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Partially fluorinated polymer networks: Surface and tribological properties

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ABSTRACT

Functionalization of epoxy-based networks by the preferential surface enrichment of perfluorinated tails to achieve hydrophobic surface is described. Two series of crosslinked fluorinated epoxy-based materials containing variable fluorine contents (from 0 to 5 wt % F) were prepared using formulations based on partially fluorinated diamine, epoxy monomer and a curing agent. The epoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA) while the curing agents were either propyleneoxide diamine (JEFFAMINE) or 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA). The selected fluorinated epoxies (FE) were: 2,2,3,3,4,4,5,5,6,6,7,7,8,9,9,9-hexadecafluoro-8-trifluoromethyl nonyloxirane (FED3) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro nonyloxirane (FES3). The influence on surface properties of the architecture of FE, and the molecular structure of the unit building blocks was analyzed and discussed. It was found that both series showed high hydrophobicity and oleophobicity, independently of the crosslink density, bulk composition, and curing conditions. XPS measurements showed a surface composition much richer in fluorinated segments than expected from bulk composition. Fluorine enrichment was also manifested at the polymer/aluminium interface for JEFFAMINE-based networks. This observation is discussed in terms of the molecular weight dependence of surface tension and configurational entropy of the thermosetting matrix. At least for the range of this study, while increasing the amount of fluorine incorporated in both network series, dynamic friction is reduced due to surface migration of fluorine species during polymerization

1. Introduction

The polymer surface acts as such an important bridge between the polymer bulk and the outer environment and many specific surface properties, such as wettability, paintability, adhesion susceptibility, biocompatibility and so on, must be incarnated through it [1,2]. These properties often demand special molecular structures which just cannot be satisfied only by single homopolymer material. Then, the surface modification has been developed as an effective way to obtain the acceptable surface of the materials to broaden their application. Conventional polymer surface functionalization is always depended on the chemical or physical techniques including corona, plasma or flame treatment chemical reaction, surface grafting, surface coating or etching of finished articles and so on. However, the complicated processes and the specialized equipment are always required by using these techniques. Especially, for the intricate articles, the completed and uniform functional surface cannot be easily achieved. In addition, the expensive post-treatment has also greatly limited the application of these methods. Then, much attention has been focused on the exploitation of the new low-cost, reliable methods for the large-scale polymer surface functionalization [3]. Among them, the selective migration of functionalized additives in host polymer to achieve the designed surface is being aspiring researched as a method with high potentiality [4–9]. Due to the thermodynamic incompatibility among the components in a polymer blend, the component with the lowest surface energy will spontaneously aggregate at the air interface to reduce the system's interfacial tension if the blend is equilibrated in air. Based on the above concept, large numbers of the functional additives have been developed and extensively applied in many fields for their obvious effect on the surface functionalization. The typical structure of functional additives were usually composed of two parts: the functional chain segments to modify the material's surface and other chain segments to assure its compatibility with host polymer [10,11]. When the objective is to increase the hydrophilicity, an additive containing high polarity chain segments should be introduced. On the other hand, fluorine-based component was usually introduced into the primary chain of host polymer when the additive was applied to enhance the surface hydrophobicity of the

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material, because its low surface energy and good selective migration to air interface [12–14].

In a previous study [15] we reported the synthesis and characterization of two series of partially fluorinated crosslinked epoxy-based polymers, each with distinct differences in the molecular structure of the unit building blocks. The fluorine migration and/or reaction-induced phase separation taking place in a reactive epoxy solvent containing a perfluorinated tail attached to a diamine was analyzed. The morphology and composition of partially fluorinated networks was investigated on a micrometer scale combining scanning electron microscopy and X-ray analysis. Aliphatic diamine-cured samples were homogeneous for all fluorine proportions. In contrast, aromatic diamine-cured blends showed fluorine-rich zones dispersed in a continuous epoxy-rich phase. A completely different morphology, characterized by a distribution of irregular fluorine-rich domains dispersed in an epoxy-rich phase, was obtained when curing blends initially immiscible.

Pursuing this research line, the aim of this work is to point to a clear relation between the surface and tribological properties and the different morphologies generated along with the associated thermal properties of epoxy-based networks to which perfluorinated groups are attached. The resulting networks contain variable fluorinated tail content, and have distinct differences in the molecular structure of the unit building blocks.

2. Experimental

2.1. Materials and samples preparation

The chemical structures of reactants are shown in Fig. 1. The selected fluorinated epoxies (FE) were: 2,2,3,3,4,4,5,5,6,6,7,7,8,9,9,9-hexadecafluoro-8-trifluoromethyl nonyloxirane (Sigma–Aldrich, FED3) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro nonyloxirane (Sigma–Aldrich, FES3). The diamine employed was propyleneoxide diamine (JEFFAMINE D-230, Huntsman). Partially fluorinated JEFFAMINE monomers (F-JEFFAMINE) were prepared by reaction of FE with a known excess of diamine at 100 °C for 120 min in sealed tubes. In this step the fluorinated epoxide was chemically bonded to the diamine. Subsequently, the remaining unreacted amine groups were cured using an epoxy monomer based on Diglycidyl ether of bisphenol A (DER331, Dow, DGEBA), with a mass per mol of epoxy groups equal to 174.3 g mol^{-1}. Curing reaction was carried out at 100 °C for the time necessary to obtain total conversion of the reactants in the presence of 10 wt % toluene [16]. The diamine was used at a stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. The resultant fluorinated networks, containing from 0 to 5 wt % F, were called FE-DGEBA-JEFFAMINE.

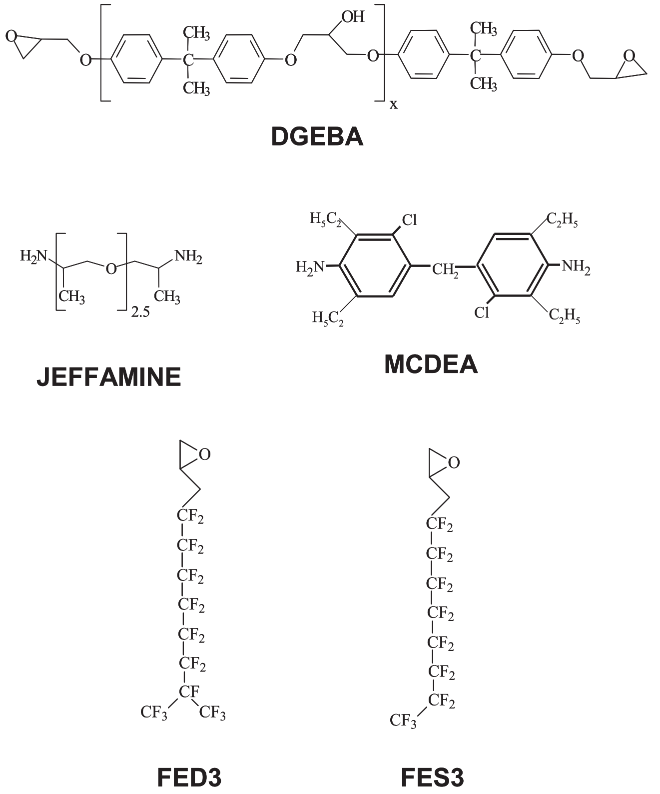

Fig. 1. Chemical structure of the epoxy monomer (DGEBA), amines (JEFFAMINE and MCDEA), and fluorinated epoxides (FES3 and FED3).

Selected amounts of F-JEFFAMINE prepared by reaction of FES3 with JEFFAMINE using r = eq. amine/eq. epoxy = 4, were blended with DGEBA. These blends were cured with an aromatic amine hardener, 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA) (Lonza). The resultant partially fluorinated networks, containing from 0 to 5 wt % F, were called FES3-DGEBA-MCDEA. The hardener was used at a stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. The dissolution temperatures was 90 °C while curing reaction was carried out at different temperatures (150 and 180 °C), for the time necessary to obtain total conversion of the reactants [17]. After curing, samples were post-cured by a stepwise increase of the temperature up to 200 °C for 1 h.

2.2. Measurements

Films of both series of fluorinated networks were prepared onto aluminium substrates. The films obtained were peeled off the substrate and the static contact angle (SCA) on the two sides of the films was measured. SCA determination was made by the sessile drop method. Drops of doubly distilled water and hexadecane (Merck) were formed on the surfaces of plaques of the specimens. The contact angles, θ, were measured with an MV-50 camera, zoom 6× and acquired with the software Image NIH. This method facilitates surface tension measurements of solids and is sensitive to chemical changes within the first 5 Å of a material's surface. The experiments were performed at 25 ± 1 °C and at about 65% relative humidity. The contact angles were detected 1 min after application of the drop to determine the equilibrium contact angle of the liquid on the solid, suggesting that underwater surface restructuration can be neglected in the time frame of the measurements described here [18]. The volume of the drop was always about 5 µl. For each sample and liquid, θ value was the average of 5–10 determinations. The accuracy of the contact angle measured was within 1.5°. As a check of the method, contact angle of commercial sample of poly (tetrafluoroethylene) (MG4-FF/HD, Heroflon™) was measured every time before analyzing polymer samples.

Friction measurements were made with steel sliding on the solid polymers as recommended by the ASTM D1894 protocol [19]. Unless otherwise specified, kinetic coefficient of friction, μ, was determined at 25 °C, the relative speed of sliding of the specimens was 0.01 cm seg^{-1}, and the normal load applied was 1 kg.

The surface topography of the polymers was analyzed by tapping mode atomic force microscopy (Agilent 5500 SPM). The images and root-mean-square roughness (RMS) values were taken in a 5 × 5 µm^2 area at room temperature.

X-ray photoelectron spectroscopy (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 Kα (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. High resolution scans with 0.1 eV steps were conducted over the regions of interest. Surface charging effects were compensated by referencing the binding energy (BE) to the C_{1s} line of residual carbon set at 284.6 eV BE [20]. Spectral decomposition assumed mixed Gaussian–Lorenzian curves and was performed by using background subtraction and a least square fitting program. Sputtering of the sample surface was performed with an argon ion gun under an accelerating voltage of 3 kV. All the samples were measured after 0 and 120 s of Ar^+ sputtering. The fluorine-to-carbon (F/C) ratio was determined from curve fitted C_{1s} window spectra, according to the different carbon environment.

3. Results and discussions

3.1. Surface properties

The surface properties and composition of the samples were analyzed using static contact angle (SCA) measurements, AFM and XPS.

Among the various modern tools available for the analysis of surface tension measurements of solids, contact angle analysis is considered a standard method for establishing the surface quality of a given material. θ_{adv} is an indicator of the hydrophobicity or low surface energy, whereas θ_{rec} reflects the hydrophilic nature of the surface [21]. Hysteresis ($\theta_\Delta = \theta_{adv} - \theta_{rec}$) is product of surface chemical heterogeneity, roughness, reorganization, hydration, or contamination [22]. As θ_Δ is characteristic of fluoroalkyl pendant groups that undergo surface reorganization [23], and the networks synthesized here have a high crosslink density which inhibited surface reorganization, we report SCA measurements for the surface study of final materials.

It is well known that the wettability behaviour of real surfaces is controlled by surface morphology other than surface chemical composition. In fact, it is well known that both surface roughness and surface heterogeneity strongly affect the contact angle measurements as pointed out by the classical studies of Wenzel [24,25] and Cassie [26].

AFM was carried out on the two series of networks to evaluate the contribution of surface morphology to the wettability. Surface roughness parameters, such as RMS, measure surface height and peak-to-valley distance. Some typical phase (right) and height (left) images for neat systems and both series with variable fluorine concentration are illustrated in Fig. 2, while the values of RMS roughness are reported on Table 1. It is worth noting that all the JEFFAMINE-based samples presented a very smooth surface with RMS roughness values well below 2 nm, indicating the absence of significant surface roughness. However, the RMS values of MCDEA-cured samples are not small, and consequently, the influence of the surface roughness on the contact angles cannot be ignored.

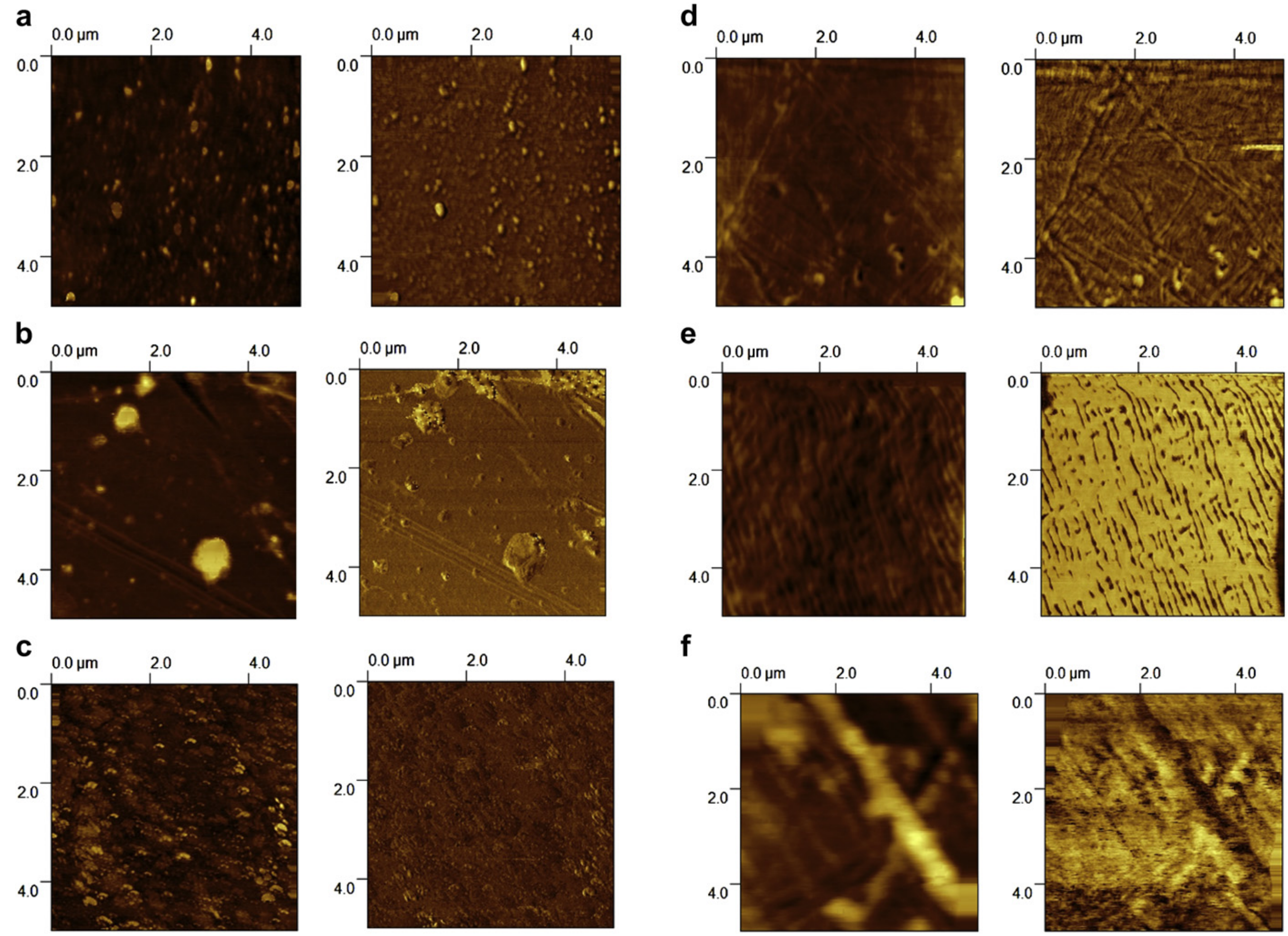

Fig. 2. AFM height (left) and phase (right) images of: a) DGEBA-JEFFAMINE, b) DGEBA-MCDEA, c) FED3-DGEBA-JEFFAMINE, 0.5 wt % F, d) FES3-DGEBA-MCDEA, 0.5 wt % F, e) FED3-DGEBA-JEFFAMINE, 3 wt % F, f) FES3-DGEBA-MCDEA, 3 wt % F.

Table 1
RMS roughness determined with AFM for FED3-DGEBA-JEFFAMINE and FES3-DGEBA-MCDEA systems.

Sample	F-content (nm)	RMS roughness (wt %)
FED3-DGEBA-JEFFAMINE	0	0.8 ± 0.5
	0.5	0.6 ± 0.5
	1	0.5 ± 0.5
	3	0.3 ± 0.5
	5	1.2 ± 0.5
FES3-DGEBA-MCDEA	0	35 ± 5
	0.25	37 ± 2
	0.5	32 ± 2
	1	39 ± 8
	3	37 ± 5
	5	38 ± 10

Figs. 3 and 4 show contact angle measurements performed with liquids of different polarities of the air side corresponding to both series with variable fluorine concentration. The results discussed here essentially refer to the surfaces exposed to air, i.e., the airside of the films, where an interesting surface modification as a function of fluorine contents was found. The surface properties of the substrate side of the films will be discussed in the following section. The water contact angle (θ^{W}) of neat systems, Fig. 3, DGEBA-JEFFAMINE and DGEBA-MCDEA, were 72° and 89°, respectively. These values are typical of a surface of medium polarity.

The JEFFAMINE-based fluorinated networks containing FES3 and FED3 showed a hydrophobic behaviour with water contact angles higher than 90° for samples containing only 1 wt % fluorine. Thus, a very hydrophobic film surface was exhibited. The end-group plays a role on the surface modification, particularly for low fluorine concentrations. The effect of the architecture of the FE is clear: the contact angle of samples containing FED3 (with two CF_3) is slightly higher than FES3 (with one CF_3) although often within the experimental error. Then, θ^{W} increases further ($\theta^{W} = 109°$) until the bulk fluorine content reached the value of ~5 wt %. When the bulk fluorine content was further increased to the value of ~7 wt %, θ^{W} did not reflect these changes in the bulk composition. Interestingly, higher contact angle was obtained for the JEFFAMINE-based system with about 5 wt % of fluorine (107°), as compared to previous studies in which a fluorinated acid (same length of FES3) was covalently attached to the polymer by an ester bond (92°) leading to JEFFAMINE-based network with similar fluorine content [16]. Probably, the observed differences are related with the architecture of the networks compared and they are a direct consequence of the crosslinking density dependence on the surface energy. At the interface, the two classes of materials display different molecular organization characteristics. When fluorinated monomer is an acid, the fluorinated tail remains as a long pendant chain connected to the gel by one reacted epoxy functionality. However, the reaction of the epoxy fluorinated monomer changes the functionality of the diamine (from 4 to 3). This fact slightly alters the crosslink density of the network which contains the fluorinated tail placed in a branch.

The wettability of MCDEA-based fluorinated networks revealed some interesting aspects. It seems that the morphology greatly influence the surface energy of the samples, reflected in SCA values. Formulations initially homogeneous that phase separate during polymerization show θ^{W} higher (10°) than those measured for the rest of the samples containing comparable fluorine concentration initially immiscible (see Fig. 3). MCDEA-cured blends located inside the miscibility window showed fluorine-rich zones dispersed in a continuous epoxy-rich phase. A completely different morphology, characterized by a distribution of irregular fluorine-rich domains dispersed in an epoxy-rich phase, was obtained when curing blends initially immiscible. As we have discussed before, all the fluorinated networks (initially immiscible or phase separated during curing) presented comparable surface roughness to neat system (see Table 1). These results indicate that the second phase is not "on" the surface modifying its topography. The observed differences in wetting behaviour can possibly be correlated with fluorine concentration present on the surface. It can be concluded that the introduction of a small amount of a fluorinated epoxide in an epoxy-amine formulation initially homogeneous results in a large reduction of the surface wettability.

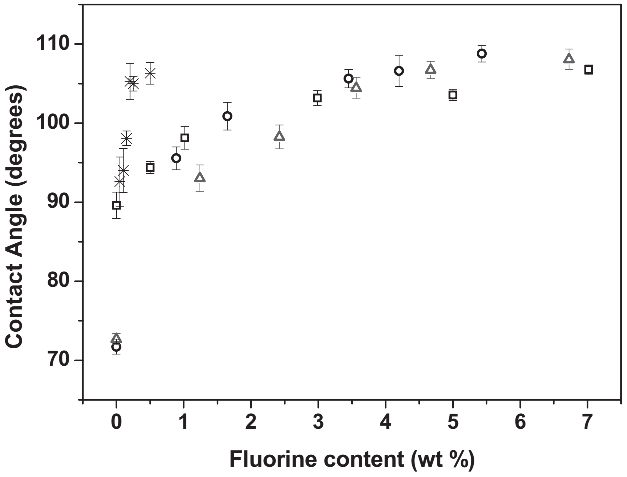

Fig. 3. Contact angles of water on the air side as a function of the amount (wt %) of fluorine content deposited on films of FES3-DGEBA-JEFFAMINE (triangles), and FED3-DGEBA-JEFFAMINE (circles), FES3-DGEBA-MCDEA initially heterogeneous (squares), and FES3-DGEBA-MCDEA initially homogeneous (asterisks).

Further measurements were done to receive additional information about the oleophobicity of the fluorinated networks. This parameter controls fundamental characteristics of coatings, i.e., the stain release and the antigraffiti resistance. Fig. 4 summarizes the hexadecane contact angle, θ^{HD}, on the fluorinated network surfaces as a function of the bulk fluorine content. In the case of the non-fluorinated MCDEA-cured sample, HD wets the surface completely. For both series with low fluorine concentrations, similar trends

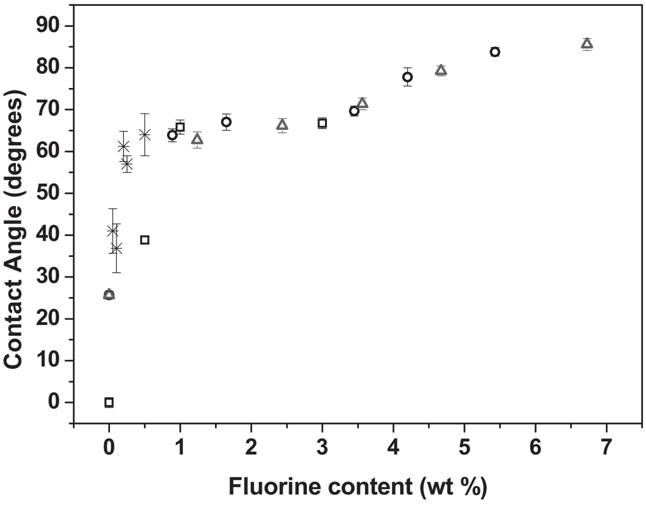

Fig. 4. Contact angles of hexadecane on the air side as a function of the amount (wt %) of fluorine content deposited on films of FES3-DGEBA-JEFFAMINE (triangles), and FED3-DGEBA-JEFFAMINE (circles) and FES3-DGEBA-MCDEA initially heterogeneous (squares), and FES3-DGEBA-MCDEA initially homogeneous (asterisks).

were found with very high value of contact angles in all cases. For small fluorine contents (0.25 wt % for MCDEA-, and 1 wt % for JEFFAMINE-cured samples), a contact angle of 60° was measured for both systems. Apparently, incorporation of a negligible amount of fluorinated species into the epoxy-based material results in a strong increase of hexadecane contact angle. The addition of more fluorine in the system results in further increase in θ^{HD} up to 85° until the bulk fluorine content reached the value of 6 wt %. The plot clearly evidence that the same oleophobicity is reached independently of the FE employed. Moreover, it is remarkable that MCDEA-cured samples initially miscible (asterisks) showed higher values of θ^{HD} when comparing with the immiscible ones (squares), as also shown in Fig. 4.

It should be noted that θ^{W} and θ^{HD} for the fluorinated epoxy surfaces with $F = 5$ wt % are higher than those measured in this work for the reference polytetrafluoroethylene Heroflon™, of about 103–104° and 35–36°, respectively. These observations demonstrate a higher hydrophobicity and oleophobicity of the fluorinated epoxies synthesized compared to the polytetrafluoroethylene Heroflon™. Although polytetrafluoroethylene may be regarded as the benchmark low surface energy material, this polymer has limitations due to its low oil repellency [27].

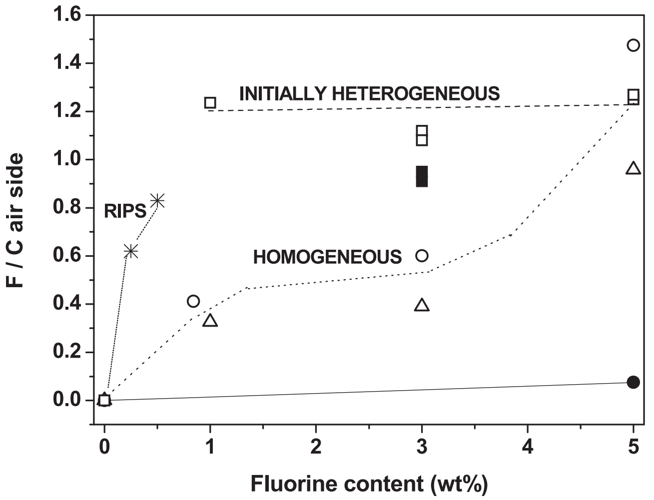

Fig. 6. XPS results of the airside surfaces in terms of F/C atomic ratios as a function of fluorine content for: FES3-DGEBA-JEFFAMINE (triangles), FED3-DGEBA-JEFFAMINE (circles), FES3-DGEBA-MCDEA initially heterogeneous cured at 150 °C (squares) and at 180 °C (filled squares), and FES3-DGEBA-MCDEA initially homogeneous (asterisks). For FED3-DGEBA-JEFFAMINE materials, F/C datum is also shown for a polished surface (filled circle). The theoretical F/C values in the bulk are also shown in the figure (solid line).

The surface characteristics achieved suggest that there is a change in the surface composition of the external layers of the films and the surface segregation of the low surface energy component which migrates toward the surface at the air interface [28]. This is confirmed by XPS analysis performed on a selection of samples containing variable fluorine concentration. This technique is a useful tool for investigation of fluorine enrichment at the outermost film surface due to its good surface sensitivity and capability of providing chemical bonding information. All spectra were collected at an angle of 45° with respect to the normal to the surface. As a result, the information obtained corresponds to depths within a range of 6 nm from the surface. Typical spectra of the C_{1s} for several fluorinated networks having variable fluorine concentration are given in Fig. 5. The shape of the measured C_{1s} spectrum is a composite of the differently bound carbon atoms. The deconvolution of this C_{1s} spectrum allows identifying the different carbon species and their contribution to the sample's surface composition. The signals of CF_3 and CF_2 groups were found to be at 294.4 eV and 292.2 eV, respectively. As shown in Fig. 5, the relative high fluorocarbon signals ($CF_3 + CF_2$) for fluorinated epoxies strongly suggest high levels of surface enrichment in perfluorinated species. This important point is addressed further in Fig. 6 which shows the outermost 6 nm fluorine over carbon (F/C) atomic ratios for both series of networks and the theoretical F/C values in the bulk (solid line) calculated according to the recipe of the reaction mixtures as a comparison. Experimental data were divided into groups. FE-DGEBA-JEFFAMINE series is homogeneous over the total fluorine content range employed in this work. For this system the overall F/C atomic ratio in the films was lower than 0.075 but in the top 6 nm of the films much more fluorine-containing species segregated, with an F/C atomic ratio higher than one when 5 wt % fluorine was added. The surface enrichment by fluorine was slightly more significant for the samples containing the fluorinated epoxy FED3 compared to FES3, which allowed a fluorine excess at the surface of 29-fold and 25-fold (1 wt % F), respectively, more than those of bulk levels. Interestingly, also shown in Fig. 6 is the composition of a polished sample containing 5 wt % F (filled circle), which coincides with the theoretical one. In the case of MCDEA-based series, all samples were quantified and its dependency on the concentration of fluorine is also shown in Fig. 6. For this series two different materials were obtained depending on the initial miscibility of reactive mixtures. Samples initially miscible (asterisks) suffer reaction-induced phase separation (RIPS) during the course of polymerization. For these phase-separated

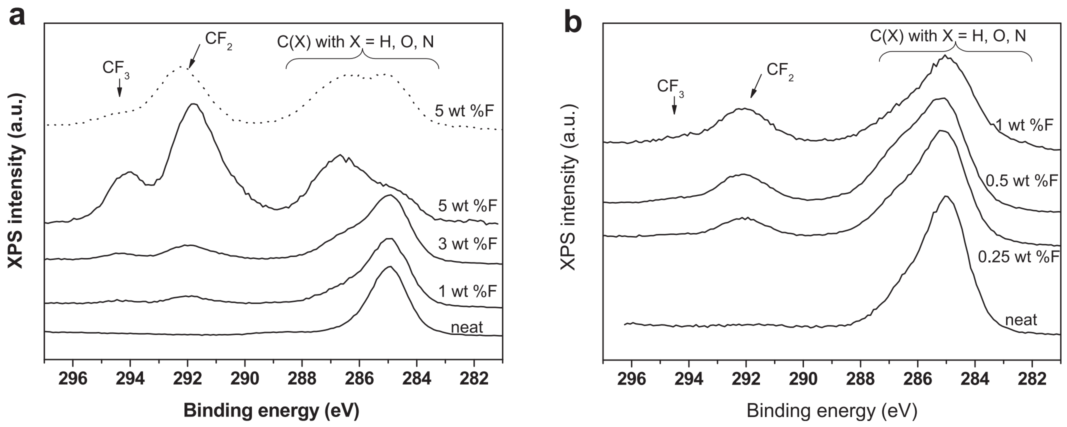

Fig. 5. High-resolved C_{1s} spectra of films of neat system, and flurorinated epoxy networks: a) FES3-DGEBA-JEFFAMINE (dashed line) containing 5 wt % F, and FED3-DGEBA-JEFFAMINE (solid lines) containing 1, 3 and 5 wt % F; and b) FES3-DGEBA-MCDEA containing 0.25, 0.5 and 1 wt % F.

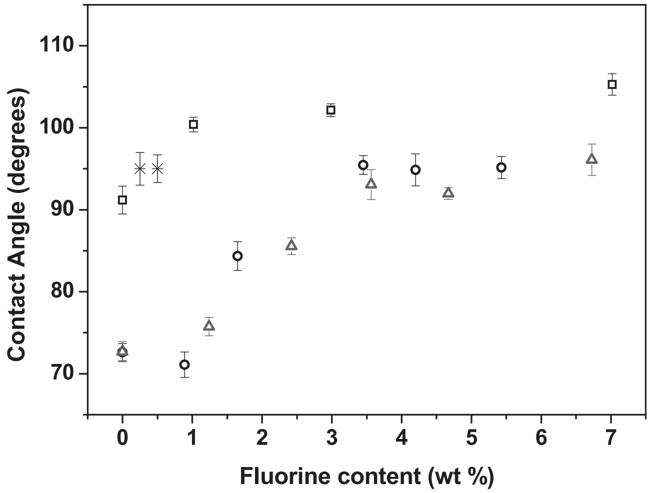

Fig. 7. Water contact angles on the aluminum side as a function of the amount (wt %) of fluorine content deposited on films of FES3-DGEBA-JEFFAMINE (triangles), and FED3-DGEBA-JEFFAMINE (circles), FES3-DGEBA-MCDEA initially heterogeneous (squares), and FES3-DGEBA-MCDEA initially homogeneous (asterisks).

samples the theoretical F/C value in the films was 0.006 when 0.25 wt % F was added, but in the outermost 6 nm of the samples there was 180-fold surface excess of fluorine compare to the theoretical bulk levels. Experimental data for samples initially immiscible (squares) show constancy in F/C ratio with bulk fluorine content. However, these results appear contradictory. For a fixed composition, XPS measurements show higher surface concentration of fluorocarbon species compared to JEFFAMINE-based systems. This phenomenon intuitively should increase water and hexadecane contact angles, yet the contact angle measurements clearly indicate constancy for both network series (see Figs. 3 and 4). The reason for the observed behaviour may be attributed to the morphology of these samples, characterized by a distribution of irregular fluorine-rich domains dispersed in an epoxy-rich phase. Since AFM results indicated that the second phase is not "on" the surface modifying its topography, XPS results suggest that fluorine-rich domains can be found in the outermost 6 nm. With the increase of cure temperature, it should be expected higher F/C values for initially immiscible samples. The higher the cure temperature, the more fluorine species dissolved in the reactive mixture, responsible of surface migration. In fact, experimental F/C values decrease with cure temperature. For instance, a sample containing 3 wt % F showed F/C = 0.94 when curing at 180 °C in contrast with F/C = 1.1 at a cure temperature of 150 °C (see Fig. 6).

It can be concluded that XPS data (Fig. 6) are in good agreement with the contact angle results (Figs. 3 and 4) for samples initially miscible, suggesting that the film wettability and oleophobicity are closely correlated with the fluorine concentration in the surface. In other words, the wettability behaviour takes its origin from the chemical surface composition and thus from the preferential surface segregation of fluorinated species during polymerization. For initially immiscible samples, highly heterogeneous, as XPS probes much deeper layers than contact angle measurements, the observed trend is not the same for both techniques.

3.2. *Surface energetic effects*

Although the preferential surface migration of components in polymer blends has been studied for many years, the essential mechanism was not sophisticated and complete. One school of thought believes that the driving force of the surface migration depends on the difference of the surface free energy between the host polymer and additives [5,11,14,29,30,31]. To keep the minimum surface energy of the whole system, the composition of the surface must be different from that of the bulk. Another thought believes that the effect of the configurational entropy is the important factor to influence the composition of the blends surface [18,32–34]. Because the highest molecular weight polymer component in a mixture experiences a large entropy penalty for residence near the surface, lower molecular weight ones will enrich on the surface to maintain the least surface free energy. This should result in greater concentration of polymer chain ends at surfaces. Finally, both flow fields and stress gradients are believed as the creators of the surface migration.

Up to this point we have assumed that when a low surface energy component migrates to the surface during curing, it reduces the surface free energy of the system. The surface tension of starting materials was found to be 46.0 (DGEBA), 32.7 (JEFFAMINE), 44.3 (MCDEA) and 16.7 (FES3) mN/m [35,36]. As expected, due to aromatic groups, DGEBA and MCDEA have high surface energy. At the end of the reaction, the surface tension of the final products may be quite different than those of the initial monomers [5]. The estimated surface tension of partially fluorinated JEFFAMINE (mono-substituted), F-JEFFAMINE, is 22.7 mN/m. The difference in the surface tension between F-JEFFAMINE and non-fluorinated components for both series of fluorinated networks would ensure a stronger driving force for the fluorinated species to migrate toward the air/film interface to minimize the surface energy. The larger difference when curing with MCDEA could explain the contact angle and XPS results analyzed in the previous section.

There are, however, important practical situations when the network is bounded by high-energy metallic substrates and the system free energy might be increased by migration of a lower surface energy component to the interface. To investigate this issue

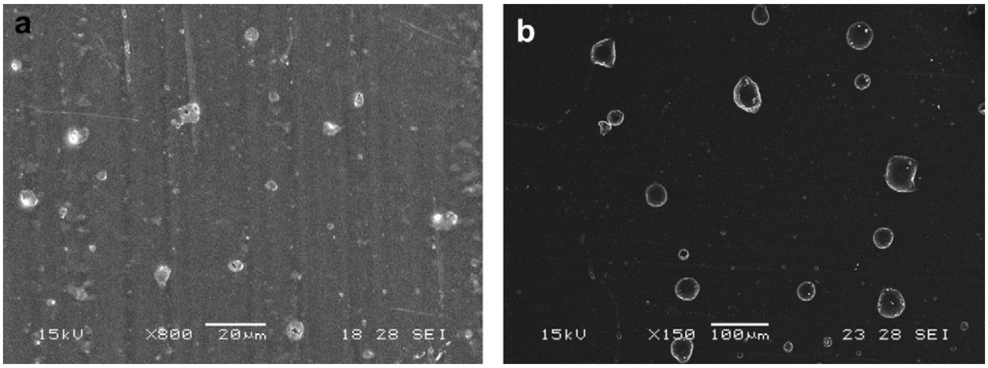

Fig. 8. SEM micrographs of FES3-DGEBA-MCDEA formulations, showing the different morphologies on the aluminum side obtained depending on the initial miscibility of the samples: a) 0.5 wt % F cured at $T = 180$ °C, system initially miscible; b) 1 wt % F cured at $T = 150$ °C, system initially immiscible.

further, fluorine enrichment at the polymer/aluminium interface was analyzed. Fig. 7 shows the experimental water contact angles on the aluminium side of the films for the different crosslinked epoxy-based polymers synthesized as a function of fluorine concentration. For JEFFAMINE-based materials, it is evident larger differences in fluorine content at the air/polymer interface (see Fig. 3) when comparing with polymer/aluminium interface (see Fig. 7). This observation confirms that migration of low surface energy fluorinated groups to the lower energy polymer/air interface is preferred. Surprisingly, the experimental results also show a clear excess of fluorinated species near the high-energy aluminium surface. More interesting, MCDEA-based networks showed similar contact angle measurement in both sides of the films for samples initially heterogeneous. These observations suggest that a second mechanism for surface migration might exist in these materials.

The reaction of the fluorinated monomer with JEFFAMINE changes the network architecture of final materials. As it was mentioned before, the fluorinated tail remains as a pendant chain connected to the gel by three reacted amine functionalities. Our findings suggest that for JEFFAMINE-cured samples, the trend towards higher levels of migration of low-energy fluorinated groups to the high-energy aluminium surface is consistent with the mechanism that considers the entropically driven end-group attraction to the surface. The enrichment of fluorinated chain ends maintains the least surface free energy by this mechanism. Lee et al. [37] investigated surface migration of polystyrene-b-poly(dimethyl siloxane) (PS-b-PDMS) copolymer additives in PS hosts. They reported that migration of copolymer to the polymer/air interface was driven primarily by the large difference in surface tension of PS and PDMS. These authors also reported that low surface energy DMS groups could even be induced to migrate to rigid high-energy aluminium substrates if the molecular weight of the PS matrix is sufficiently high.

To identify the dominant mechanism responsible for the observed differences in aluminium side contact angle behaviour between MCDEA- and JEFFAMINE-based networks, it has to be considered the influence of the flexibility of the network. The more flexible JEFFAMINE-cured samples were found to exhibit enrichment of fluorinated chain ends in order to maintain the least surface free energy by this mechanism. In the case of MCDEA-based system, wettability behaviour is controlled by surface roughness and surface heterogeneity other than surface chemical composition. In fact, all MCDEA-based materials present a complex morphology on the aluminium side. Fig. 8 shows the morphology observed for a sample containing 0.5 wt % F-content cured at 180 °C (initially homogeneous) and for a sample with 1 wt % F cured at 150 °C (initially heterogeneous). Independently on the initial miscibility of formulations, the aluminium side shows an important topography which strongly affects the wettability behaviour of these kinds of networks.

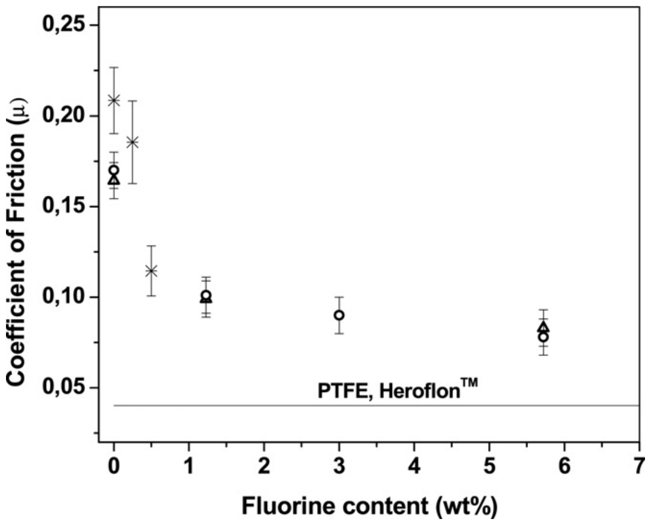

Fig. 9. Dynamic (steady state) friction of partially fluorinated networks as a function of fluorine content for: FES3-DGEBA-JEFFAMINE (triangles), FED3-DGEBA-JEFFAMINE (circles) and FES3-DGEBA-MCDEA (squares). The figure also shows the corresponding value of the reference polytetrafluoroethylene Heroflon™.

3.3. *Friction coefficient*

Fig. 9 shows the average values of the dynamic friction (at steady state) as a function of fluorine contents. For comparison purposes, corresponding value of the reference polytetrafluoroethylene Heroflon™ is also shown in Fig. 9. As can be seen, all partially fluorinated networks exhibit lower friction than the neat epoxy system. The uniquely low friction of polytetrafluoroethylene is attributed not only to its weak adhesion and low surface energy, but also to its linear structure and “smooth molecular profile” [38]. In general, branching, crosslinking, or even substitution of atoms along linear chain increases μ of a polymer. The high friction of neat systems (0.18–0.20) results from the crosslinked nature of these materials. The presence of fluorine has great effect for both series. Friction decreases significantly when a small amount of fluorofunctionalized amine oligomer is added (1 wt % F). Incorporation of 1 wt % of fluorine reduced friction by 50%. Then, friction decreases slightly when more fluorine is added.

4. Conclusions

The route described in this work offers an interesting way to a permanent surface modification of conventional epoxy-based coatings by using very small amounts of fluorinated epoxies. Two series of epoxy-based networks containing variable fluorinated tail content were synthesized and their surface enrichment was investigated by using SCA and XPS. Different fluorinated epoxies were employed in order to study the influence of the presence of more than one CF_3 group on surface properties. It was found that it was possible to develop materials with very high hydrophobic and lipophobic character for all the networks synthesized. The effects of important parameters such as bulk composition, crosslink density, and curing conditions, on fluorine species migration were investigated in detail.

It was shown that not only the total fluorine content incorporated determines the surface characteristics of the networks, but there is an important dependence on the miscibility of the system during curing. Phase separation during polymerization modifies the concentration of fluorine species capable of migration to give fluorine-rich surfaces. These evidences were further supported by XPS analysis which showed an interface between air and polymer with F/C ratio much higher than that expected from bulk composition and with a preferential surface segregation of fluorinated tails.

Enhanced fluorine migration at high-energy polymer/aluminium interface has also been reported for JEFFAMINE-based networks. A mechanism based on reduction in the configurational entropy penalty of low molecular weight chains near surfaces fairly explains this last observation.

Finally, tribological properties were analyzed in terms of friction behaviour. The coefficient of friction of partially fluorinated networks containing only 1 wt % of fluorine is reduced by 50%, independently on the nature of the diamine units. Friction decreases slightly when more fluorine is added.

The developed materials can be potentially used as functional coatings to prepare water and oil repellent surfaces or, in general terms, to modify the surface characteristics of several substrates.

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