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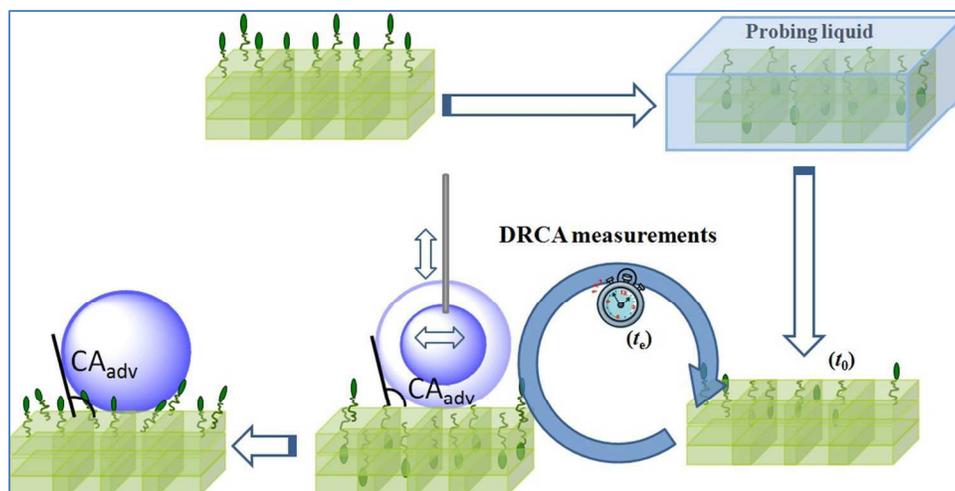
Graphical Abstract

Rearrangements of Polymer films monitored by Dynamic Recovery Contact Angle (DRCA)

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ARTICLE

Time-resolved Surface Rearrangements of Polymer films monitored by Dynamic Recovery Contact Angle (DRCA)

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Polymer surfaces can be designed to have functionalities significantly different from the bulk. However, such surfaces can be very dynamic in nature and rapidly rearrange or exchange with bulk components upon changing environmental conditions or contacts. The time-frames involved in surface rearrangements of polymer films are investigated by Dynamic Recovery Contact Angle (DRCA) through a simple, non-invasive and reconstructive approach, based on the sequential exchange of the polymer surface contact between a probe liquid (water) and air.

Introduction

Polymers are amongst the few material classes that offer the possibility to tailor the molecular composition and mesoscale morphology of the surface¹⁻⁶. This feature is of wide interest for a large number of applications, in particular functional surfaces with *e.g.* specific wettability, low friction, anti-fouling or anti-bacterial properties.

The molecular design principles to be taken in account for functional surfaces have been studied since several decades and were reviewed by Koberstein⁷: surface segregation, surface structure and surface rearrangements. The last of the three has been extensively studied⁸⁻¹² and relates to the fact that such functional polymer surfaces are known to be quite dynamic and can rapidly rearrange or exchange with the bulk components upon contact with a different surrounding environment. This may lead to substantial property changes, as a result of a simple but complete exchange of chemical groups between the top surface layers, over a distance of only a few nm^{13,14}.

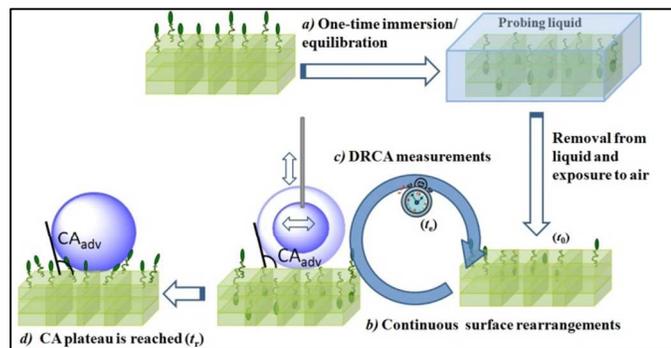
The surface reorganization on polymer films has been largely investigated on pre-conditioned materials¹⁵⁻¹⁸, which were either immersed in liquids or intentionally damaged to create new air-polymer interfaces. A number of experimental techniques, such as Contact Angle (CA), Angle-dependent X-Ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) or Rutherford Backscattering have been used to assess aspects of chemical and/or physical nature of the surface rearrangements¹⁹⁻²⁴. However, one of the consequences of the fast rearrangements is that these dynamic surfaces are difficult to characterize when not in equilibrium. Moreover, the

time interval between the surface rearrangements and the practically earliest possible start of the characterization experiment is very often shorter than, or in the same order of magnitude of, the surface rearrangements (sometimes seconds or few minutes). Hence, the time-frame needed for the surface to rearrange remains largely unknown for the majority of the systems studied.

Contact angle measurements have the general disadvantage that the procedure itself is already interfering with the surface rearrangements by contacting with a probe liquid²⁵, except in the advancing mode which addresses only the surface ahead of the area firstly wet by the liquid. Hence, static drop measurements typically used in the past to assess surface rearrangements, give results dependent on previous surface history and probing protocol^{23, 26, 27}. The advancing mode, however, is a dynamic measurement and can be used to reveal temporal information, if the history of the surface is precisely determined by consecutive measurements, as combined from the initial off-equilibrium state to the final equilibrium state, in a reconstructive approach.

In this paper, we investigate the time-frames involved on surface rearrangements occurring on low surface energy polymer films of different chemical nature, using a simple method named as Dynamic Recovery Contact Angle (DRCA), based on a sequential time-reconstruction approach. First, the original material is submersed in a high surface energy probe liquid (*e.g.* water), forcing the low surface energy groups into the bulk of the material (Scheme 1 *a*). After equilibrium has been reached the liquid is removed, the film surface is exposed

to air and rearranges in time to a new equilibrium state, against the air interface (Scheme 1 *b* to *d*).



Scheme 1: Illustration of the DRCA method: *a*) one-time immersion in a liquid forcing the chemical groups from the surface into the bulk of the polymer film; *b*) re-equilibration of the surface upon renewed contact with air, *c*) the dynamic water contact angles (CA) are measured at sequentially incremented time-intervals until *d*) a constant CA value is reached on the fully rearranged surface.

The first dynamic water contact angles were collected immediately after the film was removed from the liquid (zero time, t_0), on the pre-immersed/equilibrated surface. The advancing (CA_{adv}) and receding (CA_{rec}) contact angles were measured consecutively by increasing and decreasing the volume of the water droplet, respectively. This sequence is called DRCA measurement (see Scheme 1 and Scheme 4, in experimental). The progress of the surface rearrangement is then followed by making DRCA measurements in the same way, however, incrementing the time-intervals between each measurement (t_e) (Scheme 1, *b*-*c* and Scheme 4), until a constant value of the CAs is reached, determining the total air-exposure time needed for the surface to recover completely (t_r) (Scheme 1, *d*).

Using two low surface energy polymer films as show-case, we demonstrate how the DRCA method allows the investigation of the time-scales involved in surface-rearrangements occurring in very different polymer films with tailored functional surfaces. Moreover, both polymer systems studied, have a “surface-healing” ability based on surface rearrangements²⁸⁻³⁰. New air interfaces created upon surface-damage are self-replenished with chemical groups from the bulk, recovering the chemical composition of the surface and hence, the hydrophobic character of the polymer films. Hence, for such systems the DRCA method provides an estimation of the approximated time period needed for the surface to recover from damage, *i.e.* for self-replenishing of the surface functionality to occur. The different times of recovery encountered for the two polymer films are discussed, taking into consideration the influence of the characteristics of each polymeric system on the surface rearrangement.

Results and discussion

The two low surface energy polymer films investigated have different chemical natures, namely with perfluoroalkyl and silicone groups, but both possess proven self-replenishing ability²⁸⁻³¹. One is a “homogenous” system consisting of a poly(caprolactone)-based cross-linked network with perfluorinated dangling chains containing a polymeric spacer, chemically bonded to the network^{8, 28}. The other is essentially heterogeneous, consisting of a poly(dimethylsiloxane) (PDMS) grafted-poly(styrene-*alt*-maleic anhydride) (PSMA), with phase-separated soft PDMS domains and hard cross-linked PSMA domains³². Both polymer films were extensively characterized by chemical and physical techniques, as reported in our previous works²⁸⁻³⁰.

For the DRCA measurements the polymer films were first immersed in water for a specific period of time (e.g. one night to two days depending on the system) to expel the low surface energy components from the surface, into the films bulk. Several periods of immersion were tested and the CA_{adv} was measured. The immersion time necessary to expel all the low surface energy groups from the interface was set to the time at which no further change (decrease) of the CA_{adv} was observed, as compared to the initial CA, measured on the original dry-films before immersion.

After the pre-established immersion period, the film was removed from the water and the dynamic CAs were immediately measured on the pre-immersed/equilibrated surface. The CA_{adv} and CA_{rec} were measured consecutively, with a waiting period of 2 seconds between them (see DRCA measurement on Scheme 4, experimental). During these measurements, the contact area within the radius of the increased droplet is firstly wet and then re-exposed to air in the end of the procedure, re-setting the zero time of air-exposure within this area. Hence, in the end of each DRCA measurement the “air-exposure time” within the probed area is set back to zero. The DRCA measurement is repeated at incremented time-intervals (t_e) (e.g. $t_e = 60$ s, means one minute of air exposure).

The air exposure time-intervals (t_e) were increased step-wise, incrementing from the previous time considered (e.g. time of air exposure, $t_e = 60$ s, 120 s, 180 s, and so on ...) until no more changes were registered for the dynamic CAs measured. The time-intervals suitable for each material were pre-determined by doing a first preliminary experiment to assess the time-scale variations. Hence, the total air-exposure time needed to stabilize the dynamic CAs, defined here as (t_r), is determined as the total time required for the surface to recover up to a stable CA value (plateau) close to the value of the originally-dry sample.

Perfluoroalkyl - polymer films

The first system comprised cross-linked poly(urethane) films with perfluoroalkyl-terminated dangling chains. The films were prepared from OH-terminated poly(caprolactone) precursors reacted with a triisocyanate cross-linker in the

presence of OH-terminated poly(caprolactone)-dangling chains with perfluorooctyl end-groups⁸ (see experimental, Scheme 2). Polymer films were prepared with an overall content of 2 wt % of fluorine and dangling chains with different lengths, *i.e.* different degrees of polymerization of the polymeric spacers (DP from 8 to 24) (Scheme 2). After immersion in distilled water for 1 night (t_0), all the films showed an initial (maximum) drop of the CA in the order of 30-40° (Figure 1), as compared to the original values (Figure 2a). This clearly shows the enforced orientation of the perfluorinated components towards the bulk. Further on, the DRCA shows that all the films surfaces rearrange towards higher hydrophobicity, with a characteristic t_e of about 2 hours (Figure 1). However, these values are still on average ~5° below the original value (Figure 1 and 2 a).

In order to remove all the water, potentially retained/adsorbed in the polymer film and also to promote the mobility of the polymer network which may enhance the surface rearrangements, the films were heated during 4 hours at 40 °C under vacuum, (well above the materials' $T_g \sim 40$ °C). The CA_{adv} values on the heated films increase slightly (2-3°) for all polymeric systems, but still do not reach the original values. This indicates that either a residual amount of water is retained/dissolved in the top surface or some permanent damage/changes occurred on the surface polymeric structure (Figure 2a).

In these systems, the poly(caprolactone) chain segments have a considerable hydrophilic character. Hence, the water can penetrate very easily, eventually leading to permanent damages/changes on the polymer network, *e.g.* through hydrolysis of the ester bonds of the “bulk” polymers or the polymeric spacer of the dangling chains.

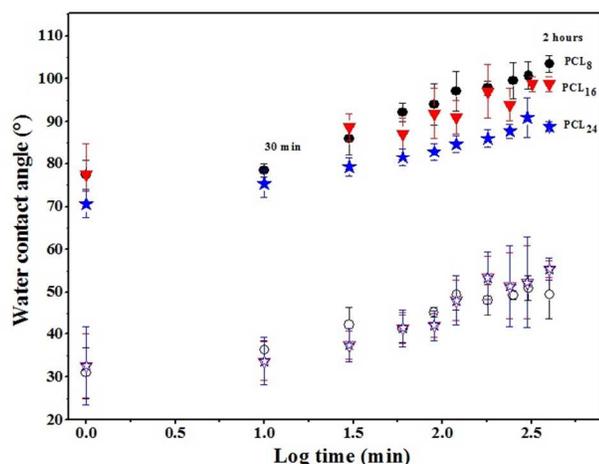


Figure 1: Advancing (solid symbols) and receding (open symbols) water contact angle (CA) versus air exposure time (t_e), for films with 2 wt % of fluorine: (●) Rf₈-PCL₈ and (▼) Rf₈-PCL₁₆ and (★) Rf₈-PCL₂₄. The time of air exposure (t_e) (in minutes) was converted to log scale for easier visualization. The CA_{adv} at log time = 0 min corresponds to the CA value measured at (t_0), immediately after a 1 night of water immersion.

An interesting observation is that the surface recovery of systems with perfluorinated dangling chains with longer

polymeric spacers (DP 16 and 24), seems to proceed slower (Figure 1). This may be due to a “shielding” of the hydrophilic groups or restrictions on the polymer spacer local segment mobility which delays the surface re-orientation. Feijen *et al.*³³ reported a similar effect for poly(alkyl methacrylates) with long alkylic side chains.

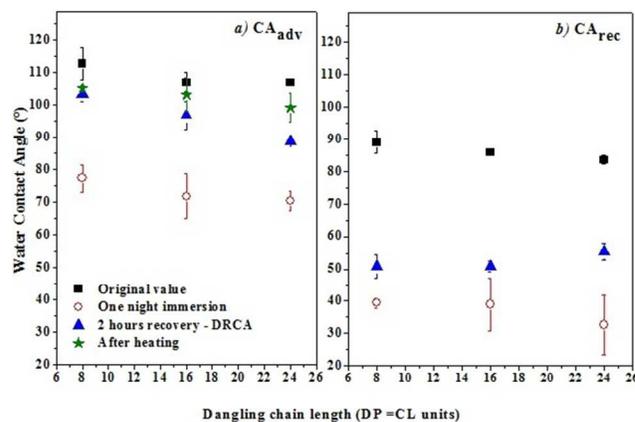


Figure 2: Advancing (a) and receding (b) water CA versus dangling chains length (DP = CL units) in different situations: (■) Original value on the dry-films, (○) measured at the (t_0) after 1 night immersion in water, (▲) DRCA result after 2 hours of recovery (t_r) and (★) after heating the final (t_f) films for one night, at 40 °C under vacuum.

The DRCA results obtained for the receding CA are, however, very different (Figure 1 and 2 b). For the same recovery time, the final receding CA are far lower than the original values. The advancing and receding CA were measured in a continuous mode, 30 seconds for each measurement and a waiting time of 2 seconds in between. Typically upon wetting of a surface, a new thermodynamic equilibrium is reached within a few tens of seconds³⁴. Hence, the receding CA measurement, although short in time scale with respect to the total recovery time, already includes some initial response of the surface, which was pre-wet when measuring the CA_{adv} , *i.e.* the recovery time is nearly reset to zero by each CA_{adv} measurement. Hence, the CA_{rec} does not provide reliable data for the reconstructive approach that we seek to achieve with the DRCA method.

Polydimethylsiloxane - polymer films

The second series of polymer systems studied consisted of poly(styrene-*alt*-maleic anhydride) grafted with PDMS (PSMA-*g*-PDMS). All films were cross-linked with adipic dihydrazide (ADH) and fully characterized^{30, 32} (see experimental, Scheme 3). Two series of films were investigated: **1**) with different weight percentage of *g*-PDMS (1000 g/mol), low (PSMA-5%*g*-PDMS1000) and high (PSMA-43%*g*-PDMS1000) and **2**) with similar wt% *g*-PDMS (43-49%) but different PDMS average molecular weight, 1000 g/mol (PSMA-43%*g*-PDMS1000) versus 2000 g/mol (PSMA-49%*g*-PDMS2000).

The films were immersed in distilled water for 2.5 days (t_0) to force the surface PDMS groups into the bulk. The DRCA results for the polymeric films with different weight

percentages of *g*-PDMS have shown that, after the immersion period, the CA_{adv} of both films only decreased 8-10° from the initial value (Figure 3).

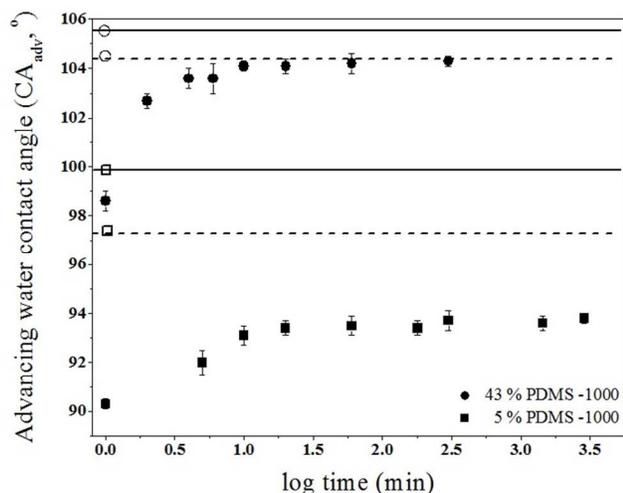


Figure 3: Advancing water contact angle versus air exposure time (t_e) for cross-linked films with: (■, □) PSMA-5%*g*-PDMS1000 and (●, ○) PSMA-43%*g*-PDMS1000. The CA_{adv} at log time = 0 min corresponds to the value measured at (t_0), immediately after a 2.5 days water immersion. Open symbols correspond to the CA_{adv} measured on the dry-sample before immersion (*solid line*) and after a heat treatment applied on the final t_r films (*dashed line*).

However, after re-exposition to air the recovery of the two films is different. The film with a higher amount of *g*-PDMS recovers 6° in $t_r \sim 3$ minutes while the other only recovers 2° in a somewhat longer time frame of about $t_r \sim 10$ minutes (Figure 3). For both films, the surface rearrangements lead to final water CA_{adv} values lower than for the original surface (Figure 3 *solid line*). Also in these cases, this effect could be due to retention/entrapment of water in the film or permanent damage of the polymer network, probably by hydrolysis of the residual anhydride or amide bonds. The CA_{adv} after heating increases slightly (1-2°) for both films (Figure 1, *dashed lines*) but still do not reach the original dry-values (Figure 1, *solid line*). This effect is much more pronounced for the film containing a low percentage of *g*-PDMS (7° difference from the initial value).

Similar DRCA experiments were carried out for films with the high percentage of *g*-PDMS and using a PDMS with a higher molecular weight (PSMA-49%*g*PDMS2000) (Figure 4). In this case, after an initial decrease of 6° upon water immersion, the original CA_{adv} is fully retrieved in a $t_r \sim 3$ minutes (Figure 4 *solid line*). After the heat treatment no further changes were observed (Figure 4 *solid line*). The PDMS grafted chains of these films are, on average, about twice as long as the PDMS-1000 chains. This may have several effects which can explain the higher stability towards water and the fast and complete recovery: easier reorientation or “migration” of the PDMS chains towards the air-interface, more difficult penetration of the water into the film and better surface coverage by the PDMS phase.

The reasons for the large differences found in the time-scales involved in the surface rearrangements can be found in the distinct chemical and structural characteristics of the systems studied.

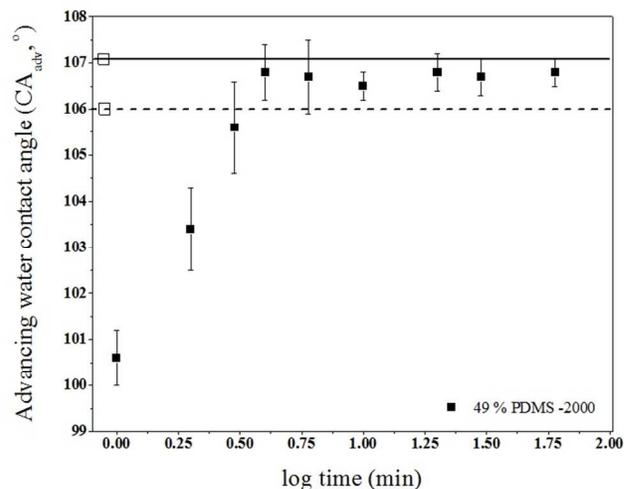


Figure 4: Advancing water contact angle versus air exposure time (t_e) for cross-linked films with PSMA-49%PDMS2000 (■). The CA_{adv} at log time = 0 min corresponds to the value measured at (t_0), immediately after a 2.5 days water immersion. Open symbols correspond to the CA_{adv} measured on the dry-sample before immersion (*solid line*) and after a heat treatment applied on the final t_r films (*dashed line*).

A first consideration to be made is the fact that the fluorine-systems have to recover from an initial decrease of $\sim 30^\circ$, as compared to the PDMS-systems with only $\sim 8^\circ$, measured after immersion (t_0). This difference in CA after the t_0 measurement is linked to the hydrophilic nature of the poly(caprolactone) component in the fluorine-systems, which allows extensive penetration of water and exposes the most hydrophilic groups through surface rearrangements⁸. In the PDMS-systems, this effect is much less pronounced due to the presence of the poly(styrene) block. Hence, this may lead to the larger total rearrangement times (t_r) as observed for the fluorine-systems.

The next considerations are related to the key parameters underlying the surface reorganization, which were identified through many studies available in the literature: (1) differences between surface and bulk energy (*i.e.* low versus high surface energy components) which results in different segregation driving forces^{7, 35} and (2) the chain segment mobility, which may depend on molecular weight²⁰, chemical architecture of the polymer segments^{20, 36, 37}, density of the network²⁷ and in some cases, concentration of the self-segregating species⁵. Additionally, from our previous work with self-replenishing polymer systems, we identified a third important parameter which prevents complete segregation of the dangling ends towards the top surface layer at the early stages of film preparation^{28, 29, 31}, namely (3) local fixation.

Since in both our systems local fixation (3) is guaranteed, by cross-linking or grafting reactions, involving one reactive end

of the dangling chains, the two first points probably play the most important roles on the surface reorientation time-scales.

As for the first (1), every segment of the PDMS dangling chain has supposedly a lower surface energy than the surrounding polymer matrix, while for the fluorinated system, only the perfluoroalkyl end-group has a lower surface energy than the surrounding poly(caprolactone) units of the network, and the rest of the dangling chain itself. Hence the driving force for surface segregation may be a few orders of magnitude higher for the PDMS system as compared to its perfluorinated counterpart.

Concerning segment mobility (2), the PDMS-g-PSMA systems were expected to be in disadvantage by the high T_g of the PSMA phase (+ 162 °C), causing a slower rearrangement. Apparently, this is not the case and the intrinsic properties of the PDMS phase ($T_g = -128$ °C)³² compensate with sufficient mobility. This is clearly visible by the increasing recovery observed for PDMS films with higher PDMS-grafts concentration.

The short time-scale observed for the surface rearrangement of the PDMS systems³⁰ was rather surprising, considering that this is a phase-separated system, as previously confirmed by DSC and AFM³⁰, see Figure 5.

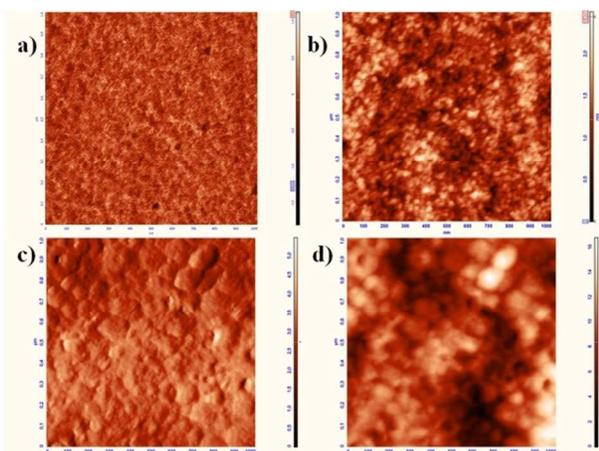


Figure 5: a) and b) AFM phase and height image, respectively, of a cross-linked PSMA film with 30 % ammonolysis; c) and d) AFM phase and height image, respectively, of the PSMA1-2000, with 9 % wt PDMS.

PDMS domains with dimensions of about 100 nm were identified from AFM topography and phase images. Apart from the differences in the phase contrast between the domains and the background (Figure 5 c and d), the root mean square (S_q) calculated from the roughness profiles, showed approximately a nine-fold increase from $S_q(\text{PSMA}) \sim 0.31$ nm for the reference PSMA film to $S_q(\text{PSMA-g-PDMS}) \sim 2.73$ nm for the films containing the PDMS-grafts, which provides further evidence for the presence of the phase-separated domains.

It was concluded that as the PDMS grafts concentration increases, the surface becomes smoother, indicating a possible full coverage of the surface with the softer PDMS phase³⁰.

Hence, considering that surface rearrangements occur mainly at the top surface layers, over a small distance up to 10 nm^{13, 14}, the soft phase domains at the PDMS systems surface may still be able to rapidly re-orient and fully cover the new surfaces. Fast and complete recovery of the surface hydrophobicity was also observed for films intentionally damaged by microtoming, indicating that the self-replenishing of new air-interfaces occurs equally in very short time-scales³⁰.

Conclusions

The time-frames involved on the surface-rearrangements of two low surface energy polymer films of different chemical nature were investigated by the DRCA method. The reconstructive approach provides an estimate of the time-of-recovery (t_r) of the surface hydrophobicity by self-replenishment of new polymeric surfaces created upon damage. Polymeric films are very often in contact with liquids and subjected to damage (wear, friction) and for certain applications, such as in the biomedical area, it may be critical to know how fast the surface rearranges/replenishes, that is, how reliable is a material concerning its surface functionality, upon routine handling.

In polymeric systems sensitive to the probe liquid (in this case water), for example, through reaction with or absorption of the water, permanent changes of the polymeric network or its morphology may occur when the material is immersed in the probe liquid for a long time. This is a limitation to the DRCA method, as it prevents a full recovery of the initial properties and will influence the DRCA estimated time-response. Nevertheless, it is still a simple, time-effective and versatile method that can be applied with different probe liquids on a wealth of polymeric systems with surface-tailored chemical groups or polymeric functional materials. Such functional materials are typically used for low-adherence, anti-fouling, anti-bacteria or lubricious purposes, and are in constant contact with fluids. Knowing the typical time-response of surface reorganization is critical to design the material in such a way that the surface functionality and high performance of the material can be maintained through its life-cycle.

Experimental

Materials and characterization

Perfluorinated – polymer films

The perfluorinated dangling chains ($\text{F}_{17}\text{C}_8\text{-PCLy}$) and the polymer bulk precursor (TMP-PCL_{24}) compounds used to prepare the films were synthesized and characterized as described elsewhere^{8, 28}. The films were all prepared with a 2 % wt fluorine concentration, in relation to the total formulation, adjusted by incorporating the necessary amount of the respective perfluorinated dangling chains (with DP from 8-24). Tolonate HDT-LV2, mainly consisting of hexamethylene diisocyanate trimer (noted as *t*-HDI), was used as cross-linker

with no further purification (Perstorp, equivalent weight of NCO (EW)NCO = 183 g; NCO functionality = 2.8, molar mass = 504.6 g/mole). Solvents p.a. grade: THF, n-heptane, NMP (N-methyl pyrrolidone) and methanol were used as received without further purification.

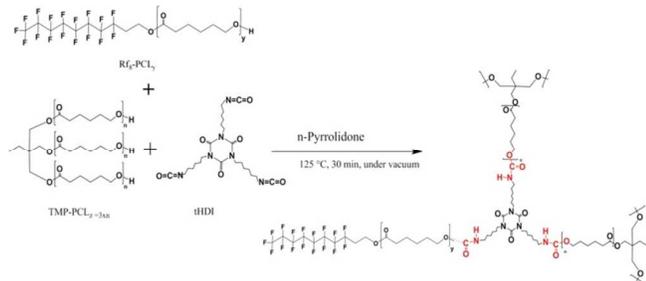
The thickness of the films was controlled by dropping always the same specific volume of the formulation on a glass slide and spreading it homogeneously to cover the complete slide. Alternatively, the same formulations were spread on aluminium panels and the thickness of the layer was controlled by a square "Doctor blade" applicator. The final thicknesses of the films were determined with a "magnetic checker" when applied on aluminum plates or by Confocal Microscopy when applied on glass slides.

PDMS – polymer films

Poly(styrene-maleic anhydride) (PSMA) latex (synthesized by standard free radical polymerization technique) was provided by Sartomer (SMA1000F, $M_n = 2,650$ g/mol). PDMS-NH₂ grades were purchased from Gelest (for PDMS1000 the manufacturer indicates a $M_n = 800$ -1,100 g/mol whereas we calculated 1,030 g/mol based on the ¹H NMR characterization) For PDMS2000 these data are 2,000 g/mol and 2,030 g/mol, respectively). Ammonia solution (Merck, 25 wt% in water) and adipic dihydrazide (ADH, DSM NeoCoating Resins) were used without purification.

Poly(urethane) cross-linked films with perfluorinated dangling chains ($F_{17}C_8$ -PCL_y, $y = 8, 16, 24$).

Typically, polyurethane films were prepared from a mixture of the polymer precursors described above^{8, 28} with a triisocyanate cross-linker (t-HDI) and using N-methyl pyrrolidone (NMP) as the solvent (45 % wt solid content) (Scheme 2). The molar ratio of NCO/OH was kept at 1.1 to ensure full conversion of OH groups of the polymer precursors. The films were drop casted on glass slides (previously cleaned with ethanol, sonicated for 10 minutes and dried/flushed with air). Typical "wet" thickness of the polymer films ~ 400-500 μm. The films were then cured at 125 °C in a vacuum oven (pressure was about 20 mbar) for 30 min.

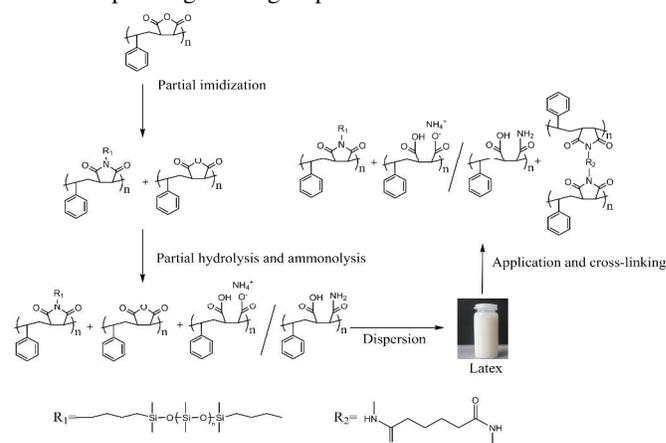


Scheme 2: Molecular structures and reaction scheme of the preparation of the Poly(urethane) cross-linked films with fluorinated ($F_{17}C_8$ -PCL_y) dangling chains.

Preparation of the Poly(styrene-alt-maleic anhydride) (PSMA)-PDMS films

In order to convert a known fraction of the anhydride groups of PSMA into imides, a two-step reaction was performed.

The first step was the addition of an amine to a PSMA solution in acetone to obtain the corresponding polyamic acids. The second step led to ring closure of the amic acid groups to form the corresponding imide groups.



Scheme 3: Molecular structures and reaction scheme of the preparation of the Poly(styrene-alt-maleic anhydride) (PSMA)-PDMS films.

Latexes of poly(styrene-alt-maleic anhydride) (PSMA) were obtained by partial imidization with PDMS1000 or PDMS2000, followed by partial ammonolysis of the anhydride moieties in acetone as described in more detail elsewhere^{30, 32} (Scheme 3). The compositions of modified PSMA copolymers are given in Table 1.

Table 1: Composition of the PSMA-PDMS copolymers used in this study.

	Reactions with anhydride functionalities of PSMA				wt% of PDMS
	Imidization with PDMS-NH ₂ * (mol %)		Cross-linking using ADH (mol %)		
	Target (mol%)	Experim. (mol%)	Target (mol%)	Experim. (mol%)	
PSMA1-1000	1	0.8 ± 0.1	59	20	4.7
PSMA15-1000	15	13.6 ± 0.8	45	20	42.6
PSMA1-2000	1	0.9 ± 0.2	59	20	9.0
PSMA10-2000	10	9.1 ± 0.3	50	20	49.7

* Mol percentage of anhydrides that could react with PDMS-NH₂ ($M_n = 1,000$ or $2,000$ g.mol⁻¹) based on the weighed-in amount of PSMA and PDMS-NH₂. All percentages are relative to the initial amount of anhydride present along the PSMA backbone. In PSMA1-1000 the "1" indicates the targeted mol percentage of initially present anhydrides of PSMA that is imidized with PDMS-NH₂ and the "1000" stands for the approximate M_n of the grafted PDMS-NH₂.

20 mol% of the remaining 40 mol% of the anhydride groups of the PSMA were used for cross-linking with adipic dihydrazide (ADH). When the mol% of the cross-linking increases, the brittleness of the films increases as well.

PSMA-PDMS films were prepared by applying the latexes containing the cross-linker (adipic dihydrazide by drop casting, to glass substrates (cleaned by ethanol), immediately followed by a curing step in an oven at 160 °C. 20 mol% of the remaining 40 mol% of the anhydride groups of the PSMA were used for cross-linking with adipic dihydrazide (ADH) in order to perform microtoming experiments. The typical thickness of films for DRCA measurements was around 10-15 μm .

Characterization techniques and DRCA procedure

Dynamic water Contact Angle (CA) and Dynamic Recovery Contact Angle (DRCA) measurements were performed on a Dataphysics OCA 30 at room temperature, using de-ionized water as probe liquid. Water droplets were measured in advancing and receding mode and the reported results are the average of three separate drop measurements at different locations at the films surfaces. The error bars provided correspond to the fitting error as provided by the Dataphysics calculation software. For the sake of testing the DRCA reproducibility, for some of the films, several replicas were measured and the sample standard deviation typically ranged between ± 2 to 5° .

The initial immersion period was determined as follows: the films prepared on glass substrates were immersed in water for a specific period of time (e.g. one night to two days) to expel the low surface energy components from the surface into the films bulk, and achieve an equilibration state. Several periods of immersion were tested for each of the polymer systems, and the CA_{adv} was measured after different immersion periods. The immersion time necessary to expel all the low surface energy groups from the interface was set to the time at which no further change of the CA_{adv} was observed, as compared to the initial angle measured before immersion.

The time t_0 was determined as follows: After immersing the film in water for the equilibration period established as described above, the surface of the film was carefully cleaned using a soft tissue (KimTech from Kimberly-Clark – dust free) to remove the excess of water or gently blown by an air flow to avoid contamination from the paper. Note that after this wiping step an adsorbed film of water is probably still present in the film, as reported by several authors, who studied wetting of surfaces at the molecular scale^{38, 39}.

Immediately after this soft wiping, a water droplet of 0.5 μL was placed on the surface of the film in order to prevent immediate interaction with air, and the Dynamic CAs were measured. The advancing (CA_{adv}) and receding (CA_{rec}) contact angles were measured consecutively, using the continuous mode of the Dataphysics software, with a waiting period of 2 seconds between the advancing and receding CA measurement. This measurement set the zero time (t_0) and after it, the complete film was exposed to air. After a certain period of air exposure (e.g., $t_e = 60$ s) another droplet of water (0.5 μL) was placed on the same spot as used for the t_0 measurement. The air exposure time intervals (t_e) were incremented step-wise taking in consideration the previous time measured (e.g., considering time-steps of 60 seconds, if the first exposure time is $t_{e1} = 60$ s,

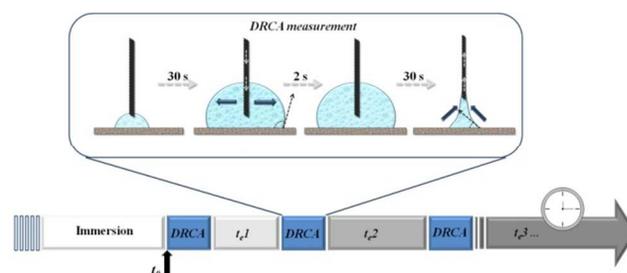
the next will be $t_{e2} = 120$ s, $t_{e3} = 180$ s, $t_{e4} = 240$ s and so on ...) The dynamic CAs were measured for sequentially incremented time-intervals until no further changes were registered for the dynamic CAs values measured, which determined the air-exposure time period for the complete rearrangement, t_r .

For the fluorine systems, the DRCA measurements were carried out by measuring every time in the same spot and also on different spots of the films surface. No significant differences were observed between these two.

The DRCA measurements were carried out as follows, with the “sessile needle-in” continuous mode and the following parameters (see Scheme 4): for the CA_{adv} measurement, a starting droplet of 0.5 μL was placed on a spot of the film surface. Its volume was continuously increased by the needle dispenser, with a constant rate of 0.5 μLs^{-1} , up to a final volume of 15.5 μL . After 2 seconds waiting, the 15.5 μL water droplet volume was continually decreased, by retracting the water through the needle and with the same 0.5 μLs^{-1} rate, until a final volume of 0.5 μL is reached. By this DRCA procedure, the water droplet initially placed on the film is removed by default from the surface in the end of the measurement, letting the contact area re-exposed to air, i.e., each measurement “re-sets” the exposure time to zero in the area probed by the droplet. The next t_e measured is incremented taking in consideration the previous t_e measured, e.g., if the initial time of air exposure after the droplet is removed, is $t_{e1} = 60$ s, the next will be $t_{e2} = 120$ s, $t_{e3} = 180$, etc...

The time-intervals suitable for collecting a DRCA measurement on each material (t_e , with e = minutes or seconds of air exposure) were determined by doing a first preliminary experiment to assess the time-scale variations. The total time-interval needed to stabilize the dynamic CA's at a constant value, corresponds to the time needed for the surface changes to recover into a stable state after the initial water-induced rearrangements take place, which is named here as t_r .

The total air-exposure time needed to stabilize the dynamic CAs at a constant value close to the one of the original-dry film, which is named here as t_r , corresponds to the time needed for the surface to recover into a stable state, after the initial water-induced rearrangements have taken place.



Scheme 4: Schematic of the total time-line of the DRCA-Dynamic Recovery Contact Angle measurements: t_0 = DRCA measurement immediately after immersion and t_{ex} = DRCA measurements at the incremented x time (minutes or hours depending on the system).

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