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Thermally cured low surface-tension epoxy films

R.D. van de Grampel[a,1], W. Ming[a,*], W.J.H. van Gennip[b], F. van der Velden[a],
J. Laven[a], J.W. Niemantsverdriet[b], R. van der Linde[a]

[a]Laboratory of Coatings Technology, Materials and Interface Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands
[b]Schuit Institute of Catalysis and Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

A simple method is described on the preparation of low surface-tension epoxy films via thermal curing. First a partially fluorinated diamine was synthesized by reacting perfluoroalkyl epoxide with a known excess of diamine. Then a mixture of the fluorinated diamine and diglycidyl ether of bisphenol-A was thermally cured, resulting in films with surface tensions as low as 15 mN/m by using less than 2 wt% of perfluoroalkyl epoxide. The fluorinated species segregated preferentially at the film surface to minimize the coating-air interfacial energy. The surface tension of the epoxy films can be adjusted by varying the type of the fluorinated epoxides and their amounts. The surface enrichment of fluorine was verified by angle-resolved X-ray photoelectron spectroscopy (XPS), showing a more than 80-fold excess in the outermost ∼9 nm compared to the theoretical bulk concentration. Deeper depth profiles on the fluorine content were qualitatively revealed by dynamic secondary-ion mass spectrometry (DSIMS) measurements.

Keywords: Epoxy films; Low surface tension; Depth profiling

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1. Introduction

In the past several approaches have been explored for the modification of polymer surfaces, including chemical reactions, surface grafting, blending, plasma treatments, corona discharge treatments, and adsorption of block-copolymers [1]. In particular, fluorinated surfaces have gained considerable interest because of the advantageous surface properties induced by the fluorine atoms, such as excellent hydrophobicity and oleophobicity (due primarily to the low surface tension) and low coefficients of friction [2]. Self-stratification strategies [3,4] have been used to create coatings in which desired surface and bulk properties are well balanced and only a very small quantity of fluorinated species is needed to provide a surface with low surface tension. The fluorinated species would migrate toward the air/film interface to minimize the interfacial energy [5–20].

Epoxy resins have been extensively used in coatings, electronic parts, composite materials, and adhesives [21]. Fluorinated epoxies [22–25] have recently been used to prepare films with low surface tension by cationically photocuring the epoxy moiety by employing, essentially, the self-stratification strategy. The use of a compound containing both a perfluoroalkyl group and a photopolymerizable group ensures a permanent surface modification.

In this paper, we describe the preparation of low surface-tension epoxy films based on the thermal curing of the epoxy by a diamine. First a partially fluorinated diamine is prepared, and then a mixture of the fluorinated diamine and an epoxy is thermally cured to obtain low surface-tension films. This approach is not only interesting from a fundamental point of view but also technologically attractive: an inexpensive bulk material with a fluorinated surface can be obtained in an easy way. The surface enrichment of the fluorinated species has been characterized by several techniques including contact angle measurements, X-ray photoelectron spectroscopy (XPS) and depth

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* Corresponding author. Tel.: +31 40 247 3066; fax: +31 40 244 5619.
E-mail addresses: robert.vandegrampel@ge.com (R.D. van de Grampel), w.ming@tue.nl (W. Ming).

[1] Present address: General Electric Plastics, P.O. Box 117, 4600 AC Bergen op Zoom, The Netherlands.

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profiling dynamic secondary ion mass spectrometry (DSIMS).

2. Experimental

2.1. Materials

An epoxy resin, diglycidyl ether of bisphenol-A (DGEBA, Epikote 828, epoxy equivalent weight (EEW) $\cong 187$), was supplied by Shell, Amsterdam, The Netherlands. As curing agent a polyoxypropylene diamine [Jeffamine D230, Huntsmann, amine-hydrogen equivalent weight (AHEW) = 60] was used. The perfluoroalkyl epoxides (Fig. 1), including (2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)oxirane (EP-F6), [2,2,3,3,4,4,5,5,6,7,7,7-dodeca-fluoro-6-(trifluoromethyl)heptyl]oxirane (EP-F7), (2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxirane (EP-F8), 2,2,3,3,4,4,5,5,6,6,7,7,8,9,9,9-hexadecafluoro-8-(trifluoromethyl)nonyl]oxirane (EP-F9), and (2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10, 11,11,11-heneicosafluoroundecyl)oxirane (EP-F10) were purchased from Aldrich and used as received.

2.2. Sample preparation

First, a partially fluorinated diamine was prepared by reacting Jeffamine-230 (at a known excess) with a small amount of a fluorinated epoxide at 100 °C. In this step the fluorinated epoxide was chemically bonded to Jeffamine-230 as confirmed by ^{1}H NMR and IR. Subsequently, the fluorinated diamine, Jeffamine-230, and Epikote 828 (the molar ratio of epoxy/NH was kept at 1:1) were mixed together with 10 wt% of toluene. The ratio of the fluorinated diamine and Jeffamine-230 was varied to adjust the fluorine content in the final film. This mixture was exposed to ultrasound for 5 min to remove air that may otherwise result in bubbles during epoxy solidification. Finally, the mixture was cast on clean aluminum panels with a 100 μm wet film thickness with a doctor blade applicator, and cured immediately for 2 h at 100 °C. Under these conditions smooth transparent films with a layer thickness between 50 and 60 μm were obtained.

2.3. Surface characterization techniques

2.3.1. Contact angle measurements

Advancing contact angles were obtained by means of the sessile drop method, using a Krüss G10 set-up. During the measurement of the advancing contact angles the needle remained inside the drop. The droplet was monitored by a CCD-camera and analyzed by Drop Shape Analysis software (DSA Version 1.0, Krüss). The complete profile of the sessile droplet was fitted by the tangent method to a general conic section equation. The derivative of this equation at the baseline gives the slope at the three-phase contact point and thus the contact angle. In this way angles were determined both at the right and the left side. Reproducibility was within 0.5°. Surface tensions of the modified epoxy films were determined by the geometric mean method of Owens and Wendt [26], using the advancing angles of two wetting liquids: deionized water and diiodomethane [27]. Surface tension of liquid samples was measured by the Wilhelmy plate method on a Kruss Digital Tensiometer K10T.

2.3.2. XPS

XPS measurements were performed using a non-monochromized VG Mg Kα X-ray beam operated at 20 mA emission at 12.5 kV and a VG Clam II hemispherical analyzer. As fluoropolymers can undergo degradation when irradiated by X-rays [28], XPS measurement time was limited to 10 min or less. Under these conditions surface damage due to radiation was minimized. Angle-resolved XPS spectra were collected at takeoff angles of 0, 26, 37, 46, 53, and 60° from surface normal. All C_{1s} peaks corresponding to hydrocarbons were calibrated at a binding energy of 285.0 eV to correct for the energy shift caused by charging.

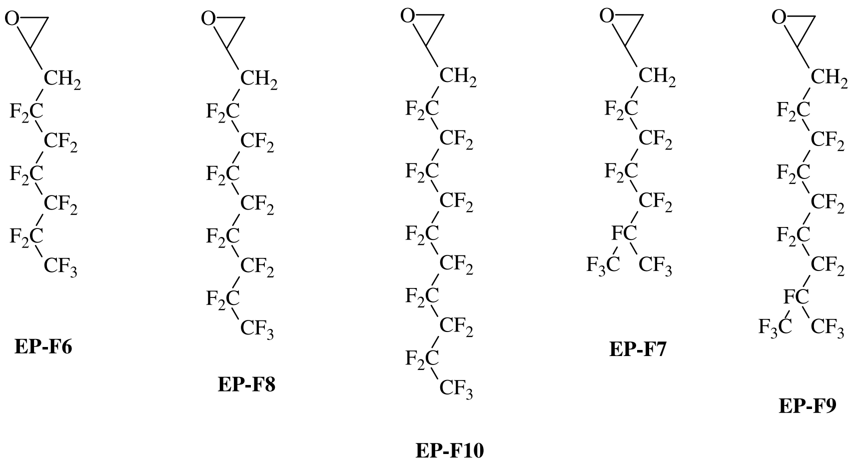

Fig. 1. Chemical structures of the fluorinated epoxides used.

For peak fitting the program XPSPEAK Version 4.0 of Kwok [29] was used. All peaks were fitted with a 30% Lorenzian and a 70% Gaussian peak shape.

2.3.3. DSIMS

All dynamic SIMS measurements were performed on a VG Ionex system equipped with a MIG-102 Ga^+ ion source, a LEG 31 F electron flood gun, and a M12-2 s quadrupole, using 10 kV Ga ions with a total current on the sample of approximately 5 nA. A polystyrene sacrificial layer of about 77 nm was used to avoid the distortion of the depth profiling during the pre-equilibrium phase [30–32].

3. Results and discussion

3.1. Surface tension of starting materials

To achieve surface segregation, a difference in surface tension of the components is necessary. From the classical Gibbs adsorption law it follows that in multi-component systems the surface will be preferentially enriched with the component with the lowest surface tension. This principle also applies to the epoxy–amine system.

The surface activity of the monomers is dependent on their amphiphilic structure and in particular on the balance of hydrophobicity–hydrophilicity of the groups. In order to give an indication of the surface activity of the different monomers, their surface tensions were determined using the Wilhelmy plate method. In addition an estimation of the surface tension was also made by the so-called group contribution theory (Parachor-method) [33].The experimentally determined surface tensions of Epikote 828, Jeffamine-230, and EP-F8 were found to be 46.0, 32.7, and 16.7 mN/m, respectively (Table 1), which are in good agreement with the theoretically estimated values by the Parachor-method.

The direct addition of a fluorinated epoxide to an Epikote 828/Jeffamine-230 formulation appeared to be unsuccessful, as the cured films exhibited a large amount of surface defects. Therefore, a pre-polymer, partially fluorinated diamine, was first synthesized by reacting the fluorinated epoxide with a large, but known, excess of Jeffamine-230. The excess is very important to ensure that there are still NH groups available for diamines to further react with Epikote 828. The surface tension of partially fluorinated diamine decreased drastically when a small fraction of NH groups were substituted by EP-F8, as shown in Fig. 2. For instance, the addition of 0.5 mol% (with respect to NH) EP-F8 effectively reduced the surface tension from 32.7 to 26.0 mN/m. On the other hand, from Parachor calculation it was estimated that EP-F8-mono-substituted Jeffamine-230 had a surface tension of 24.6 ± 3.0 mN/m, suggesting that the surface tension of the partially fluorinated diamine is predominantly governed by the EP-F8-mono-substituted species.

Table 1
Surface tension of the components used at 20 °C

	Epikote 828 (mN/m)	Jeffamine-230 (mN/m)	EP-F8 (mN/m)
Wilhelmy plate	46.0	32.7	16.7
Parachor estimation	46.6 ± 3.0	34.3 ± 3.0	17.0 ± 3.0

The difference in the surface tension between the EP-F8-modified diamine and Jeffamine-230 is about 8 mN/m, and the difference between the EP-F8-modified diamine and Epikote 828 is as much as 22 mN/m. The large difference in the surface-tension between the fluorinated species and non-fluorinated components would ensure a strong driving force for the fluorinated species to migrate toward the air/film interface to minimize the surface energy.

Next, the surface segregation of fluorinated species was investigated by making formulations based upon a mixture of partially fluorinated diamine, Jeffamine-230, and Epikote 828. It was found that the existence of a small amount of fluorinated Jeffamine did not show any significant effect on the reaction between epoxy and Jeffamine.

3.2. Wettability of surface-modified epoxy films

The wetting behavior of the surface-modified epoxy films containing different fluorinated epoxides was investigated via contact angle measurements. The advancing water contact angles (θ_{H_2O}) on these epoxy films as a function of the concentration of fluorinated epoxides (the concentration of the fluorinated epoxide is based on the total weight of the fluorinated epoxide, Jeffamine-230, and Epikote 828) are shown in Fig. 3. On the film from Epikote 828 and Jeffamine-230, the water contact angle was 76°. When the fluorinated epoxides were added, the wettability of the cured film decreased gradually with increasing fluorinated epoxide concentration, pointing to a preferential surface segregation of fluorinated species.

The dependence of θ_{H_2O} on the amount of EP-F8 for the modified epoxy film is depicted in Fig. 3. It can be seen that the θ_{H_2O} value reaches a plateau at about 108° at an EP-F8

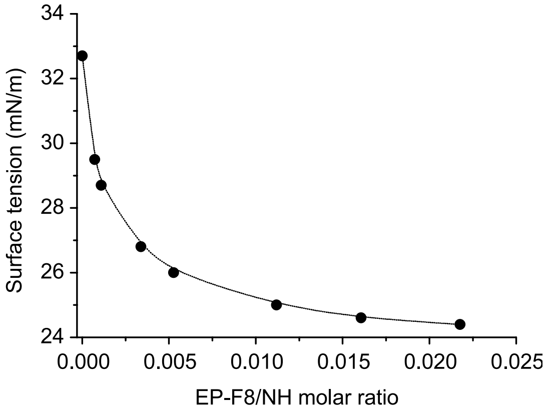

Fig. 2. The surface tension of partially fluorinated Jeffamine-230 as a function of the molar ratio of the incorporated EP-F8 and NH.

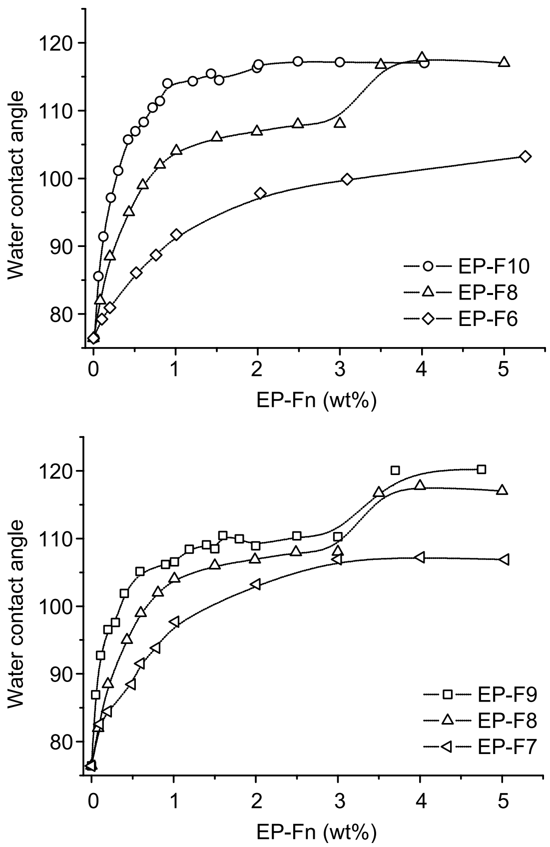

Fig. 3. Advancing contact angles of water as a function of the content of different fluorinated epoxide in the coating films.

concentration of about 1.5 wt%. This plateau value is comparable to that in a recent study by Sangermano, et al. [24], in which a C_8F_{17}-containing epoxide was photocured together with non-fluorinated epoxides; they observed a water contact angle plateau at about 105° when the fluorinated epoxide concentration was between 0.3 and 1 wt%. At this first plateau the surface tension was determined to be 15.6 mN/m. This value is lower than, e.g. the surface-tension of polytetrafluoroethylene (20.1 mN/m) [34]. The addition of more EP-F8 (>3 wt%) in the formulations led to severe dewetting in the final cured epoxy film. On parts of this film, where the coating film was still intact, a second plateau was found with θ_{H_2O} values as high as 118°. This sudden increase in the contact angle indicates a significant reorganization in these surfaces leading to serious dewetting in the film. On the other hand the dewetted areas of the coating film were found to be not completely depleted of fluorinated species, as evidenced by a contact angle of 106°. This seems to parallel the spreading of a liquid drop on a non-mixing liquid for which it is possible to have lenses and monolayers together at one surface [35]. Dewetting with the epoxy films modified by EP-F10 occurred already at a concentration of about 1 wt% of EP-F10. Just before dewetting took place the surface tension of the modified epoxy film was 14.2 mN/m.

At the second plateau, for films containing either EP-F8 or EP-F10, the surface-tension was determined to be 9.3 mN/m. This low surface tension obtained for the modified epoxy films is very close to values of a close-packed perfluoroalkyl ($CF_3(CF_2)_7$–) surface, which exhibits surface tensions of 8.7 mN/m [36]. Although the contact angle data give insufficient information to draw any firm conclusion with respect to orientation of the fluorinated species at the solid–air interface, the reduction in the surface tension from 44 to 9.3 mN/m with increasing concentration of the fluorinated epoxide does suggest that the perfluoroalkyl chains may be orientated to some extent at the surface, allowing CF_3 groups to be exposed to air. It can be concluded that the introduction of a small amount of a fluorinated epoxide in an epoxy–amine formulation results in a large reduction of the surface wettability.

It can also be seen in Fig. 3 that, for the epoxy films modified by EP-F10, the initial slope is steeper than in the case of the EP-F8-modified films. This suggests that, besides the concentration, the chain length of the fluorinated tail also influences the wetting [37]. It is interesting to note that EP-F8 and the branched epoxide EP-F9 (Fig. 1), having a comparable fluorocarbon chain length, demonstrate an almost identical dependence of the θ_{H_2O} values on the concentration of the fluorinated epoxide (Fig. 3). Also the occurrence of a second plateau at about 120° is similar in both cases. The fact that the θ_{H_2O} values in the case of EP-F9 are slightly higher than for EP-F8 may be ascribed to the larger number of CF_3 groups at the surface [38].

In Fig. 3 the water contact angle on the epoxy films containing fluorinated epoxides of shorter chain lengths, EP-F6 and EP-F7 (Fig. 1), is also given. It can be clearly seen that the compounds containing 6–7 fluorocarbons exhibit a completely different behavior. First, the increase of the advancing angles of water with increasing concentration of the fluorinated epoxide is less pronounced than for EP-F8. Second, for films modified by EP-F6 θ_{H_2O} does not exhibit values higher than 100°, whereas for EP-F7-modified films the plateau value of θ_{H_2O} (about 108°) can only be reached at much higher epoxide concentrations than for EP-F8. In addition, a second plateau was not observed for EP-F6 and EP-F7. This behavior may possibly be correlated with the lower tendency to form ordered structures at the solid–air interface, as it is known that the organization of perfluoroalkyl groups at the surface increases with increasing chain length [37]. Similar to the different effect between EP-F9 and EP-F8 on the surface wettability, the influence of the EP-F7 concentration on the advancing angle of water is more pronounced than for EP-F6. Again the difference can be ascribed to the extra CF_3 group per perfluoroalkyl chain.

The changes introduced into the composition and structure of the surface layer of the epoxy films, by adding increasing amounts of the fluorinated species, can be compared with the behavior of surfactant molecules spreading on a water surface in a Langmuir–Blodgett balance [39]. At low concentrations the surfactant molecules are separate and move independently in the surface layer, but a decrease in available surface area results in the formation of an insoluble two-dimensional monolayer of surfactant molecules. If the surface area is further compressed, the surfactant molecules in the monolayer become more closely packed together and coherently orientated towards the surface. Finally, no further compression is possible and the monolayer collapses [39].

From a molecular perspective it could be expected that micro-heterogeneity in the surface is present due to the different nature of the fluorinated tails and the hydrocarbon matrix [40]. However, the interpretation of only advancing contact angles must be taken with care as noted by Johnson and Dettre [41].They analyzed the advancing and receding angles on a model heterogeneous surface with water and concluded that relatively small domains of low surface energy species would result in relative high advancing angles accompanied by relatively low receding contact angles. This is likely the case for our surface-fluorinated epoxy films.

It is important to prove that the perfluorinated epoxides are chemically incorporated into the epoxy–amine network and that the surface modification is not temporary. The epoxy films were, therefore, rinsed by acetone and 1,1,2-trifluoro-trichloroethane. It was found that the differences in contact angles before and after rinsing were negligible (within 1°), suggesting that the films are indeed stable and the surface modification is permanent in nature.

3.3. Surface composition of surface-fluorinated epoxy films by XPS

To confirm the surface enrichment of fluorine in the modified epoxy films XPS measurements were performed on the samples. XPS spectra were collected at an angle of 0° with respect to the normal to the surface. As a result, the information obtained pertains to the outermost 9.1 nm of the film. The C_{1s} spectra for modified epoxy films with different concentrations of EP-F8 are shown in Fig. 4. In the spectra of the modified epoxy films, two additional peaks appeared at around 292 and 294 eV, corresponding to CF_2 and CF_3, respectively. The intensity of these two peaks increased with the increasing concentration of EP-F8 in the coating formulation.

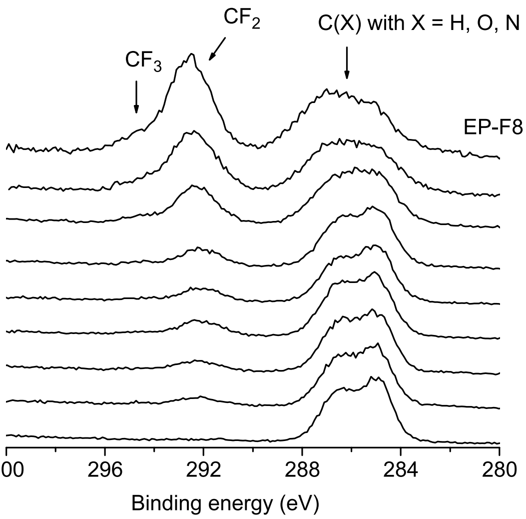

Fig. 4. Compositional dependence of the XPS C_{1s} region in the outermost 9.1 nm for a series of surface-modified epoxy films containing various amounts of EP-F8.

The F/C atomic ratio in the outermost 9.1 nm was quantified and its dependency on the concentration of EP-F8 is shown in Fig. 5. The overall F/C atomic ratio in the films was lower than 0.02, but in the top 9.1 nm of the films much more fluorine-containing species segregated, with an F/C atomic ratio of 1.3 when 5 wt% of EP-F8 was added. There was an 80–100 fold surface excess of fluorine compared to the theoretical bulk levels. Two plateaus for the F/C atomic ratios (Fig. 5) appear to exist, in good agreement with the contact angle results (Fig. 3), suggesting that the film wettability is closely correlated with the fluorine concentration in the surface [42].

The surface chemical composition was further examined by angle-resolved XPS (ARXPS). An example is shown in Fig. 6 on an epoxy film containing 1 wt% of the fluorinated epoxide EP-F10. Six different angles were used, giving access to compositional information over depths in the range of 4.5–9.1 nm. The F/C atomic ratio is a weighted average over the sampling depth of a film. These data show that the fluorine concentration is the highest at the coating-air interface. The profile strongly supports a gradient structure where the fluorine concentration increases from the bulk to the surface.

3.4. Depth profiles of surface-fluorinated epoxy film by DSIMS

To obtain a deeper-layer depth profiling of the fluorine concentration in the films, DSIMS measurements were

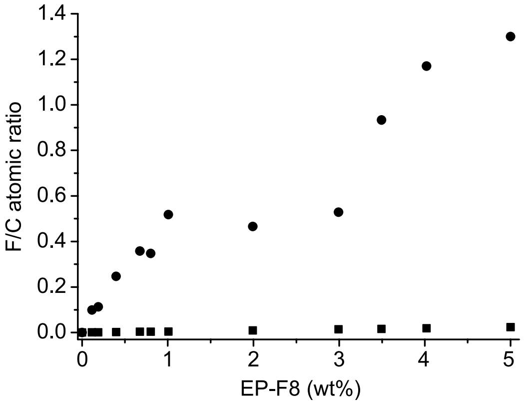

Fig. 5. F/C atomic ratio as a function of the EP-F8 amount in surface-modified epoxy films: (■) theoretical values based on a homogeneous distribution of EP-F8 in the cured film; (●) experimental value in the outermost 9.1 nm.

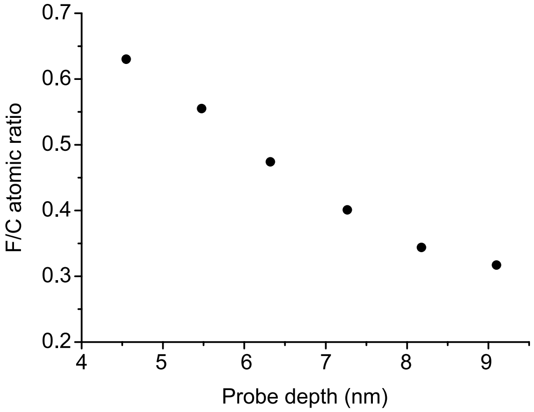

Fig. 6. F/C atomic ratio as a function of probing depth in surface-modified epoxy films containing 1 wt% of EP-F10. The theoretical F/C atomic ratio, based on a homogeneous distribution of EP-F10 in the cured film, would be 0.006.

performed. The main problem when performing DSIMS on samples that contain the sought-after information in the near-surface region is that the measured intensities near the surface are unreliable. During the initial sputtering, the so-called pre-equilibrium phase, more primary ions are implanted than subsequently removed by sputtering. Hence the matrix of each subsequently sputtered layer is different regardless of actual compositional differences, resulting in a changing intensity. To avoid the distortion of the depth profile during the pre-equilibrium phase a suitable thick sacrificial layer of approximately the identical density on top of the studied polymer layer can be easily applied [30–32]. A steady state will then have been obtained by the time the interface between the sacrificial layer and the studied polymer is reached, which has been well documented in the literature [30–32].

In Fig. 7 the qualitative depth profile of fluorinated species in the coatings containing different concentrations of EP-F8 is shown. The vertical solid line indicates the air/film interface and the thickness of the PS sacrificial layer is about 77 nm. Although the depth resolution of the SIMS profiles is at best 4.9 nm (but usually worse) [43], leading to the broadening of the distribution profile of the ion intensity in Fig. 7, the deeper-layer depth profile can be qualitatively obtained by DSIMS. The gradient distribution of the fluorinated species is clearly revealed, up to about 20 nm into the film. As the EP-F8 concentration increases, the maximum F signal also increases (Fig. 7), in agreement with the XPS results (Fig. 5). On the other hand, the ARXPS signal represents a weighted average, in which the surface layers have more weights than the deeper layers within the sampled surface volume; the DSIMS provides the real, deeper depth profile. In addition, it is obvious that the bulk F concentration also increases as a result of the increasing EP-F8 content, which cannot be revealed by conventional XPS.

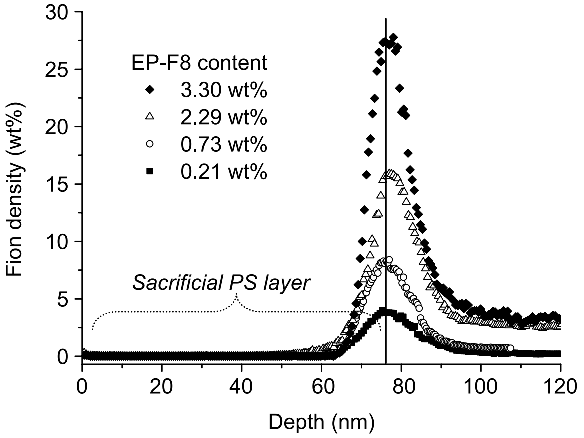

Fig. 7. Depth profiles of F signals for thermally cured films containing different concentrations of EP-F8 from DSIMS. The solid line indicates the air/film interface and the thickness of the PS sacrificial layer is about 77 nm.

4. Conclusions

The route described in this paper offers an interesting way to a permanent surface modification of conventional epoxy-based coatings by using very small amounts of fluorinated epoxies. The segregation of fluorinated species at the air-coating interface is confirmed by contact angle data, XPS, and DSIMS measurements. Through a judicious choice of the fluorinated components it is possible to control the surface tension of the final cured epoxy film. The covalently bonded fluorinated species at the coating-air interface reduce the surface tension of the material tremendously, while keeping the bulk properties virtually unchanged.

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