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Fluorinated Polyurethanes: XPS and AFM Characterization

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Summary: Fluorinated polyurethane films were obtained from 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane (IPDI) and polyethylene oxide (PEO), employing two monoalcohols with different chain lenghts as fluorinated modifiers, 1H,1H,2H,2H-tridecafluoro-1-n-octanol (EA600) and 1H,1H,2H,2H-heptadecafluoro-1-n-decanol (EA800). X-ray photoelectron spectroscopy (XPS) has demonstrated that fluorine surface enrichment takes place. Atomic force microscopy (AFM) was employed in order to characterize films surfaces, in terms of topography and differences in hydrophobicity from light and moderate tapping conditions.

Keywords: atomic force micorscopy (AFM); films; fluoropolymers; polyurethane; surfaces

Introduction

Polyurethanes are used in a wide range of applications, mainly because their properties may be easily tailored to vastly different end results, ranging from stiff, thermoset materials to soft expanded elastomers.[1] Also, fluorinated surfaces derive their characteristics from the unique molecular properties associated with the C-F bond that imparts a specific, unique chemistry and physics at interfaces. Their low surface tensions, low electrostatic loading, and low friction coefficient can play an essential role in microelectronics, antifogging and antifouling applications and are promising in medical applications.[2] The surface properties such as the contact angle generally increases, wettability and surface tension are reduced and thermal stability increases.

It is well known from the literature that small amounts of fluorine can migrate to the air-polymer interface promoting the fluorinated polymer properties in the surface, while preserving the properties of the non-fluorinated material in the bulk. Most of commercially available fluorinated polymers present a high fluorine content (50–70 wt %) which represents an obstacle for their application, such as difficulties for processability and high costs. With the aim of overcoming these limitations, the present work propose to explore the strategy of surface enrichment in order to achieve materials with a high fluorine surface concentration, preserving the bulk properties of the traditional polymers. Two fluorinated monoalcohols were employed to modify polyurethane systems, with the aim of verifying the surface enrichment and characterizing films with 1–5 wt % of fluorine content. The effect produced by the different chain lengths of the monoalcohols, was compared.

Materials and Methods

Fluorinated polyurethanes (FPUs) were synthesized from IPDI (Aldrich), PEO with average Mw≈1500 (Aldrich) as the polyol, 1,4-butanediol (BDO, Aldrich) as a

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Table 1.
Nomenclature and stoichiometric ratios[a)] in FPUs synthesis.

Material	Fluorinated agent	F (wt %)	NCO/OH in the fluorinated modifier formation	NCO/OH in the prepolymer formation
PU	–	0	–	121.5/6.8
F6PUs				
F6-1	EA600	1	121.5/1	121.5/6.8
F6-2	EA600	2	121.5/2	121.5/6.8
F6-5	EA600	5	121.5/5	121.5/6.8
F8PUs				
F8-1	EA800	1	164.7/1	164.7/9.4
F8-2	EA800	2	164.7/2	164.7/9.4
F8-5	EA800	5	164.7/5	164.7/9.4

[a)] The final NCO/OH ratio is 1 for all the samples, in the chain extension reaction stage.

chain extender and dibutyltin dilaurate (DBTDL, Aldrich) as a catalyst. Tetrahydrofuran (THF, Cicarelli) was employed as a solvent and the fluorinating agents were Fluowet EA600 and EA800, gently supplied by Clariant Ltd. PEO was dried in vacuum at 90 °C for at least 2 h and the rest of the reactants were employed as received. The reaction equipment consisted in a three necked round bottomed flask (for N_2 and reactants inlets and reflux condenser) mounted on a hot plate magnetic stirrer device. The N_2 flux circulated through silica gel before reaching the reactor.

XPS spectra were taken using a commercial VG ESCA 3000 system. The base pressure in the experimental chamber was in the low 10^{-9} mbar range. The spectra were collected using Mg Ka (1253.6 eV) radiation and the overall energy resolution was about 0.8 eV. All spectra were collected at an angle of 45° with respect to the normal to the surface. Surface charging effects were compensated by referencing the binding energy (BE) to the C_{1s} line of residual carbon set at 285 eV BE.[3] Sputtering of the sample surface was performed with an argon ion gun under an accelerating voltage of 3 kV.

AFM measurements were performed using Agilent Technologies 5500 SPM equipment. The silicon probe employed (Nanosensors), had a tip radius of curvature, cantilever force constant and resonance frequency of 10 nm, 42 N/m and 330 kHz, respectively. The amplitude of the free oscillation (A_0) and the set-point amplitude ratio, $r_{sp} = A_{sp}/A_0$, where A_{sp} is the set-point amplitude, were controlled during the experiments.

A Ramé Hart model 500 Advanced Contact Angle Goniometer with DROP-image Advanced Software was employed to determine the contact angles (CAs) of the films, using bidistilled water as a probe liquid. The sessile drop method with a 5 μl drop volume was used.

The fluorinated modifier for the FPUs is synthesized from the reaction between IPDI and EA (EA600 or EA800) in the presence of 0.15 wt% DBTDL/IPDI, at 65–75 °C during 2 h.

The total amount of IPDI necessary to complete the synthesis of the FPU is mixed with EA; the amount of the fluorinated agent is one which defines the fluorine percentage desired in the final material. Table 1 shows the nomenclature for the FPUs identification and the stoichiometric ratios employed in each reaction stage.

The IPDI-EA reaction gives rise to the formation of monofunctional isocyanate fluorinated species, which are capable of reacting in further stages and thus being incorporated in the FPU as end chains.

The prepolymer is obtained by the addition of PEO to the previous IPDI-fluorinated modifier mixture. This reaction in carried out at 65–75 °C during 3 h. Owing to the excess of NCO groups in the mixture, the prepolymer statistically consists in –NCO terminated chains. The amount of

Table 2.
FPUs surface characterization.

Material	F/C		Surface enrichment	CA
	average	experimental		
PU	–	–	–	56 ± 2
F6-2	0.0269	0.223	8.3	98 ± 2
F6-5	0.0670	0.334	5.0	101 ± 2
F8-1	0.0109	0.465	42.7	107 ± 2
F8-2	0.0223	0.570	25.6	109 ± 2
F8-5	0.0565	0.356	6.3	105 ± 2
PU[t]	–	–	–	10 ± 5
F6-2[t]	0.0269	0.260	9.7	78 ± 2
F6-5[t]	0.0670	0.346	5.16	96 ± 2

[t]Samples after ageing 170 h at 80 °C in oven.

PEO responds to the purpose of generating polyurethanes with a 75 wt % content of hard segments (HS)[a]. The stoichiometry is detailed in Table 1.

The stoichiometric amount of BDO is added to the reaction medium in THF solution, in order to obtain a final product without reactive NCO groups (NCO/$OH_{final} = 1$). Due to the consumption of NCO groups in side reactions (such as dimerization or the reaction with water introduced in the system through the reactants, N_2 flux or an imperfect sealing), a slight excess of IPDI must be used, so that the calculations are made for a value of final NCO/OH = 1.05.[4] The temperature in this stage is 55 °C in order to keep it below the solvent boiling point. The mass concentration of the solution is in the range 60–80%.

The final FPUs were spin coated on glass substrates, from 10 wt % THF solutions. These films were studied by CA, XPS and AFM, before and after being aged at 80 °C, for a week.

Results and Discussion

The completion of the reaction was confirmed by Fourier Transform Infrared Spectroscopy (FT-IR). The NCO groups present an intense, well defined peak in 2260 cm^{-1}, so that the completion of the reaction can be determined when the peak disappears. As the 2260 cm^{-1} signal diminishes, a peak in the 1740–1700 cm^{-1} range appears, which corresponds to the C=O stretching of the urethane groups. An increase in the wide absorption band in 3500–3300 cm^{-1}, is also observed due to the N-H stretching of urethane groups.

DSC measurements showed a Tg value of 30 °C in both, PU and FPUs materials. Besides, the soft segments (SSs) Tg is around −50 °C and the HSs Tg is 100 °C.

Fluorine surface enrichment was confirmed by XPS technique. Table 2 shows the experimental (XPS) and average (calculated from the formulation) atomic F/C ratio. The fluorine surface enrichment is calculated as the atomic experimental F/C, divided by the average F/C ratios. It is well documented that samples with lower F content show a higher surface enrichment.[5–8] As shown in Table 2, this work is in agreement with that tendency. In Table 2 enhanced CAs can be observed for the samples with higher average wt % F and surface F/C experimental ratio. The F8PUs show higher CAs than the F6PUs for the same average fluorine content, and the aged samples exhibit lower CAs. These results mean that: i) EA800 enhance fluorinated moieties migration to the surface, reaching higher surface fluorine content and enrichment, reducing wettability. However CA seems to be linearly related with F/C ratio independentely of the lenght of the fluorinated chain. ii) the ageing may cause a

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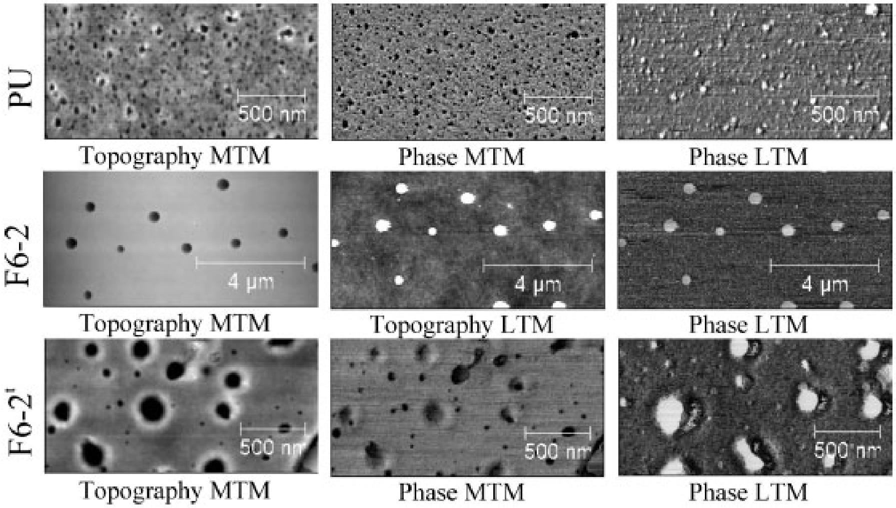
[a]The mass of the fluorinated modifiers was not taken into account in the wt % HS calculation.

morphological change in the surfaces which lowers the CAs, since the F/C ratios remain almost constant, and the neat PU, where fluorine do not play a role, shows the same tendency. In order to confirm these hypotheses and understand the changes underwent by the films surfaces, AFM was employed to study the samples.

In Figure 1 the topography and phase tapping mode AFM images of some PU and FPUs are shown. The operational conditions (i.e., r_{sp}) were manipulated in order to generate low and moderate tip-sample forces. They are referred to as LTM (light tapping mode) and MTM (moderate tapping mode). MTM ($r_{sp} \approx 0.4$–0.7) is sensitive to the tip-sample interactions, so it provides information about surface stiffness variation related to changes in Young's modulus. [9,10] In contrast, LTM ($r_{sp} \approx 0.8$–0.95) derives the chemical resolution from hydrophilicity differences of the phase at the surface.[10–13] This is explained by a thin adsorbed water layer on the sample surface. When the tip-sample interaction is weak (LTM) the attractive forces due to adhesion and capillary forces from tip–water layer interactions are expected to dominate the amplitude damping of the cantilever, which feeds back the control loop to generate the height and phase images.[13] A surface region of larger amplitude damping is recorded as higher in topography and hence brighter in height image, as well as brighter in phase images. A reversal in the image contrast has been reported for both, height and phase images when changing from MTM-AFM to LTM-AFM because of different hydrophilicity regions in the sample.

In Figure 1 the neat PU topography appears as a continuous phase with spots with no long range order. The surface is covered in a 10–15% by hole-like spots. The F6-2^t sample is also covered by 10–15% hole-like spots. One should remember that the PU measured CA was 56° and the F6-2^t CA was 78°. In contrast, the F6-2 film showed a 98 °CA, and although the MTM topography is also a continuous phase with hole-like spots, here the area which they cover is only a 3%. It is noticeable that the phases of the continuous and spots areas have different CA values contributing to the total surface wettability.

Also, the spots seem to represent the phase with the lower CA, in spite of having the same average and similar surface fluorine concentrations, the F6-2^t sample has a lower CA than F6-2 film. LTM



Topography MTM Phase MTM Phase LTM

Topography MTM Topography LTM Phase LTM

Topography MTM Phase MTM Phase LTM

Figure 1.
AFM Topography and Phase images measured in MTM and LTM conditions.

measurements show that thermal ageing induces blocks reorganization in fluorinated polyurethane copolymer, creating a surface richer in the low CA components. Figure 1 also shows a reversal of height contrast in the F6-2 images and a reversal of the phase images for all the samples, when changing from MTM to LTM-AFM. This means that when measuring in LTM conditions the attraction forces are detected together with the tip-sample interactions. More hydrophilic material attracts more strongly the water layer on the sample surface, then hydrophilic areas are recorded higher in height LTM images. Also, the water layer between the tip and the sample increases damping showing hydrophilic areas brighter in phase images. So, the spots might be more hydrophilic than the continuous phase, which explains the CA decrease after thermal ageing due to the spot like surface coverage increase from 3% to 10–15%. The hydrophilic character of spots areas should be related with SS higher concentration. The PU spots-structure defines a nano structured two phases material: spots richer in SSs and a continuous area richer in HSs. The comparison between the PU and the F6-2 films indicates that the addition of fluorine into the formulation reduces the presence of the hydrophilic SSs in the surface, as the spots occupy a smaller area. The comparison between F6-2 and F6-2^t films shows that the ageing produces a surface reorganization of the blocks which brings more SSs to the surface, giving a larger area occupied by the spots. This is possible because the ageing takes place at 80 °C, an intermediate temperature between the SSs and HSs Tg's, so that only the SSs have enough mobility to reorganize.

Conclusion

FPUs have been synthesized from PEO and IPDI using EA600 and EA800 as fluorinated agents. Surface fluorine enrichment was verified for all the samples, but higher enrichments are obtained for lower bulk fluorine concentrations. The CAs have been enhanced by the addition of 1–5 wt % fluorine. EA800 has demonstrated to be more effective in enhancing the CAs than EA600. A hole-like nano-structure with no long range order has been observed in spin coated FPUs films. The holes are richer in SSs than the continuous phase, i.e. the holes are more hydrophilic. When adding fluorine into the formulations, SSs cover the surface in a lesser extent. When ageing the materials at 80 °C the SSs reorganize and cover a larger surface area, thus diminishing the CA of the sample, in spite of the fluorine presence. Thus, both the composition and the surface morphology determine the wettability. MTM and LTM-AFM techniques were useful to prove both, the morphology and the chemical differences of the samples.

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