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Modification of photocurable epoxides by new perfluoropolyalkylether alcohols for obtaining self-cleaning coatings

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Keywords

UV-curing; perfluoropolyalkylethers; self-cleaning

Abstract

Perfluoropolyalkylether (PFPAE) structures can be functionalized with alcoholic groups using an appropriate synthetic pathway: these new fluorinated alcohols can be used as surface modifying agents, through chain transfer mechanism in cationic UV-curing of an epoxy system. Notwithstanding their very low concentration (only ≤5 wt%), the fluorinated alcohols are able to induce a dramatic improvement to the surface properties of the films, without substantially modifying their curing conditions and their bulk properties, neither their transparency. As confirmed by Fourier Transform-Infra Red (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements, the fluorinated comonomers tend to concentrate selectively at the outermost layer of the epoxy UV-cured coatings, by spontaneously migrating to the free surface due to their low surface tension. The surface modification of the films depends on the concentration of the fluoroalcohols: coatings

prepared with a concentration of PFPAE comonomer higher than 2 wt% are both hydrophobic and oleophobic. Moreover, thanks to their low surface energy (as low as 17 mN m^{-1}) and reduced sliding angle (as low as 5°), photocured fluorinated copolymers show advanced coating performances such as anti-stain and self-cleaning properties.

1. INTRODUCTION

Cationic photopolymerization of epoxy monomers is a well-known process and has found a remarkable success in many industrial fields such as inks, coatings, adhesives and microelectronics [1, 2]. UV-curing techniques allow the facile and rapid synthesis of solid crosslinked polymer networks with distinctive physico-chemical properties starting from multifunctional liquid monomers. In particular, the photopolymerizable formulations are solvent free, the production rates are high, the energy required is much lower compared to thermal curing, and selectivity and flexibility in the use are guaranteed [3, 4]. Besides, cationic photopolymerization processes of epoxy monomers possess some distinct advantages, such as lack of inhibition by oxygen, low shrinkage, and good mechanical and adhesion properties of the UV-cured materials [1].

In order to impart the appropriate surface properties to UV-cured polymeric films, several chemical and physical methods have been developed, including chemical etching, plasma or thermal treatment, and surface grafting [5, 6]. To achieve this goal without substantially changing the overall bulk properties of the films, another interesting method is the use of specific reactive additives. For instance, when a low surface tension component (generally fluorinated or siloxane monomers) is added to a photocurable formulation, it migrates to the free surface, driven by thermodynamic forces, in order to minimize the total energy of the system. This spontaneous enrichment of the free surface of the low surface tension additive is an attractive, low-cost, easy, reliable method for functionalizing polymer surfaces [7-9] and obtaining materials that may be useful in different fields, such as adhesives, hydrophobic, easy-to-clean, antifouling, and self-replenishing coatings [10-13].

Perfluoropolyalkylethers (PFPAEs) are a unique family of fluoropolymers: they typically contain one or two of the repetitive units $–CF_2O–$, $–CF_2CF_2O–$, $–CF_2CF_2CF_2O–$, $–CF(CF_3)CF_2O–$, while the terminal groups can be $CF_3O–$, $C_2F_5O–$ and $C_3F_7O–$, depending on the synthesis route [14]. PFPAEs are non-toxic, even when the fluorinated chains are long [15], and they demonstrate outstanding properties,

such as high thermal and chemical resistance, low refractive index and very low surface tension [16]. In fact, the existence of polarity in the partially fluorinated polymers strongly influences the interfacial properties, leading to a reduction of adhesion and friction, to a good protection against corrosion, environmental pollution, weather aggression and graffiti: all peculiar coating characteristics [17-19].

PFPAEs can also be used as interesting building blocks for preparing monomers reactive in photopolymerization [8, 16, 20, 21]. In this work, new PFPAE oligomers were synthesized by the anionic ring-opening reaction of hexafluoropropylenoxide (HFPO) with cesium fluoride and functionalized with an -OH end group [22]. In fact, as a cationic mechanism applies in the curing of epoxy resins, alcohols act as chain transfer agent [23] and can be used to selectively modify the surface properties of the polymer [24]. The surface of epoxy coatings prepared with a concentration of PFPAE alcohol ≤5 wt% were found to be both hydrophobic and oleophobic, having a surface energy as low as 17 mN m^{-1}; moreover, they showed anti-stain and self-cleaning behavior assuring the removal of dirt particles simply by the (rain) water.

2. MATERIALS AND METHODS

2.1 Synthesis of the fluorinated alcohols $HFPO_n$-MA

Two oligo(HFPO) methylene alcohols ($HFPO_n$-MA, with n=5 and n=10) were synthesized according to a modified procedure reported in [22].

2.1.1 Materials

The oligo(HFPO) acyl fluoride was synthesized using cesium fluoride (from Sigma Aldrich, Canada) as initiator, tetraethylene glycol dimethyl ether (from Sigma Aldrich, Canada) and HFE-7100 (from 3M™ Novec™, USA) as solvents, and hexafluoropropylene oxide (generously supplied by Chemours™, USA) as monomer. Lithium aluminum hydride (LAH), diethyl ether, sulfuric acid and all other chemicals were purchased from Sigma Aldrich (Canada).

2.1.2 Procedure

For the synthesis of $HFPO_5$-MA, $LiAlH_4$ (0.2046 g, 5.391 mmol, 0.25 equiv.) was added to a 500 mL 3-necked round-bottomed flask. The oligo(HFPO) acyl fluoride M_n=1200 g mol^{-1}, (25.138 g, 20.11 mmol) was introduced into a 20 mL I-Chem™ 100 series vial in a dry box. Under a N_2 blanket in the fume hood, 50 mL of anhydrous diethyl ether (dried over molecular sieves, then refluxed with

sodium/benzophenone and distilled into a Schlenk) were transferred via cannula into an addition funnel and added dropwise to the $LiAlH_4$ and left to stir for 15 minutes. The oligo(HFPO) acid fluoride was then added dropwise via the addition funnel to the solution of $LiAlH_4$, over two hours keeping the flask (equipped with a condenser) on ice. After the addition, the mixture was left to stir for 16 hours under N_2. The solution was then poured carefully into a beaker filled with ice and 10% H_2SO_4. The mixture was then washed with concentrated H_2SO_4 (50 mL) and returned to neutral pH by 7 D.I. water washes. Excess water was removed by rotary evaporation and then under reduced pressure for 20 hours. The resulting viscous cloudy-white product was filtered through a Whatman 2 µm GMF-150 filter to remove particulates. The isolated yield was 89%.

^{1}H-NMR (400 MHz, DMSO-d_6 capillary, 25 °C) δ = 3.66 (s-broad, -CF(CF_3)CH_2O**H**, 1H), 3.45 (d, -CF(CF_3)C**H_2**O-, 2H, $^3J_{H-F}$ = 14.8 Hz).

^{13}C-NMR (400 MHz, DMSO-d_6 capillary, 25 °C) δ = 122.24-99.26 (*m*, carbons of repeat unit), 59.00 (*d*, -**C**H_2OH).

^{19}F-NMR (376.5 MHz, Benzene-d_6, F-11 as reference, 25 °C) δ = -146.04 (*q*, C***F***(CF_3) of repeat unit), -137.67 (ω C***F***(CF_3)), -131.53 (*s*, α C***F₂***), -84.34 to -80.01 (CF_3 and CF_2 of repeat unit).

GC/MS (EI) fragmentation: m/z = CH_2OH^+ (31 m/z), CF_3^+ (69 m/z), $C_2F_4^+$ (100 m/z), CF(CF_3)CH_2OH-HF^+ (111 m/z), $C_2F_5^+$ (119 m/z), $C_2F_4CH_2OH^+$ (131 m/z), $C_3F_5O^+$ (147 m/z), $C_3F_6^+$ (150 m/z), $CH_2CHOCH_2CF(CF_3)^+$, (157 m/z), $C_3F_7^+$ (169 m/z).

The synthesis of $HFPO_{10}$-MA was performed following the same procedure reported above. The isolated yield was 93%.

^{1}H-NMR (400 MHz, DMSO-d_6 capillary, 25 °C) δ = 3.47 (*d*, -CF(CF_3)C**H_2**O-, 2H, $^3J_{H-F}$ = 14.8 Hz), 3.17 (*s*-broad, -CF(CF_3)CH_2O**H**, 1H). Some impurities were present: 5.28-5.14 (*d*, -CF(CF_3)**H**), 1H) attributable to the HFPO II hydrogen end cap, 3.34 (*s*, -O(C**H_2**CH_3), 4H), 0.62 (*s*, -O(CH_2C**H_3**), 6H) attributable to diethyl ether.

^{13}C-NMR (100 MHz, DMSO-d_6 capillary, 25 °C) δ = 121.94-99.47 (*m*, carbons of repeat unit), 59.02 (*d*, -**C**H_2OH). Impurities: 72.38 (*s*, -O(**C**H_2CH_3)), 17.97 (*s*, -O(CH_2**C**H_3)) attributable to diethyl ether.

^{19}F-NMR (376.5 MHz, Benzene-d_6, F-11 as reference, 25 °C) δ = -146.31 (*q*, C***F***(CF_3) of repeat unit), -137.91 (ω C***F***(CF_3)), -131.87 (*s*, α C***F₂***), -84.96 to -80. 43 (CF_3 and CF_2 of repeat unit). Impurities: -148.18 – -148.03 (*d*, -C**F**(CF_3)H), 1H) attributable to the HFPO II hydrogen end cap.

GC/MS (EI) fragmentation: m/z = CH_2OH^+ (31 m/z), CF_3^+ (69 m/z), $C_2F_4^+$ (100 m/z), CF(CF_3)CH_2OH-HF^+ (111 m/z), $C_2F_5^+$ (119 m/z), $C_2F_4CH_2OH^+$ (131 m/z), $C_3F_5O^+$ (147 m/z), $C_3F_6^+$ (150 m/z), $CH_2CHOCH_2CF(CF_3)^+$ (157 m/z), $C_3F_7^+$ (169 m/z).

2.2 Photoinduced polymerization

2.2.1 Materials

The epoxy resin used in this work was 1,6-hexanediol diglycidyl ether (HDGE, Grilonit® RV 1812 by EMS, Switzerland). A series of blends were prepared by addition of the PFPAE alcohols $HFPO_n$-MA (n=5 and 10), synthesized on purpose for the work as reported above. Triphenylsulfonium hexafluoroantimonate salts, 50 wt% in propylene carbonate, purchased from Sigma Aldrich (Italy), was used as the cationic photoinitiator.

2.2.1 Procedure

Photocurable formulations were prepared by adding to HDGE monomer different amounts of the two fluorinated alcohols up to 5 wt%, and 2 wt% of the photoinitiator. The UV-sensitive mixtures were coated onto a glass substrate, using a wire-wound applicator, and then irradiated by means of a high-pressure mercury arc lamp Dymax ECE, using a light intensity of 150 mW cm^{-2} for 5 minutes. Samples with different thickness, going from 100 µm to 300 µm, were prepared.

After irradiation, the samples were stored for at least 24 h at room temperature before properties evaluation, to allow a complete dark postcuring reaction, typical of cationic process. The films were then peeled away from the substrate, labeling the side in contact with the substrate as 'glass side', and the other one as 'air side'.

In order to check the conversion of the photopolymerization reaction, real-time Fourier Transform-Infra Red (FT-IR) spectroscopy analyses were performed using a Nicolet™ iS50 FT-IR spectrometer (Thermo Fisher Scientific). Simultaneously with the FT-IR scan acquisition, thin films (i.e. about 10 µm on a Si wafer as substrate) of the reactive monomeric mixtures were irradiated with a UV Hamamatsu LC8 lamp, provided of an optical fiber, having an intensity equal to 100 mW cm^{-2}. Polymerization conversion was followed by monitoring the decrease in the absorbance due to epoxy groups in the region 900–920 cm^{-1} as a function of irradiation time.

2.3 Polymer characterization

Attenuated Total Reflectance (ATR) FT-IR analyses were performed on the reactive monomeric mixtures and the cured polymers with a Nicolet™ iS50 FT-IR spectrometer (Thermo Fisher Scientific), using a diamond probe. ATR FT-IR spectra were also used to calculate the monomer-to-polymer conversion by measuring the area of the absorption band of the reactive functionality (epoxy group in the region 900–920 cm^{-1}).

The insoluble fraction (gel content) of the crosslinked samples was evaluated by the weight loss of the network after 24 h extraction by chloroform at room temperature (ASTM D2765).

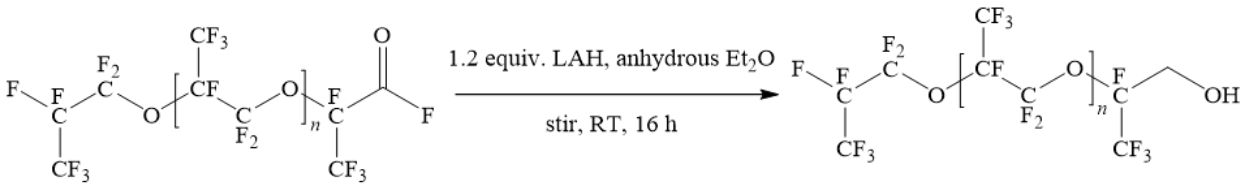
Differential scanning calorimetry (DSC) thermograms were recorded using a Mettler Toledo DSC1 STARe System in the temperatures ranging from -60 °C to 150 °C using a heat/cool/heat method at a heating and cooling scanning rate of 10 °C min^{-1}, under nitrogen flux. The glass transition temperature (T_g) was determined using the midpoint of the heat capacity jump on the second heating cycle thermogram.

A PHI 5000 VersaProbe instrument (Physical Electronics) was utilized for X-ray photoelectron spectroscopy (XPS) analysis. A monochromatic Al Kα X-ray source (1486.6 eV, 15 kV voltage, and 1 mA anode current), a power of 25.2 W, and a pass energy of 187.85 eV were used. Analyses were carried out with a takeoff angle of 45° and with a 100 µm diameter X-ray spot size.

Static contact angle measurements were performed with a FTA 1000C instrument, equipped with a video camera and image analyzer, at room temperature with the sessile drop technique. Three to five measurements were performed on each sample and the values averaged. The measuring liquids were water and hexadecane, whose surface tension are 72.1 mN m^{-1} and 28.1 mN m^{-1}, respectively. The surface energy was calculated by the Owens-Wendt geometric mean method [25]. For the sliding angle measurements [26], the same FTA 1000C apparatus was employed, equipped with a tilting stage. After placing a 20 µl liquid drop on the test surface, the film was tilted at 0.5 ° s^{-1}.

3. RESULTS AND DISCUSSION

Two $HFPO_n$-MA alcohols were synthesized by the reduction of the corresponding oligo(HFPO) acyl fluoride with lithium aluminum hydride prepared as described in previous works [27, 28] (Scheme 1).

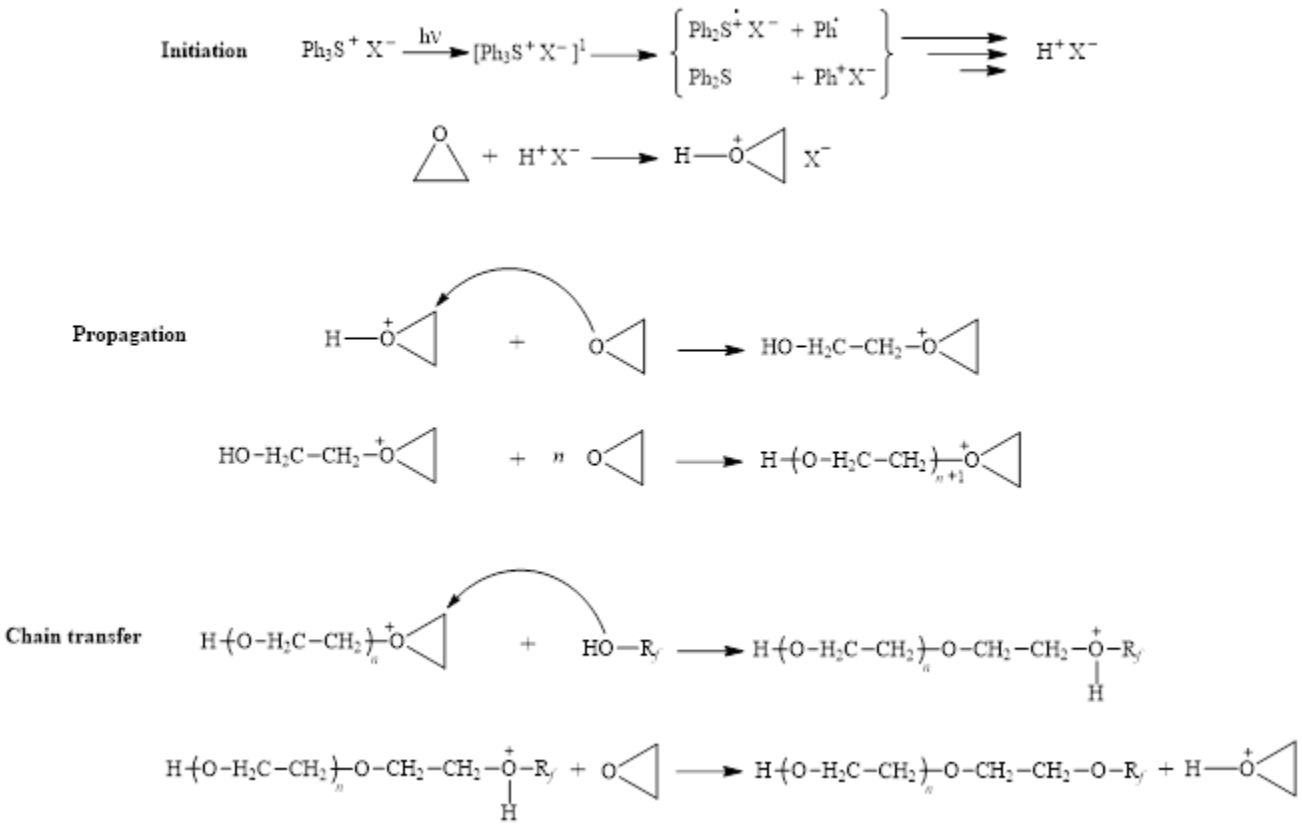


Scheme 1. Synthetic path leading to the $HFPO_n$-MA monomers.

The alcohols were obtained in good yield and high purity. The structures were confirmed by NMR, GC-MS, MALDI-TOF (see Supporting Information, Figure S1-S12). The reaction allowed a high control

of the fluorinated molecular length: two oligo(HFPO) methylene alcohols were prepared, namely $HFPO_5$-MA and $HFPO_{10}$-MA, having M_n=1170 and M_n=2020 respectively, as evaluated by ^{19}F-NMR (Figure S3 and Figure S9 of the Supporting Information).

$HFPO_n$-MA were used as chain transfer agent in the photoinduced cationic polymerization of a difunctional diepoxide (i.e., HDGE) commonly used as a resin in UV-cured coating formulations. Scheme 2 shows The mechanism of the photopolymerization reaction of an epoxy monomer and of the chain transfer due to the presence of an alcohol. The $HFPO_n$-MA alcohols were added in low amount (≤5 wt%) to the diepoxide, assuring by visual inspection that no phase separation was occurring; a sulphonium salt was chosen as a photoinitiator.



Scheme 2. Mechanism of the photoinduced polymerization of an epoxy monomer and the chain transfer occurring in the presence of a fluorinated alcohol (R_f stands for the oligo(HFPO) chain).

In Fig. 1 the conversion curve as a function of irradiation time for HDGE is reported and compared with the systems containing 2 wt% and 5wt% of $HFPO_n$-MA. Data were obtained by monitoring the reaction in situ during irradiation, measuring the disappearance of the oxirane ring by transmission FT-IR spectroscopy on thin films. As expected for cationic photopolymerization, even if the reactions

did not take place in an inert atmosphere, there is no induction time and the conversion initially increases very rapidly. Then it slows down in all systems: while the crosslinking polymerization proceeds, the physical state of the medium changes from a viscous liquid to a viscoelastic rubber (as indicted by the DSC data discussed below), causing a dramatic variation of the mobility of the reactive species and changing the propagation rate. All the investigated systems reached a conversion of more than 80% in less than 10 min. It is evident that the presence of the fluorinated alcohols, even if added in very low concentration, has a slight influence on the curing reaction, and on the initial rate of polymerization. This effect can be due to the occurrence of the chain transfer reactions and to the reduction of the system viscosity with the addition of the monofunctional $HFPO_n$-MA. Photopolymerization kinetics data were also confirmed by photo-DSC (Figure S13 in the Supporting Information).

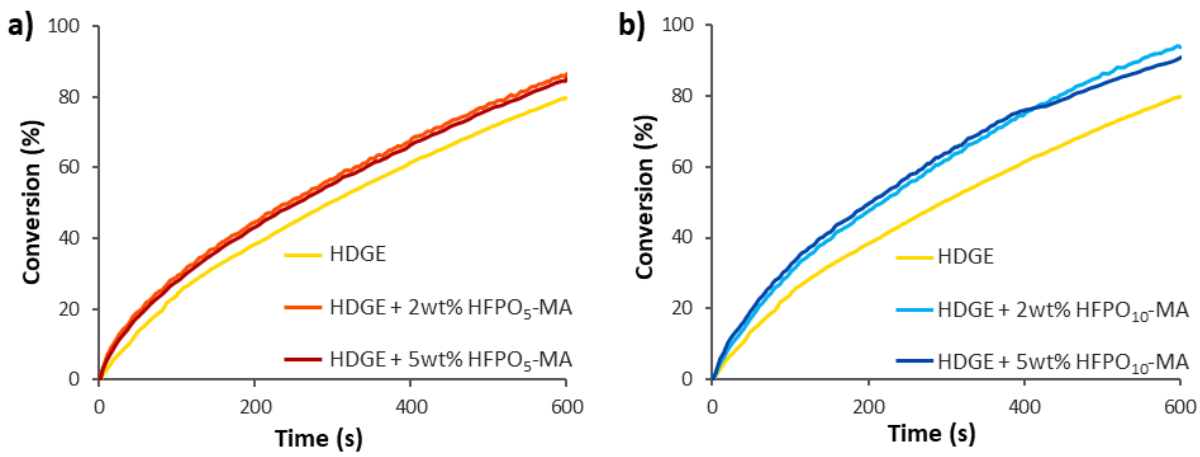


Fig. 1. Conversion of the oxirane FT-IR band at 910 cm^{-1} during irradiation of HDGE and HDGE with $HFPO_5$-MA (a) and with $HFPO_{10}$-MA (b).

Photocured coatings on glass slides were then prepared for characterization. ATR FT-IR spectroscopy was conducted to control the polymer on both sides of the film (spectra are reported as Figure S14 in the Supporting Information) and check their final conversion. Interestingly, in the spectra of the copolymers the C–F stretching band at 1240 cm^{-1} confirms the presence of the fluorinated comonomer; in particular the band is present on both sides of the film but is more intense on the air side (i.e., the free surface of the coating). The decreasing of the O–H stretching band at 3500 cm^{-1} with respect to neat HDGE is due to the propagation and chain transfer reactions.

In Table 1 the final conversions measured by ATR FT-IR spectroscopy are reported, together with the value of the insoluble fraction of the coatings (gel %). Data show that the experimental

photopolymerization conditions assure a quantitative and uniform crosslinking of the polymeric films. In particular, higher degrees of final conversion are obtained, compared to the values reported in Fig. 1, due to the higher light intensity employed for photocuring the samples analyzed by ATR FT-IR and especially to the dark postcuring reaction, typical of cationic systems. In fact, ATR FT-IR spectra were recorded after storing the samples for 24 h at room temperature after irradiation, and not in real-time as for the conversion curves of Fig. 1.

The curing reaction of pure HDGE monomer gave rise to films having a glass transition temperature of -6 °C (measured by DSC). The copolymers containing $HFPO_n$-MA were rubbery as well (being the T_g of pure $HFPO_n$-MA lower than -50 °C [29]), and their glass transition temperatures were found unchanged with respect to HDGE: the physical state of the copolymers was thus independent of the presence of the fluorinated monomer. Also the bulk mechanical properties (analyzed by dynamo-mechanical tests) were found to be unaffected by the inclusion of a low amount (i.e., ≤5 wt%) of $HFPO_n$-MA comonomer. Moreover, all the prepared photocured copolymeric films were transparent.

Table 1. Final conversion measured by ATR FT-IR spectroscopy and insoluble fraction measured by extraction in CH_2Cl_2 of HDGE, HDGE + 2wt% $HFPO_5$-MA and HDGE + 2wt% $HFPO_{10}$-MA.

Coating	Final Conversion (%)		Insoluble fraction
	Air side	Glass side	(%)
HDGE	97	99	92
HDGE + 2 wt% $HFPO_5$-MA	98	99	95
HDGE + 2 wt% $HFPO_{10}$-MA	98	99	95

Static contact angle measurements as a function of the fluorinated alcohol concentration were performed with a polar liquid (i.e., water) to evaluate the hydrophobic character of the coatings. The values are plotted as a function of $HFPO_n$-MA concentration in Fig. 2. It is possible to observe that depending on the fluorinated alcohol concentration, the water wettability changes: the contact angle of the air side increases with an asymptotic trend that already levels off at above 2 wt% content of the PFPAE alcoholic additive. At the plateau, the water wettability of the films overtakes 90°, which is considered the threshold value for hydrophobicity.

As shown in Fig. 2, the PFPAE alcohol with a higher molecular weight ($HFPO_{10}$-MA) is slightly more efficient as a surface modifier: higher values of water contact angle on the air side are obtained compared to systems containing $HFPO_5$-MA.

For all the investigated photocured coatings the modification was permanent: the films were stored in air, the wettability was checked after 24 h and after two weeks from the film preparation and the contact angle values were almost unchanged. This is an indication that the fluoroalcohol is covalently linked to the network as it takes part in the polymerization process through a chain transfer mechanism involving the hydroxyl groups [23, 24]. As a further proof of the chemical bonds between the fluorinated comonomer and HDGE network, some extraction tests were performed (results are reported in the Supporting Information, Figure S15).

From Fig. 2 one can notice that indeed the additive strongly modifies the air side of the film, while the glass side (i.e., the side in contact with the substrate during photocuring) experiences a more limited increase of water contact angle. Interestingly, wettability data on the air side are very similar to that typically shown for highly fluorinated materials (like semifluorinated polymers), suggesting that the external surface of the film is very rich in fluorine in spite of the low total amount of fluorinated alcohol added to the resin. This effect could be a consequence of the spontaneous surface segregation of the lower surface energy component, in our case the fluorinated alcohol, that has migrated towards the less polar surface, therefore the one exposed to air. Surface segregation of low surface energy chains is a well-known phenomenon detected before [8, 9]. Photocured films containing comonomers of different polarity can show a chemical composition changing along their thickness: in order to minimize the total free energy of the system, the component of lower surface tension is enriched on the free surface of the sample, and its concentration gradually decreases from the surface to the bulk.

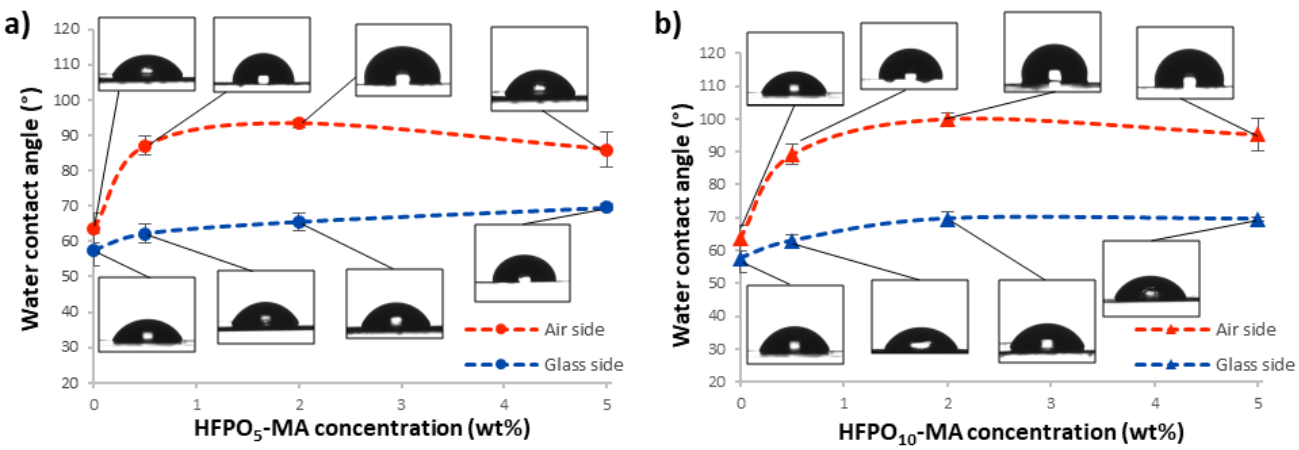


Fig. 2. Static water contact angle of HDGE + $HFPO_5$-MA (a) and HDGE + $HFPO_{10}$-MA (b), measured both on the air side and on the glass side, as a function of the fluorinated comonomer concentration. Insets are images of the water drops deposited on the photocured films.

The surface segregation is due to the migration of the fluorinated comonomers while in the liquid state, before curing: after crosslinking takes place, the surface segregation is made permanent with an increasing hydrophobicity of the final films only on the air side. According to the literature results for similar systems, there is no migration and segregation of the fluoromonomer on the surface in contact with a polar material like glass. However, as shown in Fig. 2, for the investigated systems the spontaneous surface segregation of the fluoroalcohol is not complete and, when the $HFPO_n$-MA comonomer is added, the water contact angle on the glass side increases of approximately 10°.

The surface segregation of the PFPAE additive was also confirmed by preliminary XPS measurements: in a HDGE + 2 wt% $HFPO_{10}$-MA film, the theoretical F concentration should be 1.4 wt%, while a concentration of 64.5 wt% was detected on the air surface. This result indicates that most of the fluorinated comonomer is located in the outermost layer of the crosslinked network.

The oleophobic properties of the photocured HDGE-based coatings were evaluated by measuring the static contact angle with a nonpolar liquid (i.e., hexadecane). As reported in Fig. 3, the hexadecane contact angle values of the air side indicate that an oleophobic surface is obtained: from a contact angle of 10° shown by the pure epoxy resin, a maximum contact angle around 70° could be reached with the addition of only ≈2 wt% of fluorinated comonomer.

Therefore, omniphobic coatings (i.e., showing simultaneously hydrophobicity and oleophobicity) were easily obtained.

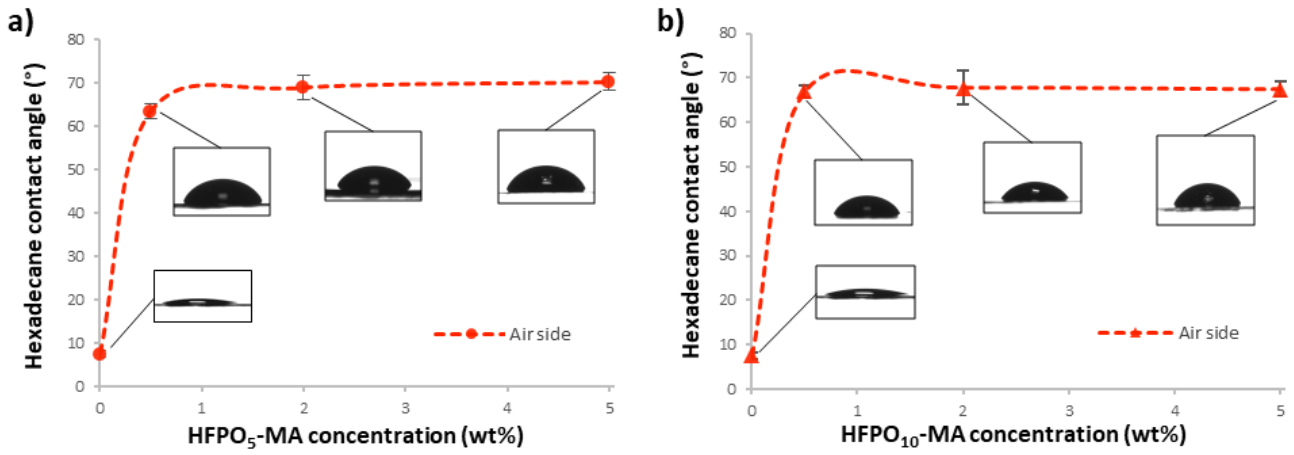


Fig. 3. Static hexadecane contact angle of HDGE + $HFPO_5$-MA (a) and HDGE + $HFPO_{10}$-MA (b), measured on the air side, as a function of the fluorinated comonomer concentration. Insets are images of the hexadecane drops deposited on the photocured films.

As expected on the basis of the wettabilities, the surface energy γ of the copolymers is quite low due to the presence of fluorine. Values are collected in Table 2: the surface energy strongly decreases in the presence of the fluoroalcohol, and especially the polar component γ^p is the most responsible of the decrease of γ values. In fact it is as low as 4 mN m^{-1}, while for the neat HDGE cured polymer γ^p=15 mN m^{-1}.

Table 2. Surface energy γ, divided in its dispersive (γ^d) and polar (γ^p) components, on the air side of HDGE, HDGE + 2 wt% $HFPO_5$-MA and HDGE + 2 wt% $HFPO_{10}$-MA.

Coating	Surface energy (mN m^{-1})		
	γ^d	γ^p	γ
HDGE	27	15	42
HDGE + 2 wt% $HFPO_5$-MA	13	6	19
HDGE + 2 wt% $HFPO_{10}$-MA	13	4	17

Low surface energy can guarantee a difficult wettability of most surfaces and repellency towards most liquids: anti-graffiti and anti-staining properties, for example, can be foreseen. The comparison of droplets of different liquids (i.e., water-based ink and olive oil) on glass slides with or without the fluorinated HDGE + 2 wt% $HFPO_5$-MA coating (Fig. 4) confirms that the copolymers can have interesting applications. Moreover, Fig. 4 also shows the transparency of the copolymeric films.

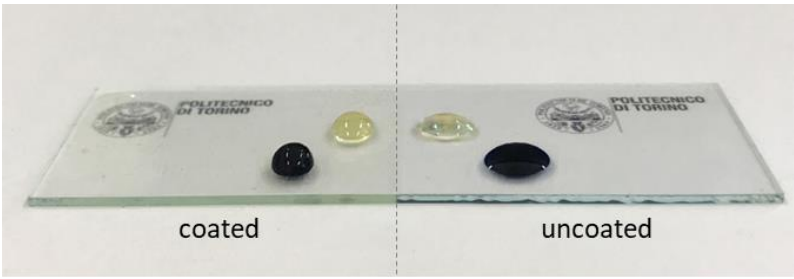


Fig. 4. Anti-stain properties of HDGE + 2 wt% $HFPO_5$-MA coating. A drop of water-based blue ink and extra virgin olive oil was deposited on the coated glass slide (left) and on the uncoated glass slide (right).

The copolymers surface behavior was also tested by the sliding angle, i.e. the angle at which the drop of a test liquid slides away on the surface of the film. The measured values are reported in Table 3. It can be observed that both using water or hexadecane the sliding angles of HDGE-based copolymers are extremely low, in fact they are lower than 10°.

Table 3. Sliding angle measured with water and hexadecane on the air side of HDGE + 2 wt% $HFPO_5$-MA and HDGE + 2 wt% $HFPO_{10}$-MA.

Coating	Sliding angle (°)	
	Water	Hexadecane
HDGE + 2 wt% $HFPO_5$-MA	7 ±3	8 ±1
HDGE + 2 wt% $HFPO_{10}$-MA	5 ±1	8 ±3

The low values of sliding angle obtained for the cured fluorinated copolymers lead to the assumption that the surfaces of the films have potential self-cleaning properties. Fig. 5 collects a series of shots of the action of a drop of water deposited on a HDGE + 2 wt% $HFPO_{10}$-MA coating covered with a fine powder of red pepper: the drop slides over the polymer film and removes the particulate, which preferably leaves the coating and stays in the water drop.

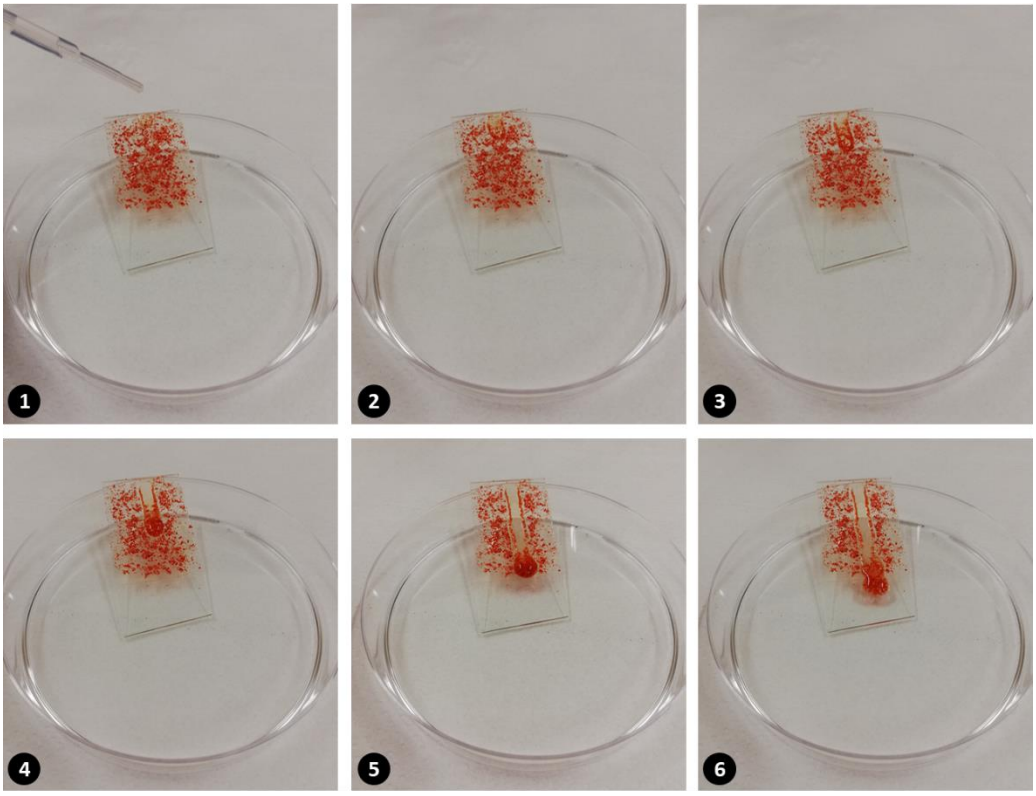


Fig. 5. Self-cleaning properties of a HDGE + 2 wt% $HFPO_{10}$-MA film coated on a glass slide. The surface of the coating was covered with a fine red pepper powder; a drop of water was deposited on the sample, which was tilted of 30°. A sequence of images was captured while the water drop was sliding on the surface of the film, removing the powder.

4. CONCLUSIONS

Cationic UV-curing technique was used to polymerize an epoxy monomer in the presence of two synthesized monofunctional PFPAE alcohols ($HFPO_n$-MA) with different molecular weight, with the aim of inducing a selective surface modification toward a lower wettability of the cured coating in a simple and effective way. Very high degrees of final conversion of the photocured films were achieved, also exploiting the dark postcuring reaction typical of cationic systems. When the fluoroadditives were introduced in the UV-curable mixture, notwithstanding the low concentration (always lower than 5 wt%), completely hydrophobic and oleophobic surfaces were obtained on the air side, showing contact angles ≈95° and ≈70° with water and hexadecane, respectively. Whereas, on the substrate side, only a limited decrease of the wettability was observed with the addition of the PFPAE alcohols: this effect could be a consequence of the surface segregation of the fluorinated comonomer, which spontaneously migrates towards the less polar surface before and during photocuring. The surface modification obtained is permanent because the alcoholic additive is covalently linked to the network as it takes part in the polymerization process through a chain transfer mechanism. Due to their low surface energy, the UV-cured coatings demonstrated remarkable anti-stain properties. In addition, the fluorinated copolymers showed extremely low sliding angles (<10°), which guaranteed interesting self-cleaning properties.

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