoro I, Kamiya H. Surface modification of BaTiO3 particles by silane coupling agents in different solvents and their effect on dielectric properties of BaTiO3/epoxy

composites. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2009;352:88–93.

[21] Dalle Vacche S, Oliveira F, Leterrier Y, Michaud V, Damjanovic D, Månson J-AE. Effect of silane coupling agent on the morphology, structure, and properties of poly(vinylidene fluoride–trifluoroethylene)/BaTiO3 composites. J Mater Sci 2014;49:4552–64. doi:10.1007/s10853-014-8155-x.

[22] Williams S, Venkateswaran N, O'Donnell TDB, Crisalli P, Helmy S, Napoli MT, et al. Assessing Stability, Durability, and Protein Adsorption Behavior of Hydrophilic Silane Coatings in Glass Microchannels. Journal of Analytical & Bioanalytical Techniques 2016;7:1–8. doi:10.4172/2155-9872.1000318.

[23] Swentek I, Wood JT. Measuring polymer composite interfacial strength. Composites Part B: Engineering 2014;58:235–41. doi:10.1016/j.compositesb.2013.10.069.

[24] Wu S. Polymer interface and adhesion. New York; Basel: Marcel Dekker; 1982.

[25] Vitale A, Quaglio M, Cocuzza M, Pirri CF, Bongiovanni R. Photopolymerization of a perfluoropolyether oligomer and photolithographic processes for the fabrication of microfluidic devices. European Polymer Journal 2012;48:1118–26. doi:10.1016/j.eurpolymj.2012.03.016.

[26] Bongiovanni R, Medici A, Zompatori A, Garavaglia S, Tonelli C. Perfluoropolyether polymers by UV curing: design, synthesis and characterization. Polym Int 2012;61:65–73. doi:10.1002/pi.3149.

[27] ASTM D 870 – 02 Standard Practice for Testing Water Resistance of Coatings Using Water Immersion.

[28] Arkles B, Pan Y, Mi Kim Y. The Role of Polarity in the Structure of Silanes Employed in Surface Modification. Silanes Other Coupling Agents, vol. 5, 2009, p. 51–64. doi:10.1163/ej.9789004165915.i-348.37.

[29] allnex Group. UV Curable resins for Filament Winding 2018.

[30] Vitale A, Priola A, Tonelli C, Bongiovanni R. Nanoheterogeneous networks by photopolymerization of perfluoropolyethers and acrylic co-monomers. Polymer International 2013;62:1395–401. doi:10.1002/pi.4436.

[31] Pape PG. 29 - Adhesion Promoters: Silane Coupling Agents. In: Kutz M, editor. Applied Plastics Engineering Handbook, Oxford: William Andrew Publishing; 2011, p. 503–17. doi:10.1016/B978-1-4377-3514-7.10029-7.

[32] ASTM D5573-99(2012) - Standard Practice for Classifying Failure Modes in Fiber-Reinforced-Plastic (FRP) Joints. 2012.

[33] Machalická K, Eliášová M. Adhesive joints in glass structures: effects of various materials in the connection, thickness of the adhesive layer, and ageing. International Journal of Adhesion and Adhesives 2017;72:10–22. doi:10.1016/j.ijadhadh.2016.09.007.