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Polymer 46 (2005) 3986–3991

polymer

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Solventless coupling of perfluoroalkylchlorosilanes to atmospheric plasma activated polymer surfaces

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Received 9 September 2004; received in revised form 4 March 2005; accepted 4 March 2005
Available online 19 April 2005

Abstract

Perfluoroalkylchlorosilanes are found to readily undergo surface coupling reactions with atmospheric pressure dielectric-barrier discharge activated polymer substrates to yield hydrophobic/oleophobic surfaces. Trichlorosilane variants give rise to much better levels of surface functionalization compared to their monochlorosilane analogues.

Keywords: Plasma; Polysiloxane; Hydrophobicity

1. Introduction

Fluorinated polymer surfaces are appealing in terms of their liquid repellency, chemical inertness, and low coefficient of friction [1]. These attributes find application in biomedical devices [2], anti-fouling finishes, filter media [3], and release coatings [4]. Current methodologies for imparting such performance include fluorine gas treatment [5], plasma polymerization [6], sputter-deposition [7], and coating from a solution of preformed polymers [8]. All of these approaches tend to suffer from either being expensive, restricted to batch processing, safety hazards, or the generation of solvent waste. In this study the direct grafting of perfluoroalkylchlorosilanes onto atmospheric pressure dielectric-barrier (silent) discharge activated polymer substrates is described. Silane coupling chemistry is already widely recognized as a convenient means for functionalizing silica [9–12], titania [13], alumina [14], mica [15], iron [16], hydroxylated PTFE [1] or PET [17] substrates as well as low pressure plasma oxidized polydimethylsiloxane [18, 19]. In all of these cases, hydroxyl groups are considered to be a pre-requisite for the chlorosilane coupling reaction to proceed on the surface. Here it is shown that atmospheric pressure dielectric barrier discharge pre-treatment of a polymer surface generates reactive sites, which readily undergo chlorosilane coupling. The relative efficiencies of monochloro- versus trichloro-silane coupling chemistries onto atmospheric pressure dielectric barrier discharge activated polymer substrates are investigated. Potential benefits of this approach include the ease of continuous processing, absence of solvents and vacuum equipment, and implicit low cost.

2. Experimental

Glass slide (Chance Propper) and polyethylene film (ICI) substrates were ultrasonically cleaned in a 1:1 mixture of propane-2-ol (BDH, Analar grade) and cyclohexane (BDH, Analar grade) for 30 s and dried in air prior to usage.

A parallel-plate silent-discharge reactor was used to activate the polymer film surface. This constituted a high-voltage, thyristor-switched power source applying 11 kV pulses at 328 Hz between two horizontal parallel-plate aluminium electrodes with an inter-electrode gap of 2 mm, where the lower electrode was earthed and covered with a dielectric material (polyethylene). The substrate under investigation was placed on top of the dielectric layer and

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doi:10.1016/j.polymer.2005.03.009

subjected to the electrical discharge operating in air for 10 s [20].

1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTCS, $CF_3(CF_2)_7(CH_2)_2SiCl_3$, Fluorochem) and 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (PFDMCS, CF_3-$(CF_2)_7(CH_2)_2SiMe_2Cl$, Fluorochem) were chosen as the coupling reagents. Vapour phase exposure comprised placing each substrate in a sealed 60 cm^3 container in the presence of a dry nitrogen atmosphere and 0.02 ml of chlorosilane. Chemical bonding of the fluorinated overlayer to the substrate (rather than just physisorption) was tested by rinsing in 1,3-bis(trifluoromethyl)benzene (99%, Aldrich, a solvent capable of dissolving any surface physisorbed chlorosilane).

X-ray photoelectron spectroscopy (XPS) analysis of each substrate surface was undertaken before and after treatment with a Kratos ES300 electron spectrometer. This was equipped with an unmonochromated Mg K_α X-ray source and a concentric hemispherical analyser operating in the FRR mode (22:1). Photoelectrons were collected at a take-off angle of 30° from the substrate normal. XPS core level spectra were fitted using Marquardt minimisation computer software assuming a linear background and equal full-width-at-half-maximum (FWHM) for all the Gaussian component peaks. The following experimentally determined sensitivity factors were employed C(1s):F(1s):O(1s):Si(2p):Cl(2p) equals 1.00:0.67:0.57:0.72:0.42, respectively.

Surface hydrophobicity and oleophobicity were assessed by probe liquid contact angle measurements performed with a video capture apparatus (AST Products VCA2500XE) using sessile 2 μl droplets of de-ionised water and decane, respectively.

3. Results

Glass slides were employed as a reference substrate, since chlorosilane coupling agents are commonly used in conjunction with silica surfaces. PFDTCS (perfluorodecyltrichlorosilane) vapour was found to react with glass to yield a well adhered hydrophobic/oleophobic surface exhibiting elemental abundances consistent with almost complete coverage of the substrate, Table 1. In the case of polyethylene, PFDTCS was found to adsorb onto the surface, but could be easily removed by washing in 1,3-bis(trifluoromethyl)benzene solvent. However, silent discharge pre-treatment of polyethylene in air was found to significantly improve the chemical coupling of PFDTCS to the surface. In this case, solvent washing made very little difference and elemental abundances closely matched those seen for the glass reference substrate (i.e. approaching the theoretical values for complete coverage). Therefore, the film thickness must be at least comparable to the XPS sampling depth (~2 nm) [21]. The small drop in the concentration of fluorinated functionality seen after solvent washing can be accounted for in terms of the loss of low-molecular-weight-oxidised polyethylene chains [31] or the removal of a loosely bound layer of physisorbed PFDTCS coupling agent [22,23]. The latter explanation is more plausible on the basis of a similar decrease being noted for the glass substrate, Table 1.

Prior to dielectric barrier plasma activation, the C(1s) XPS spectrum of polyethylene consisted of a single peak centred at 285.0 eV corresponding to $\underline{C}_xH_y$, Fig. 1. Silent-discharge pre-treatment of polyethylene gave rise to the appearance of a high binding energy shoulder attributable to oxidised moieties [24]. Exposure of this oxygenated surface to PFDTCS vapour dramatically changed the C(1s) envelope, with the emergence of a distinct high binding-energy component signaling the presence of fluorinated functionalities ($\underline{C}$–CF at 286.6 eV; $\underline{C}F_2$ at 291.2 eV; and $\underline{C}F_3$ at 293.3 eV) [24]. The concentration of these groups increased with PFDTCS exposure, in parallel with the surface percentage of fluorine and water contact angle, Fig. 2. A plateau was reached after around 18 h, corresponding to thicknesses greater than the XPS sampling depth.

The mono-chlorosilane analogue of PFDTCS, 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (PFDMCS) was found not to be as effective at modifying the glass substrate, Table 1. Mechanistically, at best, the functionalized layer is only capable of reaching mono-molecular coverage, because of the monochloro nature of the PFDMCS coupling agent (this being less than the XPS sampling depth of ~2 nm). A similar trend was observed for the dielectric-barrier-discharge treated polyethylene substrate, where prolonged monochlorosilane exposure provided only a minor improvement, Fig. 2. Furthermore,

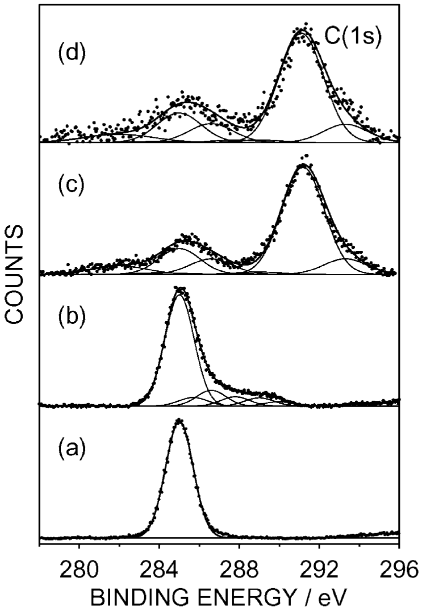


Fig. 1. C(1s) XPS spectra of: (a) clean polyethylene; (b) 10 s silent discharge oxidised polyethylene; (c) 10 s silent discharge oxidised polyethylene exposed to PFDTCS; and (d) solvent washed (c).

Table 1
XPS and contact angle values following 18 h perfluorodecyltrichlorosilane (PFDTCS) versus perfluorodecylmonochlorosilane (PFDMCS) exposure to glass, polyethylene (PE), and dielectric barrier discharge activated polyethylene (DBD-PE) substrates

Substrate	%C	%F	%O	%Si	%(CF_3+CF_2) of C(1s)	Contact angle (H_2O)/°	Contact angle (Decane)/°
Theoretical value for PFDTCS layer	34.5	58.6	6.6	3.3	80.0	–	–
Glass	22.9±2.7	0	52.9±1.3	24.2±1.9	0	18.0±2.0	Wets
Glass/PFDTCS	33.1±3.4	49.3±5.8	10.6±5.4	6.5±3.1	73.9±1.2	113.2±1.3	74.2±3.7
Glass/PFDTCS/ washed	26.7±2.1	47.8±4.5	15.8±5.1	9.6±1.5	64.5±4.6	105.1±2.9	71.2±2.6
PE	100	0	0	0	0	112.8±2.1	Wets
PE/PFDTCS	87.5±4.6	9.4±5.6	2.1±0.7	1.0±0.4	1.7±1.7	113.6±3.9	82.7±3.0
PE/PFDTCS/ washed	83.4±3.2	1.3±0.1	9.4±1.9	5.8±1.2	~0	112.0±1.8	Wets
DBD-PE	82.5±1.5	0	17.5±1.5	0	0	65.8±1.4	0
DBD-PE/ PFDTCS	33.0±1.0	56.5±1.5	6.2±0.2	4.3±0.3	73.9±2.8	142.6±4.1	83.7±3.3
DBD-PE/ PFDTCS/ washed	34.6±0.9	50.9±0.5	7.6±1.1	6.9±0.3	65.5±5.6	135.6±4.4	79.2±3.3
Glass/PFDMCS	16.3±1.0	19.5±1.2	43.4±0.4	20.9±0.1	–	96.0±4.7	47.6±4.1
Glass/ PFDMCS/ washed	23.7±2.8	18.2±3.0	39.4±2.8	18.7±1.2	–	91.4±2.2	49.9±4.3
Clean PE/ PFDMCS	99.6±0.1	0	0.6±0.1	0	–	115.6±1.7	Wets
Clean PE/ PFDMCS/ washed	99.4±0.6	0	0.6±0.4	0	–	108.8±3.6	Wets
DBD-PE/ PFDMCS	80.0±0.9	3.7±1.0	15.2±0.9	1.1±0.7	–	77.5±2.8	Wets
DBD-PE/ PFDMCS/ washed	77.0±4.6	1.6±0.3	17.7±1.3	3.6±3.6	–	82.3±3.5	Wets

the speed of reaction (rate of %F increase) was far slower compared to glass (although it was marginally quicker than virgin polyethylene), Fig. 3. Collectively these observations can be taken as being indicative of the silanol groups on glass being more reactive compared to the active sites generated by dielectric barrier treatment of polyethylene.

4. Discussion

Silent discharges are non-equilibrium plasmas which can operate at atmospheric pressure [25]. In the case of a parallel-plate dielectric barrier discharge (also known as a silent discharge) bright filamentary streamers of electrons and positive ions extend between two planar electrodes, one of which is covered by a dielectric material. Such limited current 'microdischarges' are characteristic of a silent discharge. Within each alternating cycle of high voltage, electrons arriving at the dielectric surface build up sufficient apace charge to oppose the applied field, thereby causing the current to terminate and preventing complete spark-over to the substrate. Free electron collisions generate a plentiful supply of electrons, excited neutrals, ions, and photons. Low energy electron-induced atomic and molecular excitations within the plasma together with ion-electron recombinations create a purple 'glow' and visible streamers. Common uses of dielectric barrier discharges are ozone production, the destruction of air borne pollutants [26,27], generating high intensity VUV excimer radiation [28–30], and improving the wettability and adhesive properties of polymer surfaces [31,32]. The mechanism responsible for increasing the surface energy of polymer surfaces during air dielectric barrier discharge exposure is understood to entail the reaction of in situ generated ozone with the activated surface to yield a variety of oxidized carbon groups (e.g. carbonyl, alcohol, hydroperoxide, acid, etc.) [20]. Such activated surfaces would be expected to be susceptible towards reaction with chlorosilanes via coupling through a silanol intermediate (this process being catalysed by surface water) [33–35], Scheme 1. The formation of thick PFDTCS films onto glass in the present study is a manifestation of tri-chlorinated silanes being able to polymerise to form a 3D network during adsorption [9,15,23,36,37]. In the case of chlorosilane grafting onto silent discharge activated polyethylene, surface oxygenated groups must play a key role (as previously observed for grafting onto corona discharge

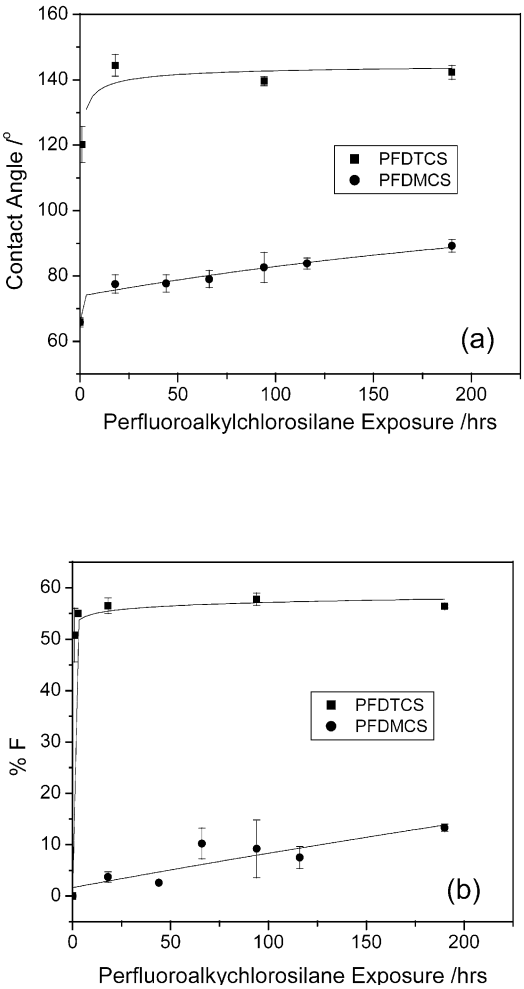


Fig. 2. Time dependence of PFDTCS and PFDMCS coupling to 10 s silent discharge activated polyethylene: (a) water contact angle and (b) %F.

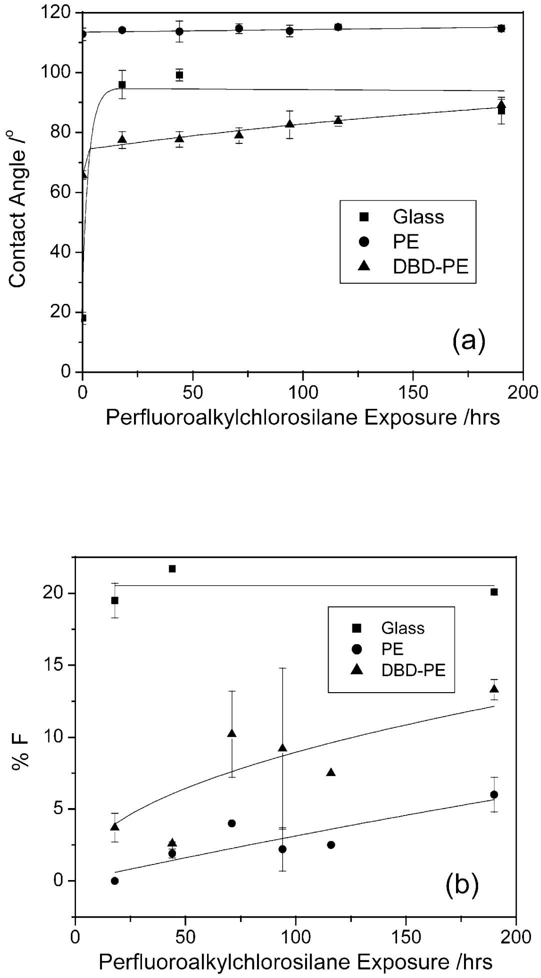


Fig. 3. A comparison of PFDMCS coupling to polyethylene, silent discharge activated polyethylene, and glass as a function of exposure time: (a) water contact angle and (b) %F.

and ozone treated surfaces) [38–41]. The increase in polymer hydrophilicity (surface energy) upon dielectric barrier discharge activation will enhance the amount of physisorbed water (something that is required for silane coupling chemistry) [34,35].

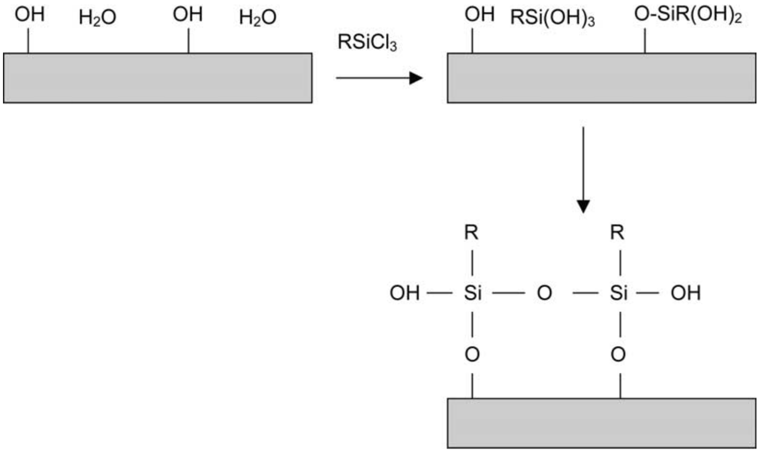
The higher water (hydrophobicity) and decane (oleophobicity) contact angles measured for PFDTCS coupled to silent discharge treated polyethylene compared to the corresponding reaction with glass (despite their identical surface compositions) can be attributed to the greater surface roughness of the former as predicted by Wenzel's law [42], Fig. 4. This stems from streamers associated with the dielectric barrier discharge causing micron scale roughening [31].

The relatively poor coupling performance of PFDMCS can be attributed to either a limiting concentration (density) of grafting sites, or these centres being less reactive towards monochlorosilanes (a kinetic limitation). The former explanation seems unlikely considering the gradual rise in grafted material over time for silent discharge activated polyethylene. This is reaffirmed by the observation that the reaction of PFDMCS proceeds much faster with glass to reach saturation due to the higher reactivity of Si–OH groups. In contrast, film formation in the case of PFDTCS appears to be unhindered by the slow production of Si–O–C linkages [43]. This can be explained on the basis that only a low level of direct attachment to the substrate is prerequisite to instigate the rapid formation of a 3D Si–O–Si cross-linked network containing perfluoroalkyl group side chains.

Similar trends in surface functionalization were found for other polymer surfaces (e.g. polypropylene).

5. Conclusions

Perfluoroalkyltrichlorosilanes are found to undergo coupling reactions with atmospheric dielectric barrier discharge activated polymer substrates much more readily than their monochloro-substituted counterparts. This enhancement can be attributed to the formation of a 3D Si–O–Si cross-linked network with perfluoroalkyl group



Scheme 1. Condensation reaction of a trichlorosilane coupling agent with a hydroxylated surface [34].

side chains. The resultant surfaces are found to display both hydrophobic and oleophobic behaviour.

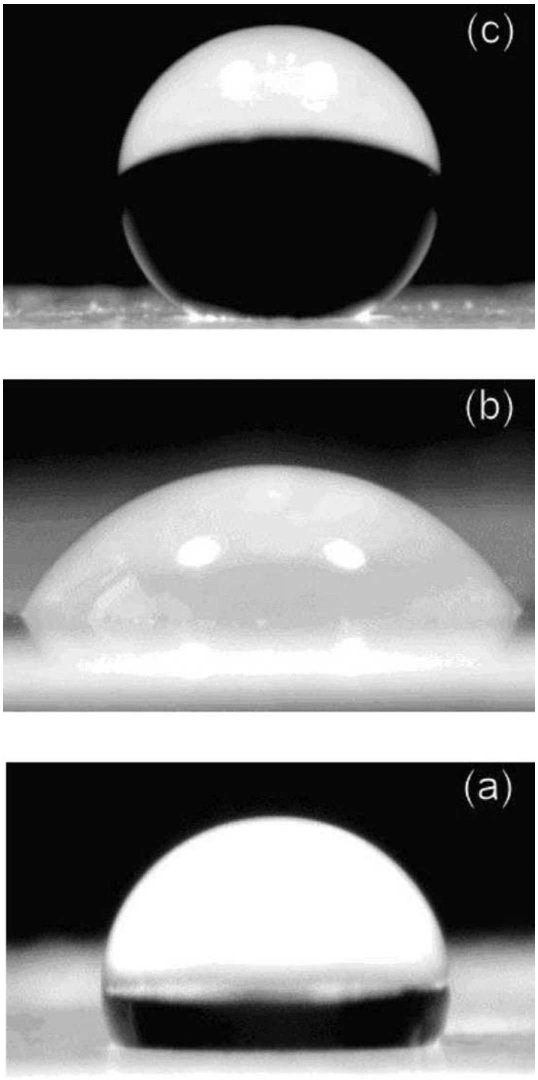


Fig. 4. Water droplet sitting on: (a) clean polyethylene; (b) silent discharge activated polyethylene; and (c) PFDTCS coupled to silent discharge activated polyethylene.

Acknowledgements

L. J. Ward would like to thank EPSRC and Dow Corning for financial support. J. P. S. Badyal is grateful to the EPSRC for an Advanced Research Fellowship.

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