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Specific, nondestructive, and durable adhesion primer for polyolefins

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Abstract Gluing polyolefins [e.g., polyethylene (PE) and polypropylene (PP)] results in a very challenging task. The main reason relies on their low surface energy, which reduces the affinity between the polyolefin surface and the chosen adhesive. To tackle this problem, the most commonly used solutions are physical surface treatments, such as plasma, corona, and flame, which introduce hydrophilic moieties on the plastics surface, thus increasing their surface energy. These approaches require special setups, are unspecific, and can induce material degradation. Furthermore, they provide a transient solution, making the storage of pretreated substrates not recommended. In this work, we developed an easy-to-apply primer for durable bonding of adhesives on PE and PP, as robust alternative to physical treatments. Our primer contains a surface-anchoring moiety and an adhesive-binding group to covalently react with the polyolefin substrate and with the glue. As a surface-anchoring moiety, we chose the perfluorophenylazide (PFPA), which is known to undergo a C–H insertion reaction upon UV activation, while as adhesive-binding groups, we selected OH functions, which can covalently react with the most common commercially available glues. When these two features (i.e., PFPA and OH) are combined in a single molecule, the reaction with the substrate does not occur and the molecule is only physisorbed, inducing no adhesion improvement. Chemisorption only occurs with bicomponent formulations, comprising a hydrophobic trifunctional PFPA and a polymer bearing OH and PFPA groups. Those induced improved adhesion on PP compared to the golden standard plasma with polyurethane-based and two-component epoxy adhesives. Storing the coated substrates at room temperature for up to two months did not alter the adhesion performance, thus further ascribing the developed primers as a promising alternative to plasma treatment.

Keywords Primers and coupling agents, Plastics, Surface treatment by chemical solutions, Adhesion by chemical bonding, Perfluorophenylazide

Introduction

The polyolefins polyethylene (PE) and polypropylene (PP) account for approximately half of the worldwide plastic production. In 2014, about 150 million tons of PE, PP, and polyolefin copolymers were produced worldwide.[1] PE is by far the most widely used (standard) plastic and is the main constituent of packaging materials. However, PE is also found in, e.g., high-quality ropes, endoprostheses, and gears. PP is instead the most abundant plastic in automobiles, where it is employed for the production of car bumpers, cable insulation, and carpet fibers. Despite their enormous industrial relevance, PE and PP without suitable pretreatment can only be bonded or coated poorly or not at all. The reason for this is that PE and PP, like most plastics, are hydrophobic by nature and have a low surface energy. Surface modification or surface activation are thus required to make these plastics bondable. Industrially approved methods

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to modify polymer surfaces and increase their adhesion include mechanical abrasion, solvent treatment, wet chemical etching,[2] adsorption of polar monomers from solution,[3] flame treatment,[4] corona,[5] or plasma activation.[6–8] Among these approaches, plasma, corona, and flame treatments have enormously developed since the first systematic investigations in 1960s,[9,10] and are now well established. In these processes, the surface is oxidized in a dosed manner, in order to introduce polar reactive groups, which increase surface energy and improve surface wetting. Although they are relatively easy to carry out and thus attractive, these processes present serious drawbacks. First of all, several different, oxygen-containing groups are randomly generated on the plastic surface.[11] The introduction of these polar groups increases the surface energy and rather nonspecific interactions between the oxidized surface and the adhesive can be obtained. However, not all the oxygen-containing groups are suited for chemical bonding with the adhesive. Secondly, for thermodynamic reasons, namely because of the rather similar bond energies of a C–H (397 kJ/mol in PE) and a C–C (370 kJ/mol in PE) bond, extensive chain scissions occur during oxidative activation. This means that strong polymer degradation is unavoidable in the oxidative processes and chain degradation weakens the adhesion.[12] Finally, the activation is not permanent because the pristine surface properties are restored over time, mainly due to hydrophobic recovery. This phenomenon is the thermodynamic response of polymers to balance concentration gradients between bulk and surface. Various mechanisms have been proposed to explain it.[13] Reorientation and diffusion of polymer chain segments, together with the functional groups, is often responsible for hydrophobic recovery. The net consequence is a progressive decrease of the surface energy of oxidatively activated polymers, which makes the activation transient and inhibits the storage of the activated polymer substrates.

In order to tackle these drawbacks, we propose a specific, nondestructive, and permanent treatment to improve the adhesion performance of polyolefins, with respect to pristine and plasma-activated analogs. In particular, we describe here adhesion promoters (primers) for, e.g., PE and PP based on azide/nitrene chemistry.[14,15] Light or temperature-activated organic azides produce highly reactive and transient nitrenes,[16] which can undergo rearrangements or insert in C-H bonds.[17,18] In order to suppress the former nitrene reactions and favor the latter, fluorine atoms as aromatic substituents are needed.[15,19] Although per- and polyfluorinated alkyl compounds (a.k.a. PFAS) are currently generating more and more concern due to their non- or low-biodegradability and dangerous accumulation,[20] perfluorophenylazides (i.e., PFPA) and their precursors are not considered to be either persistent, bioaccumulative and toxic (PBT) substances.[21,22] Thus, they have been extensively applied as photoaffinity labels in biology[23] and adhesion promoters in material science.[14,24,25] As an adhesive-affinity group, a hydroxyl function is additionally bound to the adhesion promoter.

The adhesion promoter proposed here should not have any of the shortcomings mentioned above:

1. Only hydroxyl functions are introduced as adhesive-reactive groups.
2. Selective C–H insertion does not lead to chain scission.
3. Because the grafted molecules are relatively large, rotation of the PE chains and thus hydrophobic recovery is hindered.

For these reasons, the primers described here are envisioned to overcome the adhesion performance of the oxidative processes on PE and PP, resulting in a promising alternative to improve the current industrial solutions.

Experimental methods and materials

Materials

All the chemicals were used without need of further purification and, if not herein listed, acquired from Sigma-Aldrich. The precursor pentafluorobenzoyl chloride was purchased from Apollo Scientific Ltd, UK. Dichloromethane [ROTIDRY® ≥ 99.8% (≤ 50 ppm H_2O)] and isopropanol were purchased from Carl Roth. Methanol, ethanol, and acetone were acquired from Fluka and tannic acid was purchased from Riedel-de Haën.

The PE and PP substrates (Rocholl, Nature, 200 × 300 × 2 mm^3 or 100 × 25 × 4 mm^3) and the polyurethane-based and acrylate-based adhesives were kindly provided by Sika Technology AG. As epoxy-based adhesive Araldite Rapid (two components) was used, cyanoacrylate-based adhesive LOCTITE 420 was purchased from KVT-Fastening GmbH.

Characterization

ATR-IR spectra were acquired in the range 4000–400 cm^{-1} using a Bruker Alpha FTIR spectrometer. ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra were recorded on a Bruker Ascend™ 500 MHz, using $CDCl_3$ or DMSO-d_6 as solvents. Gel permeation chromatography (GPC) was performed on a SECcurity[2] GPC Systems from PSS GmbH, Mainz, Germany. Static water and diiodomethane contact angles and corresponding surface energies were measured using a Krüss Mobile Surface Analyzer MSA Hamburg, Germany. XPS spectra were obtained using a SPECS™ spectrometer from SPECS GmbH, Berlin, Germany. Lap shear tests were performed on a Zwick/Roell Z5.0 Ulm, Germany.

Synthesis of the primers

2-[bis[2-(2,3,5,6-tetrafluoro-4-azido-benzoyl)oxyethyl] amino]ethyl 2,3,5,6-tetrafluoro-4-azido-benzoate (Triazide)

The synthesis of the triazide consisted of two steps. First the precursor 2-[bis[2-(2,3,4,5,6-pentafluorobenzoyl)oxyethyl]amino]ethyl 2,3,4,5,6-pentafluorobenzoate (triester) was produced and isolated. In the second step, the triester was converted into triazide.

In order to obtain the triester, 5.0 g (33.5 mmol) triethanolamine was dissolved in 100 mL dry dichloromethane (DCM). The solution was put under an inert atmosphere of dry nitrogen and cooled down to 0 °C. Then, 11.2 g (111 mmol) triethylamine was then added and the solution was left under stirring at 0 °C. After 30 min, 24.3 g (106 mmol) pentafluorobenzoyl chloride was added dropwise (over 2h) using a syringe pump (KDS100 Fischerbrand). The reaction was then allowed to reach room temperature (RT) and stirred overnight.

Workup: The DCM solution was washed twice with 100 mL half-saturated NaCl solution and the extracted organic phase further washed with saturated bicarbonate solution, dried with anhydrous sodium sulfate and filtered. The solvent was then removed to obtain a reddish viscous liquid that crystallized at RT (92% yield). The purity of the product was determined by TLC (ethyl acetate/heptane 50/50) and ^{1}H-, ^{13}C- and ^{19}F-NMR spectroscopy.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.45 (t, 6H) 3.06 (t, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 159.0, 146.4, 144.2, 142.1, 138.8, 136.7, 107.9, 64.8, 52.9; ^{19}F-NMR (471 MHz, $CDCl_3$) δ − 138.6 (m), − 148.8 (m), − 160.8 (m).

The triazide was finally synthesized dissolving 22.4 g (31.6 mmol) triester in 140 mL acetone. To this solution, 6.8 g (104.3 mmol) sodium azide in 45 mL deionized water was added and the reaction was left under reflux for 8 h.

Workup: The acetone was distilled off and to the remaining mixture 100 mL DCM was added and washed with an equal volume of deionized water. The organic phase was collected and the aqueous phase further extracted with 100 mL DCM. The combined organic phases were then dried with anhydrous sodium sulfate, filtered, and the solvent was removed. The desired product was obtained as a white powder after recrystallization from diethyl ether (85% yield). Its purity was confirmed by TLC (ethyl acetate/Heptane 50/50) and ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy. The presence of the azide was further attested by the appearance of an ATR-IR band at 2130 cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.43 (t, 6H) 3.04 (t, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 159.2, 146.6, 144.3, 141.8, 139.7, 123.5, 107.5, 64.6, 53.2; ^{19}F-NMR (471 MHz, $CDCl_3$) δ − 138.9 (m), − 151.2 (m).

2-(Methacryloyloxy)ethyl pentafluorobenzoate (PFP)

To begin, 5.9 g (45.4 mmol) 2-hydroxyethylmethacrylate (HEMA) was dissolved in 100 mL dry DCM and the solution was put under an inert atmosphere of dry nitrogen and cooled down to 0 °C. 11.5 g (49.9 mmol) pentafluorobenzoyl chloride was then added and the solution was left under stirring at 0 °C. After 30 min, 5.6 g (54.9 mmol) triethylamine was added dropwise (over 2 h) using a syringe pump (KDS100 Fischerbrand). The reaction was then allowed to reach room temperature (RT) and stirred overnight.

Workup: The DCM solution was washed twice with 100 mL 1 M HCl solution and the extracted organic phase further washed with saturated bicarbonate solution, dried with anhydrous sodium sulfate, and filtered. The solvent was then removed to obtain a yellowish viscous liquid (85% yield). The purity of the product was determined by ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.15 (m, 1H) 5.61 (m, 1H) 4.65 (t, 2H) 4.48 (t, 2H) 1.96 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 167.0, 158.9, 146.3, 144.5, 142.6, 138.7, 136.7, 136.1, 64.4, 61.8, 18.1; ^{19}F-NMR (471 MHz, $CDCl_3$) δ − 138.2 (m), − 148.6 (m), − 160.4 (m).

Poly(2-hydroxyethylmethacrylate)-co-(2-Methacryloyloxyethylpentafluorobenzoate (PHEMA-co-PFP) (M_w 20000 g/mol, ratio PHEMA/PFP 70/30)

First, 6.1 g (19 mmol) PFP and 8.1 g (62 mmol) HEMA were dissolved in 750 mL methanol and purged with dry argon for at least 20 min. In a separate flask, 86.3 mg (0.5 mmol) azobisisobutyronitrile (AIBN) was dissolved in 25 mL methanol and purged with dry Argon for at least 20 min. After the purging time, the monomers solution was put under reflux (at 65 °C) and kept under inert atmosphere. When the desired temperature was reached, the AIBN solution was added and the polymerization was run under stirring for 20 h.

Purification: Most of the solvent was removed by distillation and a minimum amount of ethanol was added before precipitating the polymer in heptane and drying it in a vacuum oven at 45 °C overnight. The product was obtained as a white powder (70% yield). GPC was performed to determine the polymer average M_w and polydispersity, while ^{1}H- and ^{19}F-NMR spectra were recorded to assess the polymer purity. Furthermore, ^{1}H-NMR spectroscopy was necessary to obtain the exact ratio between the two comonomers.

Poly(2-hydroxyethylmethacrylate)-co-(2-Methacryloyloxyethyltetrafluoroazidobenzoate (PHEMA-co-PFPA) (M_w 20000 g/mol, ratio PHEMA/PFP 70/30)

To begin, 5.4 g PHEMA-co-PFP was dissolved in 545 mL acetone. To this solution, 940 mg sodium azide in

180 mL deionized water was added and the reaction was left under reflux for 12 h.

Purification. The solvents were completely removed by distillation and the remaining product was dissolved in a 50/50 ethanol/acetone mixture before precipitating the polymer in heptane and drying it in a vacuum oven at 45 °C overnight. Further washings with deionized water were needed to remove the unreacted sodium azide. The final product was obtained as a pale yellow powder (90% yield). ^{19}F-NMR spectroscopy and ATR-IR were performed to confirm the desired azide substitution.

By changing the molar ratio of the monomers, polymers having PHEMA/PFPA 60/40 and 80/20 were additionally produced.

Formulation of the primer solutions

Two bicomponent primer formulations were prepared and tested. All contained 1 wt% triazide as first component, while the second component was 2 wt% PHEMA-co-PFPA(70/30) or 2 wt% PHEMA-co-PFPA(60/40). They were prepared dissolving first the polymer in a 50/50 by weight ethanol/acetone mixture and then adding the triazide.

Application of the formulation on PE or PP

Before treatment PE and PP substrates were wiped with toluene and isopropanol, respectively, to remove surface contamination. The application of the primer layer was then performed by dip coating (dip coater Model DX2-Special from L.O.T.—Oriel AG Switzerland, dipping and withdrawing speed 5.5 mm/s) or spray. After assessing the presence of the coating by ATR-IR (through the detection of the azide band), the coated samples were UV-treated (UV belt drier from Uviterno AG, Switzerland. Speed of the belt: 0.026 m/s; lamp power 1.8 kW; 1 cycle exposure time for dip-coated samples and two cycles for spray coated samples) to covalently bind the primer layer onto the plastic substrates.

Application of the adhesives and lap shear tests

The adhesives were applied on selected areas of the samples, i.e., 30 × 40 mm^2 on 2-mm-thick substrates and 12 × 25 mm^2 on 4-mm-thick substrates. The ISO 4587 and DIN EN 1465 standards were used to perform lap shear tests, pulling the samples apart at 20 mm/min in a tensile test machine by applying the force parallel to the bonding area.

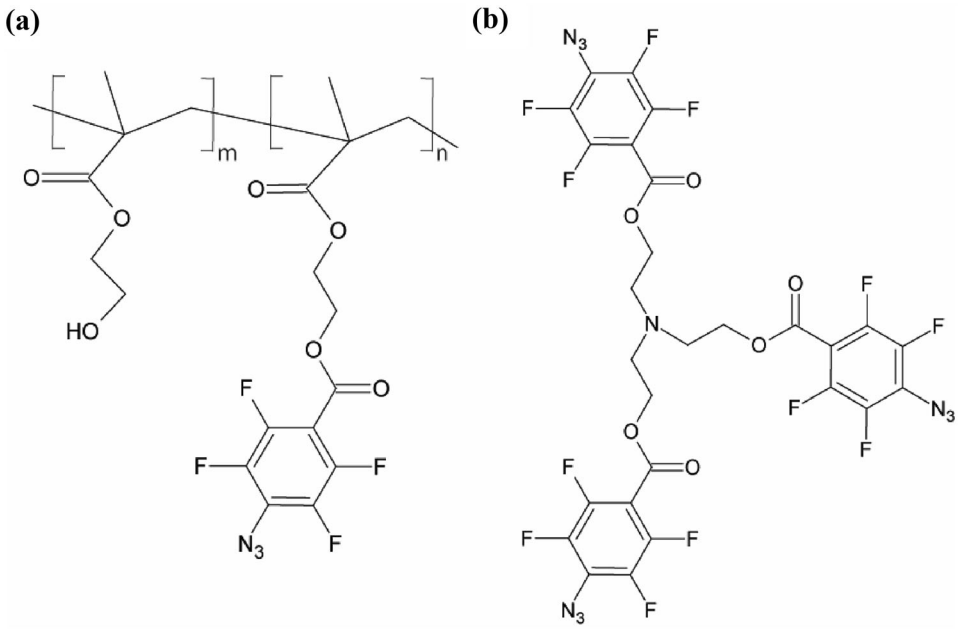
Results and discussion

Application of adhesion primer on PP and PE

In order to develop robust and thus long-lasting adhesion primers for PE and PP, we synthesized PHEMA-co-PFPA copolymers simultaneously bearing surface-reactive and adhesive-reactive groups (Scheme 1a). By changing the comonomers ratio during free radical polymerization, we obtained two adhesion primer candidates, having, respectively, 30 and 40% of surface-reactive groups. After dissolution in an ethanol/acetone mixture, each polymer was applied on the surface of PE and PP substrates via dip or spray coating, followed by UV activation.

The presence of the applied coating on PE and PP was confirmed by ATR-FTIR spectroscopy, which clearly showed the band of the azide at around 2130 cm^{-1} before photolysis and its disappearance after activation (Fig. 1a). Despite this evidence, the binding with the substrates failed and the formed film could be completely removed by ethanol wiping. The motivation behind the failure is presumably related to the different hydrophobic character of polymer and substrate.[26] Since the polymers are more hydrophilic than the substrates, they do not wet the polyolefin, allowing only the reaction with the surrounding molecules and inhibiting the covalent bonding to the substrates (Fig. 1c). In order to tackle this problem and increase the affinity between adhesion primer and polyolefins, a hydrophobic threefold surface-reactive molecule (tri-PFPA, Scheme 1b) was synthesized and added to the polymer formulation. This three-anchor primer should wet the plastic substrate and simultaneously react with it and with the copolymer. Since the latter is amphiphilic, its PFPA domains are expected to build hydrophobic interactions with the triazide and the substrate, inducing the hydrophilic domains to orient toward the air, creating a new OH-rich surface (Fig. 1c). This assumption was confirmed by applying the bicomponent formulation on PE and PP, UV activating it and measuring static contact angle (Table 1). Only the combination of tri-PFPA and PHEMA-co-PFPA resulted in a 50% decrease of the water contact angle, which can be exclusively attributed to the exposure of polar groups at the coating/air interface. Since the only formulation component bearing hydrophilic moieties is PHEMA-co-PFPA, the coating features a hydrophobic/hydrophilic gradient developing from the substrate toward the air.

By combining tri-PFPA and PHEMA-co-PFPA, the reaction with the substrate was successful and wiping with solvents did not determine material loss (Fig. 1b). To further assess the stability of the coating and the strength of the binding, the coated samples were exposed to boiling acetone for 24 h in a Soxhlet apparatus. ATR-IR spectra after Soxhlet showed also in this case no coating loss (Fig. 1d), excluding a possible physisorption and confirming covalent bond-



Scheme 1: Chemical representation of the formulation components. PHEMA-co-PFPA, m = 70, 60 and n = 30, 40 (a) and tri-PFPA (b)

Table 1: Average contact angles and surface free energy of the pristine and coated substrates

	Water contact angle (°)	Diiodomethane contact angle (°)	Surface free energy (mJ/m^2)
PE	98.9 ± 1.5	46.8 ± 1.7	34.3 ± 1.5
PE_PHEMA-co-PFPA(70/30)	89.2 ± 2.3	39.3 ± 2.6	41.1 ± 1.9
PE_PHEMA-co-PFPA(60/40)	80.5 ± 1.7	38.5 ± 2.1	47.2 ± 1.9
PE_tri-PFPA + PHEMA-co-PFPA(70/30)	53.2 ± 1.5	34.7 ± 2.9	57.4 ± 2.5
PE_tri-PFPA + PHEMA-co-PFPA(60/40)	45.3 ± 0.7	35.3 ± 1.9	61.7 ± 1.4
PP	98.8 ± 1.2	57.7 ± 1.9	31.4 ± 1.7
PP_PHEMA-co-PFPA(70/30)	91.8 ± 2.5	51.5 ± 2.1	34.8 ± 2.4
PP_PHEMA-co-PFPA(60/40)	85.7 ± 2.2	49.4 ± 1.8	39.8 ± 1.9
PP_tri-PFPA + PHEMA-co-PFPA(70/30)	53.4 ± 0.9	36.8 ± 1.5	56.1 ± 1.2
PP_tri-PFPA + PHEMA-co-PFPA(60/40)	46.5 ± 1.1	37.8 ± 0.9	60.4 ± 1.1

ing between the formulation components and the substrate.

XPS spectra quantitatively corroborated these results, revealing the same atomic percentage of fluorine on the samples surface before and after Soxhlet (Table 2). Furthermore, as expected from the chemical composition of the copolymer component, more fluorine was detected on the tri-PFPA + PHEMA-co-PFPA(60/40)-coated substrates.

Adhesion performance of the primer formulations

Once assessed the stability of the coatings against solvent extraction, the adhesion performance of the two different bicomponent formulations was tested with commercially available adhesives. Two-component epoxy (Araldite Rapid), one-component polyurethane (Sikaflex-221), one-component silane-terminated polyurethane (Sikaflex-521 UV), two-component acrylate (SikaFast-5215 NT), and cyanoacrylate (Loctite 420) were selected as most promising candidates, due to their chemical composition that allows a covalent binding with the primers. Reactions of the adhesives components with alcohols are indeed well known, thus enabling them to be permanently bound to the plastic substrate through the surface OH groups of the primers. In order to confirm this assumption, primer-coated PE and PP samples were bonded with the five selected adhesives and lap shear tests were

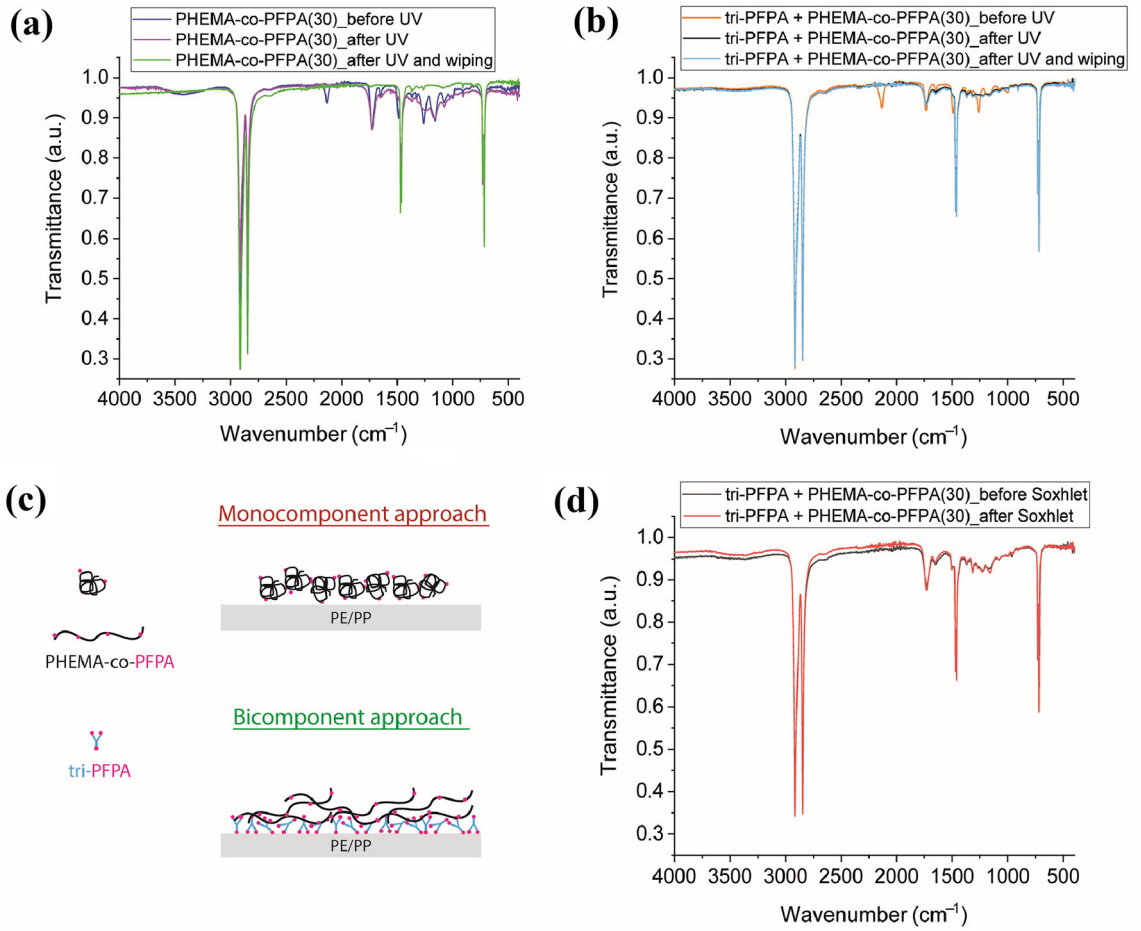


Fig. 1: FTIR spectra of PHEMA-co-PFPA(70/30) (a) and tri-PFPA + PHEMA-co-PFPA(70/30) (b) dip-coated PE substrates before and after UV activation and after solvent wiping. Schematic of the surface rearrangement of the formulation components (c) and FTIR spectra of the tri-PFPA + PHEMA-co-PFPA(70/30) dip-coated PE before and after Soxhlet extraction (d)

Table 2: Average fluorine atomic percentage detected on the coated samples before and after Soxhlet extraction

	Formulation	%F before Soxhlet	%F after Soxhlet
PE	Tri-PFPA + PHEMA-co-PFPA(70/30)	5.2 ± 0.4	4.7 ± 0.3
	Tri-PFPA + PHEMA-co-PFPA(60/40)	9.4 ± 0.5	10.2 ± 0.3
PP	Tri-PFPA + PHEMA-co-PFPA(70/30)	4.2 ± 0.5	4.1 ± 0.2
	Tri-PFPA + PHEMA-co-PFPA(60/40)	9.4 ± 0.5	9.6 ± 0.5

performed after complete curing and following the suppliers' instructions (Fig. 2a). Since oxygen plasma is the standard industrial process to impart adhesion to polyolefins, we chose this treatment to obtain our PE and PP positive controls. As negative control instead we used solvent-cleaned untreated plastic substrates. While the coatings applied on PE always performed better than the untreated ones, higher lap shear strengths than plasma-treated analogs were only obtained with polyurethane-based adhesives (Figs. 2c, 2d). Epoxy and acrylate glues adhered more on physically-activated substrates (Figs. 2b, 2e), while cyanoacrylate adhesives allowed a treatment-independent adhesion (Fig. 2f). On the contrary and in all the tested cases, both primers extraordinarily outper-

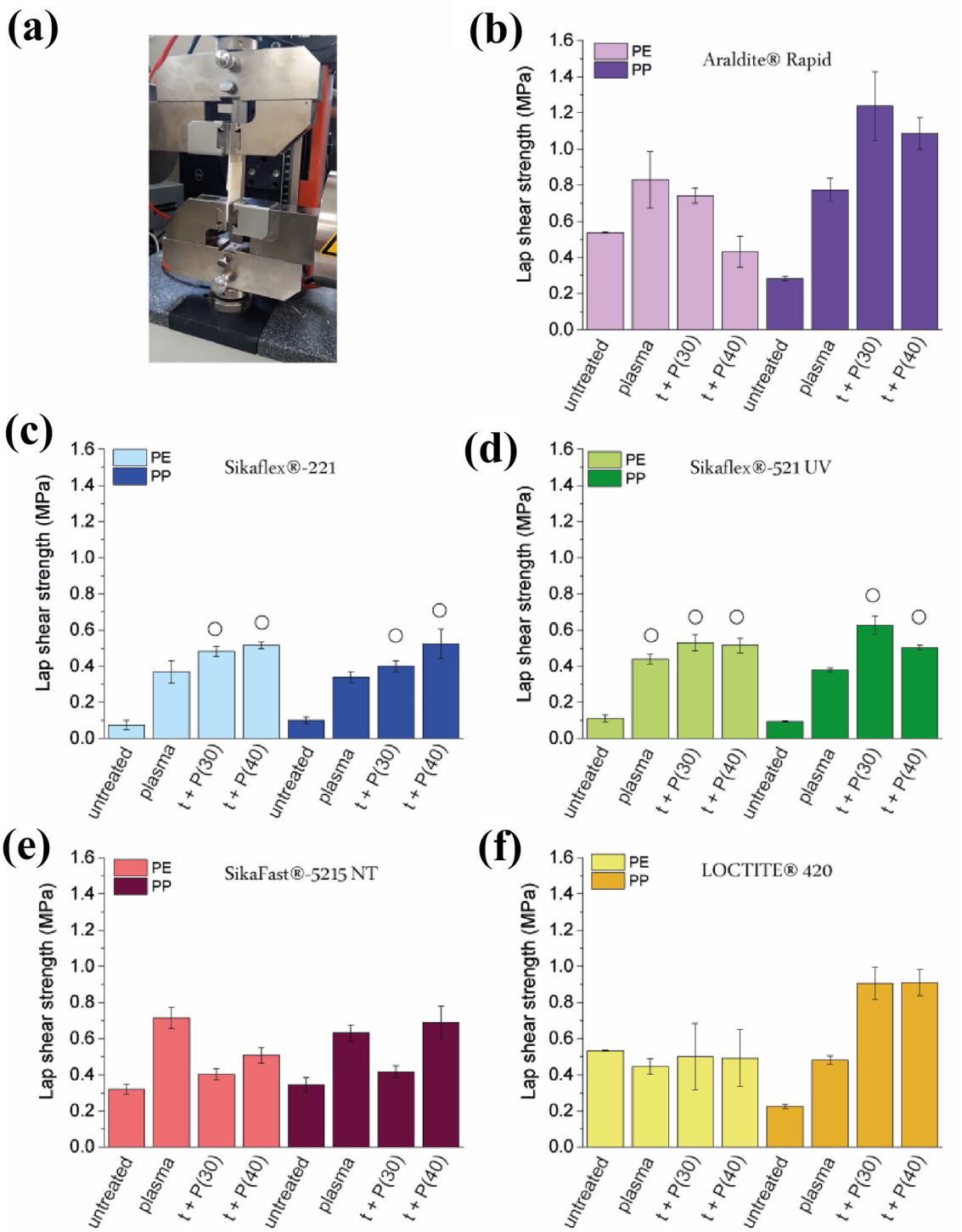


Fig. 2: Tensile lap shear tests device (a) and lap shear strength values of the tri-PFPA + PHEMA-co-PFPA(70/30) (*t* + *P*(30)) and tri-PFPA + PHEMA-co-PFPA(60/40) (*t* + *P*(40))-coated PE and PP substrates bonded with epoxy (b), polyurethane (c), silane-terminated polyurethane (d), acrylate (e), and cyanoacrylate (f)-based adhesives. The values of the negative and positive controls are also shown. The average values were calculated from six different experiments and the standard deviations are reported as errors. Cohesive failures in the adhesive are depicted with empty circles, all the other failures are adhesive between the substrate and the coating

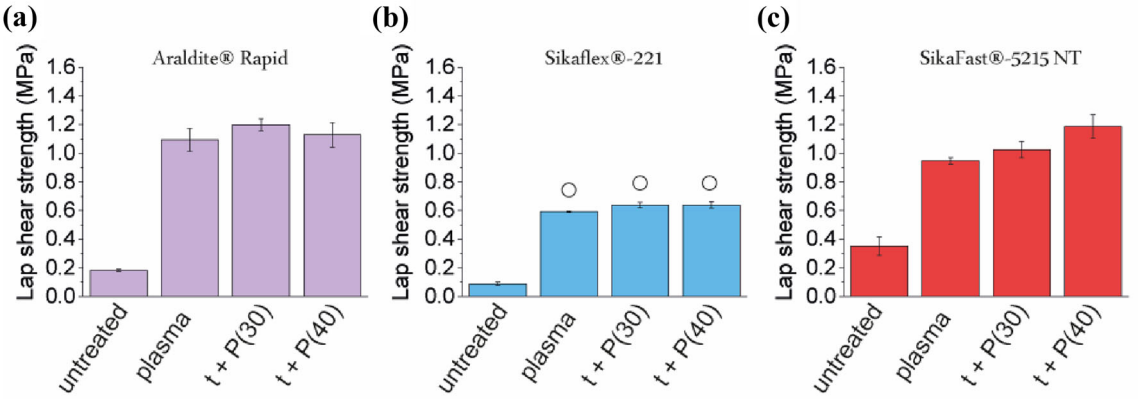


Fig. 3: Lap shear strength values of the tri-PFPA + PHEMA-co-PFPA(70/30) (*t* + *P*(30)) and tri-PFPA + PHEMA-co-PFPA(60/40) (*t* + *P*(40))-coated PE (without additives) substrates bonded with epoxy (a), polyurethane (b), and acrylate (c)-based adhesives. The values of the negative and positive controls are also shown. The average values were calculated from six different experiments and the standard deviations are reported as errors. Cohesive failures in the adhesive are depicted with empty circles, all the other failures are adhesive between the substrate and the coating

formed plasma treatment on PP, allowing 10 to 50% lap shear strength increase (Figs. 2b–2f).

The differences in absolute values depend mainly on the mechanical properties of the adhesives, which determined also the cohesive/adhesive failure at the breaking point. In particular, glues with tensile strength ≥ 10MPa (i.e., Araldite Rapid, SikaFast-5215NT, and Loctite 420) induced adhesive failures at the primer/substrate interface, while adhesives with lower tensile strength (i.e., Sikaflex-221 and Sikaflex-521UV) determined cohesive failures.

Although the two primer formulations differ for the ratio of PFPA/OH groups in the polymeric component, they did not show significant divergences in the adhesion performance. In order to assess whether there is a threshold number of PFPA anchors or polar OH functionalities to obtain good adhesion, we synthesized PHEMA-co-PFPA(80/20). Based on the expectations, the combination of the latter with tri-PFPA should result in a better performing primer than tri-PFPA + PHEMA-co-PFPA(70/30 or 60/40), due to the higher amount of OH groups, which can specifically react with the adhesive. Surprisingly, this formulation induced worse adhesion than the previously tested ones (Appendix, Fig. S1), proving that the PFPA/OH ratio plays a key role in determining the primer performance.

Since PP is the most hydrophobic polyolefin and thus the most challenging plastic to glue after PTFE, these results showed the extremely high potential of these primers as valid, nondestructive alternatives to oxidative treatments. However, the unexpected worse performance on PE, which should be easier to bind than PP, induced more investigations. Assuming that one possible reason for the adhesion failure on PE could reside in plastic additives, which migrate toward the surface, react with the primer and thus inhibit the binding with the bulk material, PE samples without additives were injection molded, coated with the primers and bonded with Araldite Rapid, SikaFast-5215 NT, and Sikaflex-221. The measured lap shear strengths confirmed the primer performances with the polyurethane-based adhesives and showed better or comparable adhesion than plasma-treated samples with acrylate and epoxy glues, respectively (Fig. 3).

This outcome confirmed our assumptions and highlighted the relevance of the substrate surface composition on the primer performance. Extensive cleaning of the additives-containing substrates with multiple solvents could be employed to overcome this pitfall. Preliminary data (Appendix, Fig. S2) on toluene-cleaned PE showed indeed improved adhesion with Araldite Rapid, although the plasma treatment remained superior.

Stability of the primer formulations over time

Since one of the drawbacks of the oxidative treatments to improve the adhesion of polyolefins relies in the hydrophobic recovery, which results in low stability over time, plasma-treated and primer-coated substrates (i.e., PP, PE with and without additives) were stored for up to two months at room temperature before applying Araldite Rapid and measuring lap shear tests. Although on PP and PE without additives all the three treatments showed unchanged adhesion performance after two months of storage (Figs. 4a, 4c), the primer coating maintained its higher quality when compared with plasma activation. On PE with additives, plasma-treated samples partially lose their adhesion properties after 30 days (Appendix, Fig. S3), while the performance of the coated substrates remained constant for two months, reaching the same lap shear strengths of the plasma oxidized PE (Fig. 4b).

Since hydrophobic recovery is highly dependent on the crystallinity of the chosen plastic[27] and after 60 days the contact angles of plasma-treated PE and PP

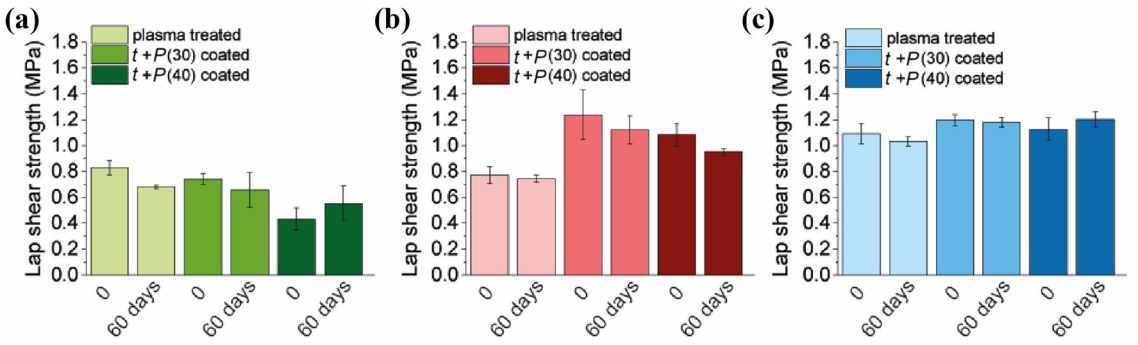


Fig. 4: Adhesion performance over time of the plasma-treated, tri-PFPA + PHEMA-co-PFPA(70/30) (*t* + *P*(30)) and tri-PFPA + PHEMA-co-PFPA(60/40) (*t* + *P*(40)) coated PP (a), PE with additives (b) and PE without additives (c) substrates bonded with Araldite Rapid. The average values were calculated from six different experiments and the standard deviations are reported as errors

show around 10° increase,[28] we hypothesize that longer storage times are needed to induce a net performance difference between plasma and primer treated. Further investigations are envisioned to assess the superiority of the latter process.[29]

Conclusions

In conclusion, we successfully developed a specific, nondestructive, and durable adhesion primer for polyolefins, which overcomes the drawbacks of conventional plasma surface treatments. The chemical composition of our primer allows its covalent bonding to the plastic substrate and a simultaneous interaction with the selected adhesive. This specificity results in outstanding adhesion on PP, reaching 10 to 50% lap shear strength increase with respect to plasma-treated substrates. On PE instead, the primer performance highly depends on the presence of additives, which inhibits the covalent bonding with the substrate and induces adhesion loss. When the primer is applied on additive-free PE, the adhesion performance improves reaching and, in some cases, overcoming plasma treatment. Interestingly, these achievements last up to two months, allowing storage of primer-coated samples instead of freshly coating them immediately before adhesion. We envision that easy application, superior performance, robustness, and durability make the hereby developed primer a promising alternative to the current physical treatments, which show industrial limitations.

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