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Surface Mobility of Polyurethane Networks Containing Fluorinated Amphiphilic Reactive Additives

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ABSTRACT: We created a model system made up of PU networks containing reactive surfactant additives in small amounts (<1%), brought in during the synthesis and able to reorient when changing the surrounding medium. The surfactants were made of fluorinated chains, sulfonamide kneecaps, and alkyl chains with a hydroxyl function able to react with the network isocyanates. The basic PU were made of a macrodiol, a diisocyanate and a triol (cross-linking agent). We were able to change their bulk glass transition easily and therefore their surface mobility by varying the respective ratios of diol and triol (a rubbery one, $T_g = -20$ °C, and a glassy one, $T_g = 40$ °C). The reactive surfactants were used to give a hydrophobic nature to the surface of PU networks when in contact with air. Several characterizations were performed, including wetting and dewetting measurements, to prove that less than 1 wt % of the fluorinated reactive additives is sufficient to confer a very hydrophobic nature to the network surface without changing its bulk properties. The influence of the network glass transition on the top surface reorganization was also investigated.

Introduction

Material surface modifications have drawn much attention during the past few years.[1,2] Wetting measurements usually show a difference between the advancing and the receding contact angle. For polymeric surfaces, this wetting hysteresis can be very large (^{2}80−^{20}90° in some cases) even for relatively smooth materials and is principally ascribed to surface molecular reorganizations at the solid−liquid interface.[3] Indeed, chain segments or lateral chains can move to the outermost surface according to the environment (water, air, alkanes,...) in order to minimize the interfacial energy. The understanding and control of the structure and mobility at polymer surfaces would present a considerable interest in different areas such as rubbing improvement, wear, antifouling paints, etc.

Furthermore, polyurethane systems constitute a group of polymers with highly versatile properties and a wide range of commercial applications due to their excellent bulk properties. Surface properties are the governing factor for many applications (such as antifouling, biocompatibility, wetting, and adhesion control...) and research has long been focused on surface modification of polymers.[2−8] It is generally acknowledged that polymers are sufficiently mobile on the molecular scale to reorganize molecularly at the surface in a relatively short time, in relation with the environment.[2−6,9−11] The interface between a polymer and the surrounding medium will rearrange itself in order to get a minimum free surface energy. Therefore it seems possible to modify the surface properties by incorporating active components (hydrophilic, hydrophobic, or amphiphilic) in the bulk material surface. Meanwhile, small molecules are easily extracted from polymers and common surfactants cannot be employed to get a permanent surface modification; different methods have been explored to solve this problem.

Copolymers with block containing highly fluorinated side chains are reported to be highly hydrophobic materials[6−8] when in contact with air; the block copolymer segregates to the surface, driven by the low surface energy of the fluorinated blocks. However, the main drawback of this approach is an alteration of the bulk properties due to the high fluorine content.

In many of the applications where the excellent mechanical properties of PU are required, surface modification is expected to preserve the bulk properties. Indeed, the need to use a small amount of surface active compounds has been pointed out by Wesslén et al.[4,12,13] They have shown that the addition in small amounts (5% weight) of an amphiphilic polymer in polyurethanes and polyurethane ureas is sufficient to confer an amphiphilic nature to the material. These modifications keep the bulk properties unaltered. In the same way, using 5% of hydrophobic polymers as additives, Santerre et al.[14] reported modified PU surfaces with wettability features equivalent to PTFE and with no detectable additive effects on the bulk structures.

We could therefore expect that reactive additives, brought in small amounts during the synthesis, would lead to surface modification of PU networks. This route would thus present a great potential in many respects:

- The surface modification would be permanent (with respect to the adjacent medium) because the additives are covalently bonded to the network.
- It would offer a continuous supply of surface active moieties in the case of eroded or abraded surfaces.
- The small amount of additives used would greatly cut down the industrial application costs.

This study pursues a double goal: (i) to synthesize and characterize polyurethane networks with a low surface energy made from a bulk modification; (ii) to use these networks as model surfaces to study surface reorganization phenomena using AFM force measurements (forthcoming paper[15]).

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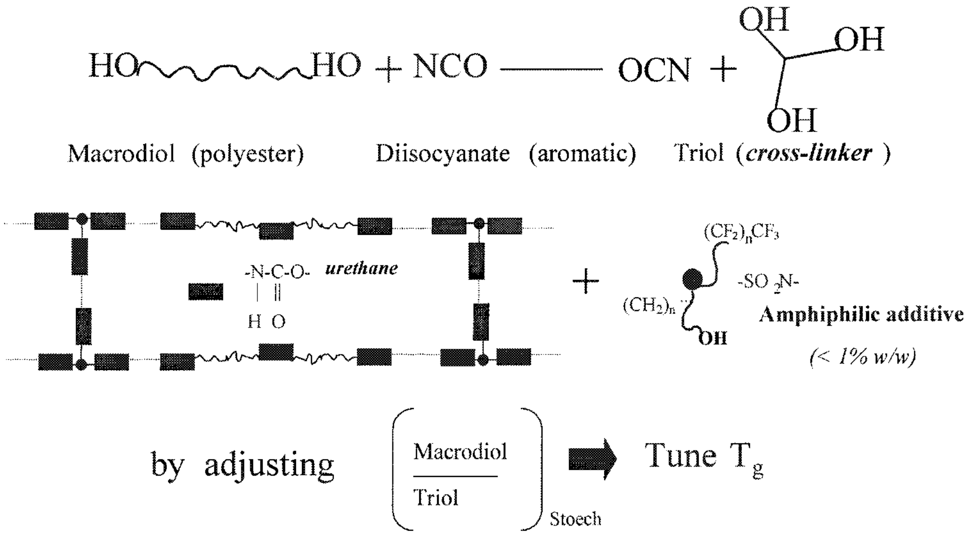
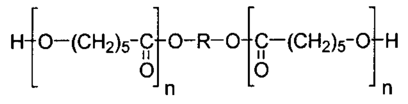


Figure 1. Route followed for the fabrication of thin PU surfaces with varying T_g containing amphiphilic additives likely to reorient with the adjacent medium.

We created a model system made up of PU networks containing reactive surfactant additives in small amount (<1 wt %). The additives, brought in during the synthesis, were able to reorient when changing the surrounding medium. The basic PU (without any surfactant additives) were made of macrodiols, diisocyanates, and triols (cross-linking agents). We were able to change their bulk glass transition easily and therefore their surface mobility by changing the respective ratios of diol and triol (Figure 1). The reactive surfactants were used to give a hydrophobic nature to the surface of PU networks when in contact with air (a rubbery and a glassy one). From this study, we tried to highlight the influence of the network glass transition on the surfactants surface reorganization.

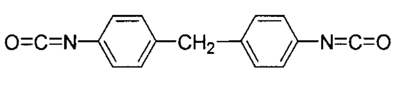
Experimental Section

Materials. CAPA 200, from SOLVAY INTEROX, was a low molecular weight ($M_w = 550$) linear polyester diol derived from caprolactone and terminated by primary hydroxyl groups. The hydroxyl value of this chemical was 208 mg of KOH/g.[16]

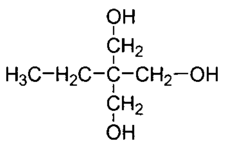


$$H\left[O-(CH_2)_5-\underset{\underset{O}{\|}}{C}\right]_n O-R-O\left[\underset{\underset{O}{\|}}{C}-(CH_2)_5-O\right]_n H$$

CAPA 212, from SOLVAY INTEROX, is similar to CAPA 200 with a higher molecular weight ($M_w = 1000$) and an hydroxyl value of 112,5 mg KOH/g. The diisocyanate used for this study was pure 4,4′-diphenylmethane diisocyanate (MDI), from ICI.

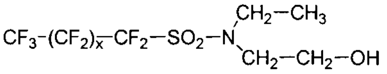


The cross-linking agent was 1,1,1-tris(hydroxymethyl)propane (TMP), from Fluka, with a purity of more than 98%.



$$H_3C-H_2C-\underset{\underset{OH}{|}}{\underset{CH_2}{|}}{\overset{\overset{OH}{|}}{\overset{CH_2}{|}}{C}}-CH_2-OH$$

The fluoro alcohol used as a reactive additive was FLUORAD FC10 (FC_{10} afterward), from 3M-France:



$$CF_3-(CF_2)_X-CF_2-SO_2-N\begin{matrix}CH_2-CH_3\\CH_2-CH_2-OH\end{matrix}$$

with $X = 6$

The tetrahydrofuran (THF) used as a solvent during the synthesis was of HPLC grade. Its purity was more than 99.7% without any stabilizer (stabilizers commonly used are alcohols, which can then react as additives with the network).

Synthesis. In this study, we were able to tune the glass transition of our network quite easily by changing the ratio [diol/triol]. This enabled us to get a rubbery or a glassy PU at room temperature while keeping the same network chemistry. Indeed, CAPA 200 and CAPA 212 have the same chemical structures but different molecular weights (chain length).

The glassy PU_g were synthesized from CAPA 200/MDI/TMP using a reactive function ratio of 1/4/3. Rubbery PU_r was synthesized from CAPA 212/MDI/TMP with a function ratio of 1/2/1 following a theoretical prediction (see the Discussion section) and some unpublished data from our laboratory).[20] Basic PU networks (without additives) were synthesized using a three-step method.

First, 50 g of CAPA were dried in the reactor under vacuum at 80 °C for 1 h. In the first step, MDI (92.7 g for the glassy and 46.3 g for the rubbery networks) was reacted with CAPA 200 (/CAPA 212). This reaction was carried out in a glass reactor for 4 h, at 80 °C (thermostated bath), under stirring and primary vacuum (rotary pump). In the second step, the reactor was brought back to room temperature and pressure; the TMP (24.8 g/8.2 g), dissolved in THF (290 cm^3/180 cm^3) was added to the prepolymer. The mixture, containing 35 wt % of reactants, was stirred until complete dissolution was attained. It was then stored for a few days at −20 °C before the preparation of the samples. Finally, cross-linking was completed in an oven, at 110 °C for 16 h.

For the PU networks containing additives (PU_gFC_{10} and PU_rFC_{10}), the same synthesis was employed. FC_{10} was dissolved in the CAPA before vacuum drying (just before the first step of reaction). In this study, 1 wt % of FC_{10} (1.7 g/1.05 g) was used and the corresponding amount of MDI was added to the solution to preserve stoichiometry.

We also performed a second kind of synthesis with additives brought in at the end of the second step. Indeed, at that point, the probability of reaction with the few isocyanate available in the network is low and the reactive additives behave more like normal nonreactive ones.

Samples Preparation. For DSC measurements, a coat of dissolved PU (30 wt %) was applied on PTFE plate and was easily removed from the plate after cross-linking.

Polymer films for contact angle measurements were made by dip coating (about 30 wt % of the reactive blend) on clean glass plates. Solvent evaporation was done at room temperature to limit bubble formation; it was then cross-linked at 110 °C for 16 h as mentioned above.

Small molecules could migrate toward the surface during PU synthesis.[21,22] Because these impurities can easily modify the contact angle measurements, we decided to clean each film thoroughly. Samples were extracted with hexane (from SDS, spectroscopic grade, purity>99%) in a Soxhlet for 10 h. They were also rinsed with methanol and distilled water. Finally, samples were vacuum-dried at 70 °C during 24 h. They were then kept in Joseph papers before measurements.

DSC Measurements. A Dupont 990 thermal analyzer was used in this study. Samples were cut off from films prepared as described above (~10−20 mg). DSC traces were run under helium between −130 and +100 °C with a heating rate of 10 °C/min. T_g was evaluated on the second run after a faster cooling (>10 °C/min) in order to eliminate the aging phenomena. For each polyester (CAPA 200 and 210) and PU results were obtained on more than two different samples coming from different syntheses. The glass transition temperature T_g was taken at the onset of the phenomenon. The values for the model networks (TMP + MDI) were taken from previous works.[24]

Dynamical Mechanical Analysis (DMA). DMA measurements were carried out using a dynamical mechanical analyzer DMA 2980 from TA Instrument from −100 to +120 °C and 1 Hz with a heating rate of 3 °C/min. The experiments were performed under tension mode (sample of 25 mm × 5 mm ×1 mm).

Secondary Ion Mass Spectrometry (SIMS) Analysis. Depth profile was collected using a magnetic sector SIMS (CAMECA IMS3/4f, CAMECA Instruments Limited). Primary ion: Cs^+, 10 kV. Secondary polarity: negative, 4.5 kV. In addition to the gold coating, the optional electron gun was used to compensate the charge up effect. In depth profiling, the intensities of secondary ions, $^{14}N^-$, $^{19}F^-$,$^{12}C^-$, and $^{197}Au^-$, were collected as a function of sputtering time. The depth of sputtered holes (3.8 μm) was subsequently measured using a surface profiler (Dektak, Veeco/Sloan Technology Ltd.).

Contact Angle Measurements. Contact angles of probe liquids on PU network surfaces were measured by the sessile drop method, using a video camera equipped with a homemade image analysis. Liquid droplets were manually deposited on the surface or withdrawn from it by a microsyringe. Advancing (θ_a) and receding contact angle (θ_r) were measured by increasing or decreasing the volume of droplet until the three phase boundary line moved over the surface. Methylene iodide was used to determine the dispersive interactions and water was used for "polar" (or non dispersive) ones. The results reported here consist of the average of at least 40 measurements taken from five different samples. The standard deviations obtained for θ_a were systematically better than ± 1.8° and for θ_r better than ± 2.5°.

Evaluation of Surface Energies. The surface energy estimation of a solid remains problematic because of the several rough assumptions usually used. In this study, we basically wanted to compare the PU surfaces to draw some general conclusions. Of course, the absolute values of the surface energy are only approximate.[23]

Nevertheless, several methods are currently used to estimate the surface free energy (γ_s) of solids from contact angle data. Girifalco and Good[28] and Fowkes[29] have suggested that the dispersive component of the work of adhesion might be proportional to the geometric mean of the dispersion component of the liquid and solid cohesion energies. Kaelble[30] and Owens and Wendt[31] have extended the Girifalco−Good−Fowkes approach by using the same geometric mean for polar interactions, thus obtaining:

$$W_a = \gamma_{lv}(1 + \cos\theta) = 2\sqrt{\gamma_s^d \gamma_{lv}^d} + 2\sqrt{\gamma_s^p \gamma_{lv}^p} \qquad (1)$$

This method is one of the most frequently used in the literature but it has been criticized because polar interactions depend on the probe liquids chosen.[31−34]

In this study, the approach is quite different. Using a simplified one-step approach, Fowkes [35] suggested the use of methylene iodide contact angles to give a direct estimate of γ_s^d for a polar surface. Methylene iodide is a liquid of high surface tension; with over 95% of its surface energy being due to dispersive interactions, the second term in eq 2 can be neglected.

$$\gamma_s^d = \gamma_{CH_2I_2}^d (1 + \cos\theta)^2/4 \qquad (2)$$

Using water as a second probe liquid, specific interactions with water, I_{sw}, were obtained by the relation:

$$I_{sw} = \gamma_{H_2O}(1 + \cos\theta) - 2\sqrt{\gamma_s^d \gamma_{H_2O}^d} \qquad (3)$$

Although I_{sw} reflects the nondispersive character of the solid probed, it should not be reduced to γ_s^{nd}, which is independent of the probe liquid. Nevertheless, to estimate γ_s, we used the geometric approximation with I_{sw}:

$$I_{sw} = 2\sqrt{\gamma_s^{nd} \gamma_l^{nd}} \qquad (4)$$

This approximation has also been used in this study to show the weak contribution of γ_s^{nd} vs γ_s^d.

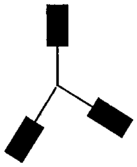
Results and Discussion

Before performing any synthesis, we tried roughly to predict the final T_g of our networks by applying the Fox equation,[17] generally employed for thermoplastic blends. Indeed, the glass transition temperature of blends could be estimated from the weight fraction and the glass transition of each components. In the case of thermosets, the equation becomes:[18]

$$\frac{1}{T_g} = \frac{W_{polyester}}{T_{g(polyester)}} + \frac{W_{cross-link}}{T_{g(cross-link)}}<frx \qquad (5)$$

The main (crude) assumption is a network composed of soft polyester chains

$M_w = 550$, $T_{g(expt)} = -78$ °C and M_w 1000, $T_{g(expt)} = -73$ °C, and hard cross-links (made from all the diisocyanate and triol brought in) with known T_g



$T_{g(expt)}$ = 168 °C. The system is considered miscible without any phase segregation. Indeed, the CAPA based PU networks appear homogeneous in SAXS measurements.[18,19]

Therefore, taking a reactive function ratio of 1/4/3 (CAPA200/MDI/TMP) and 1/2/1 (CAPA212/MDI/TMP) would yield a glassy and a rubbery network with theoretical T_g values of $T_{g(theor)}$(glassy) = 46 °C and $T_{g(theor)}$(rubbery) = −22 °C.

Table 1. DSC Experimental Results and Theoretical Predictions for the Glass Transition Temperatures of the Basic and Modified PU Networks

sample	$T_{g(expt)}$ (°C)	$T_{g(theor)}$ (°C)
basic PU_g	38−39	46
PU_gFC10	37−39	
basic PU_r	−16 to −18	−22
PU_rFC10	−17 to −18	

DSC Analysis. The PU were synthesized following the above predicted ratio. The results of DSC measurements are reported in Table 1. Since the glass transition spreads over more than 20 °C, the T_g value was taken at the onset of the phenomenon. This zone corresponds to the temperature where the mobility starts to increase in the network. Neither endothermic nor exothermic peaks were seen in the thermograms, showing that cross-linking had ended and that the solvents had completely evaporated.

This should be noted that our crude predictions were not far off from the DSC results. This goes to show the full potential of a theoretical approach.

Furthermore, the same order of magnitude was obtained for the PU with and without additives. Indeed, T_g was estimated to be about 39 °C for PU_g and −17 °C for PU_r. These results suggest that the FC_{10}, with a concentration less than 1 wt %, has no detectable effect on the bulk structure. It is worth noting that if surface properties are definitely modified by the reactive additives (see below), the bulk properties are insignificantly changed.

DMA Analysis. The dynamic mechanical measurement is one possible method to characterize coarsely a thermodynamically phase separation between soft and hard segments. In that case, the curves tan (α) vs temperature at a fixed frequency show two maxima. The DMA results that show (Figure 2) only one relaxation for each PU indicate that the networks exhibit a one-phase structure in agreement with SAXS measurements done on the same kind of systems by others authors.[18] Furthermore, we tried to correlate the *thermal* DSC results with the *mechanical* DMA ones. We instead talk in that situation about the α-relaxation associated with the glass transition. To be consistent, since we measured the T_g at the onset of the phenomenon (when the mobility starts in the network), we took the value at the beginning of the tan (α) peak. In all four cases, the T_α (1 Hz) matches the T_g. The addition of the reactive surfactant does not alter the mechanical and thermal bulk properties. We see also (Table 2) that the bare and modified networks "bulk" Young moduli (22 °C) are here indistinguishable one from the other (DMA resolution). The influence of the additives on top surface mechanical properties made with an AFM will be published elsewhere.[15]

SIMS Analysis. This analysis was planned to give us an atomic signature of the presence of fluorine moieties in our samples. It establishes that additives are well spread throughout the entire sample (Figure 3) as expected. Furthermore, this result is an indirect proof that additives are held in the networks through chemical bonds. Indeed, since all the samples were thoroughly extracted in hexane with a Soxhlet for at least 10 h, we may then suppose that the additives present in the networks did react with the isocyanate.

Contact Angle Measurements. Advancing and receding contact angles with water and methylene iodide are reported in Table 3. Since advancing and receding contact angles are different, hysteresis ($\theta_a - \theta_r$) has been reported. Results of wetting and dewetting measurements will be interpreted in terms of surface energies in the next part.

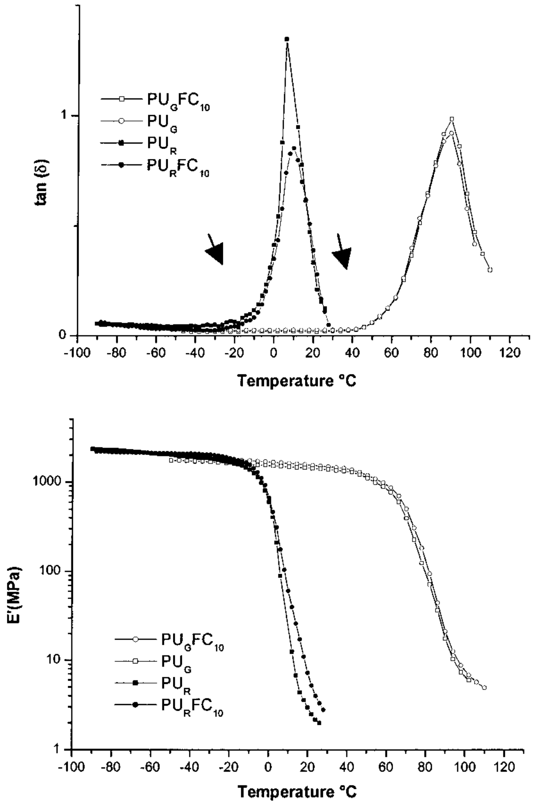


Figure 2. Dynamic mechanical analysis spectra for the four different PU networks studied: (up) storage moduli; (down) tan (α) at 1 Hz The arrows indicate the region where the mobility starts in the networks: 40 °C for bare and modified glassy networks and −20 °C for both rubbery ones.

Table 2. Young Modulus Values from DMA Measurements at 22 °C

PU (bare/modified)	*E* (MPa)
glassy	~ 1500
rubbery	~15−20

Before analyzing Table 3 and Figure 4, we would like to make a few statements on the wetting hysteresis phenomenon and its possible interpretations. For an ideal, perfectly smooth, chemically homogeneous, rigid, insoluble and nonreactive surface, θ_a should be equal to θ_r. However, hysteresis is often present, particularly in polymers. Advancing angles reflect the interface between the solid "equilibrated" against the gaseous medium (often apolar air), corresponding to the interaction of the test liquid with the low energy components of the surface. Receding angles reflect the interface between the solid and the liquid corresponding to the interaction with high energy components of the surface.

As we said in the Introduction, the high mobility of polymers allows surface reorientation of the outermost surface (or buried) moieties to minimize the free surface energy [36] and wetting hysteresis could be ascribed to those surface reorganizations. But many other factors could contribute to hysteresis: roughness (physical heterogeneity),[37] chemical heterogeneity,[38] diffusion or swelling of the test liquid into the material,[39] or deformation of the solid surface under (the vertical component of) the liquid surface tension.[40]

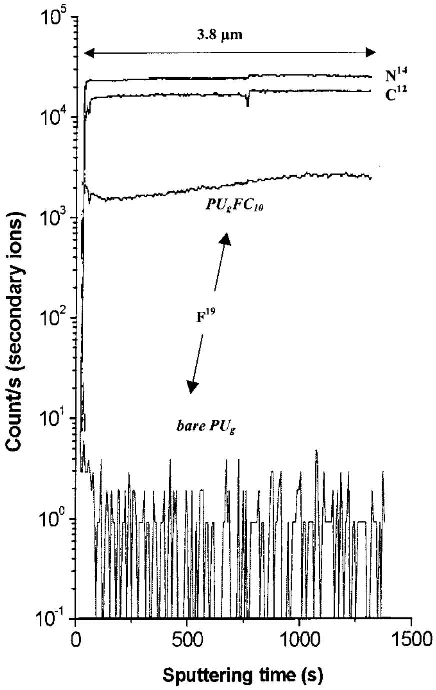


Figure 3. For clarity reasons only the SIMS results for the glassy networks are presented. The intensities of secondary ions (count/s) are a function of the sputtering time easily convertible in depth at the end of the experiment (3.8 μm in this case). The C^- and N^- ions showed up at the same intensity for bare and modified PU. Fluorine ion F^- appears as trace (noise) in the bare PU. Of course, the same trend is observed for the rubbery networks.

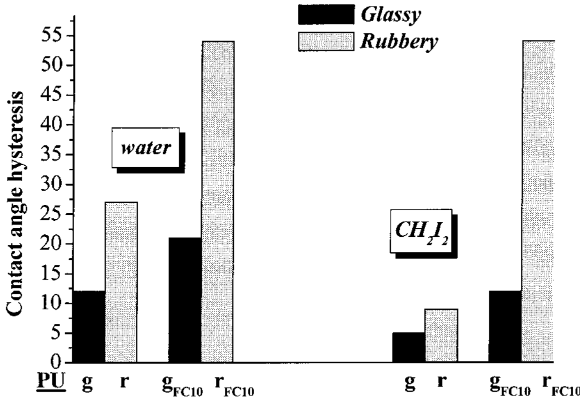


Figure 4. Contact angle hysteresis for bare and modified PU in bar graph format.

Obviously, these different contributions are generally linked. One must therefore be vigilant when interpreting hysteresis uniquely in terms of surface reorganizations. Thanks to the experimental conditions used in this study, roughness (RMS = 0.25 nm as seen by tapping AFM), swelling and surface heterogeneities have a slight influence on measured contact angles. On the basis of the difference in contact angles of PU with and without additives, which is quite significant, we could legitimately interpret the hysteresis difference in terms of surface reorganizations.

Evaluation of surface energies. Surface energies calculated from Fowkes method (eqs 3 and 4) are reported in Table 4 as well as the approximation for γ_s^{nd} and γ_s (eq 5). The first observation we can make is that our networks are hydrophobic materials. Even for dewetting, the surface energy is mainly due to dispersive interaction. Indeed, the most important nondispersive contribution is obtained on dewetting, for the bare and modified rubbery PU (PU_r and PU_rFC_{10}), and it corresponds to 21% of the total surface energy. Furthermore, it is rather satisfactory that both basic PU have a very close but distinguishable wetting and dewetting behavior related to surface mobility; the glassy dispersive and nondispersive contributions to the surface energy are always bordered by the rubbery ones.

As expected, the reactive additive incorporation leads to a great drop of PU surface energy in contact with air (wetting). Both γ_s^d and I_{sw} are affected (decrease of about 25 mJ/m^2 for each component), and γ_s^d (around 46 mJ/m^2), which corresponds to 90% of the total surface energy, drops to 24 mJ/m^2 for PU_gFC_{10} and to 20 mJ/m^2 for PU_rFC_{10}. Contact angle measurements made by Owen and Kobayashi [41-45] on fluorinated materials (using the same theoretical framework) lead to dispersive surface energies ranging from 14 mJ/m^2 for PTFE (CF_2 groups) to 7 mJ/m^2 for fluorosilicones containing CF_3 groups. Fluorosilicones used by these authors are well above their T_g and it is interesting to note that their surface energies are similar to our PU_rFC_{10}. With less than 1 wt % of fluorinated compound, the PU_rFC_{10} surface behaves as a system containing exclusively CF_3 and CF_2 groups (Figure 5). PU_gFC_{10} surface energy is a bit more important (24 mJ/m^2); this is most likely due to a drop in the surface mobility and a slightly lower fluorine content at the surface as “seen” by SIMS.

Analysis of surface energies on dewetting gives information about the importance of network mobility (on a short time frame due the contact angle method used in this study). For PU_gFC_{10}, a slight increase of surface energy is observed on dewetting but remains very low compared to the basic glassy PU_g ones (about 20 mJ/m^2 difference). The low network mobility in glassy PU_g does not allow a fast molecular reorientation when in contact with a high surface tension liquid. The high energy groups are then hidden (buried just below the outermost surface) by the fluorinated chains remaining at the surface.

Indeed, the PU_gFC_{10} dispersive dewetting values never reach the PU_g ones (around 48 mJ/m^2). However, the high network mobility of the PU_rFC_{10} leads to a fast recovery of high energy groups in contact with the probe liquid. In this case, surface energy on dewetting matches the basic PU ones (PU_r and PU_g), meaning that the reactive additives are no longer present at the outermost

Table 3. Contact Angles Results

	methylene iodide			water		
sample	θ_a	θ_r	$\Delta\theta$	θ_a	θ_r	$\Delta\theta$
PU_g	29.5 ± 1.2	25.2 ± 1.8	4.3 ± 3.0	72.8 ± 0.8	60.8 ± 2.1	12 ± 2.9
PU_gFC_{10}	71.6 ± 0.7	59.9 ± 1.8	11.7 ± 2.5	99.3 ± 0.5	77.5 ± 2.5	21.5 ± 3.0
PU_r	30.9 ± 1.3	23.3 ± 2.4	7.6 ± 3.7	79.0 ± 1.2	51.9 ± 2.2	27.1 ± 3.3
PU_rFC_{10}	78.8 ± 1.2	25.3 ± 2.1	53.5 ± 3.3	104.3 ± 1.0	52.8 ± 1.4	51.5 ± 2.4

[a] Advancing θ_a and receding θ_r angles with corresponding hysteresis $\Delta\theta = \theta_a - \theta_b$ values.

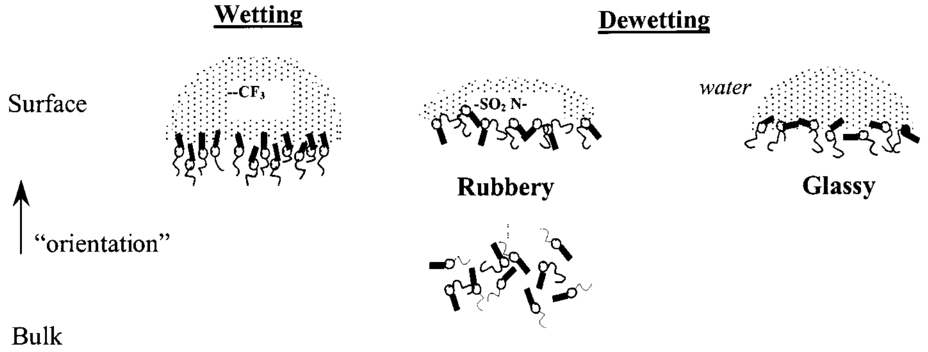


Figure 5. Sketch of the surface conformations likely taken by the additives for wetting (low surface energy moieties) and dewetting (high surface energy moieties) probed with water. The shapes of water droplets wetting more or less the PU surfaces are also represented to illustrate the contact angle meaurements. The squiggly lines represent the aliphatic chains and the rigid rods the fluorocarbon ones.

Table 4. Calculated Surface Energies (mJ/m^2)

sample	γ_s^d (±2−4%)		γ_s^{nd} (±5−10%)		γ_s (±1−3%)	
PU_g	46.5[a]	48.2[b]	4.6	9.3	51.1	57.5
PU_gFC_{10}	23.0	30.0	1.3	6.9	24.3	36.9
PU_r	45.9	48.9	2.7	13.5	48.9	62.4
PU_rFC_{10}	19.0	48.2	1.0	13.3	20	62.5

[a] Wetting. [b] Dewetting.

surface with a high energy surrounding. It is also worth noting that for, modified PU, the wetting and dewetting rubbery values are bordering the glassy ones too, as seen further up for the bare PU_g and PU_r networks.

We could then reasonably think that the hysteresis differences measured on the bare PU are due to the network mobility itself and that the hysteresis observed with the modified ones comes from the mobility of the additives bound to the surface. In the future, to really support this conclusion, we will have to perform dynamic contact angle measurements to possibly separate both mobilities: a first, fast decrease due to additives reorganization followed by a second, slower decrease due to the network reorientation.

To check if the bulk structure behaves in the same way, we slightly abraded our surface and performed afterward wetting measurements on the "bulky" surface. We observed the same trends for water contact angles. This result together with the SIMS measurements show that the modification is effective through the whole sample and suggests that additives are uniformly dispersed in the medium. Finally, we performed contact angles measurements on the PU networks containing the nonreactive additives (brought in at the end of step 2). After several Soxhlet extraction on the modified networks, the water contact angles dropped close to the value of the bare networks (102−85° for PU_rFC_{10} and 98−77° for the PU_gFC_{10}). For normal modified PU the contact angles did not change at all. This last experiment suggest that additives brought in the first step of the synthesis did react quite well with the network isocyanates.

Conclusions

This study showed a potentially interesting surface modification approach which confers a permanent modification (no solvent extraction) with a very small amount of materials without changing the bulk properties. Indeed, the incorporation in small amount (<1 wt %) of fluorinated compounds susceptible to react with the PU networks led to a very hydrophobic material (with air) without altering its bulk properties. Influence of network mobility was also pointed out by receding contact angles measurements. In contact with polar liquids (dewetting), the rubbery PU reorients itself to present polar groups on the surface, whereas for the glassy network, the reorientation is more difficult, even blocked, creating a less hydrophilic surface. The large hysteresis differences observed with the modified PU were attributed to the reactive surfactants' mobility.

Finally, the PU elaborated in this study constitute a model system that could be used to understand surface reorganization phenomenon on a smaller scale (nanometers). AFM surface force measurements carried out in different media will highlight the chemical, frictional, and mechanical aspects of the outermost PU surface.[15]

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