Conversion of Poly(ethylene-alt-tetrafluoroethylene) Copolymers into Polytetrafluoroethylene by Direct Fluorination: A Convenient Approach to Access New Properties at the ETFE Surface*

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ABSTRACT: Direct fluorination of poly(ethylene-alt-tetrafluoroethylene) copolymer (ETFE) was carried out on commercially available ETFE films with pure fluorine gas at ambient atmosphere. Reaction temperature was either 95 °C or 150 °C and exposure time was 20 hours. Analysis of the fluorinated samples was performed by attenuated total reflection Fourier transform Infrared, confocal micro-Raman and 1H and 19F magic angle spinning nuclear magnetic resonance spectroscopies, scanning electron microscopy, electron diffraction and X-Ray photoelectron spectroscopies, contact angle determination, atomic force microscopy and nanoindentation measurements, and compared to those of the virgin ETFE copolymer. Integrity of the bulk materials was verified by investigating the thermal behavior of the polymers by thermogravimetric analysis and differential scanning calorimetry. Evidence for the formation of a homogeneous layer of polytetrafluoroethylene with a thickness of several microns at the surface of the copolymers with no degradation of the materials was observed. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1517–1527, 2011

KEYWORDS: direct fluorination; fluoropolymers; poly(ethylene-tetrafluoroethylene) copolymer (ETFE); polytetrafluoroethylene (PTFE); surfaces

INTRODUCTION Fluorinated polymers are high value-added materials for various applications, due to their unique properties such as thermal stability, chemical inertness (to solvents, oils, water, acids, and bases), low values of the refractive index, permittivity, dissipation factor, and water absorption as well as excellent weather durability and resistance to oxidation.1–7 Hence, they find relevant applications in many fields of high technology like aeronautics, semiconductors, engineering, chemical industry, optics, textile finishing, automobile industry, and wiring insulation. Among these polymers, polytetrafluoroethylene (PTFE) is regarded as the most attractive fluorinated material as it exhibits exceptional thermal and inertness properties: in contrast to polyvinylidene fluoride (PVDF), it is stable in basic media and insoluble to all organic common solvents. PTFE is produced by major companies involved in fluorochemicals: Asahi Glass Chemicals, Daikin, DuPont, Dyneon and Solexis under the Fluon®, Polyflon™, Teflon®, Dyneon™, and Algoflon® trademarks, respectively. This homopolymer is usually synthesized by radical polymerization of TFE (discovered for the first time by Plunkett in 1938) through emulsion or suspension processes. This monomer can be copolymerized with various fluoroalkenes (vinylidene fluoride, VDF, hexafluoropropylene, FEP, and perfluorooalkyl vinyl ethers, PFA) leading to melt processible statistical copolymers that exhibit a lower melting point than that of PTFE. TFE can also be copolymerized with hydrogenated comonomers such as ethylene (E) or vinyl ethers (VEs) to...
lead to alternated ETFE\textsuperscript{15} or poly(TFE-alt-VE) copolymers marketed by DuPont or Daikin under the Tefzel\textsuperscript{10} and Zeffle\textsuperscript{10} trade names, respectively. These remarkable alternated copolymers arise from the well-known acceptor–donor copolymerization.

It is common knowledge that perfluorinated polymers are by far the most chemically and thermally resistant polymers,\textsuperscript{8,16} but partially fluorinated polymers offer other advantages, such as facilitated processability at lower temperatures, lower creep tendency (thanks to stronger intermolecular interactions), higher transparency, increased hardness (hardness decreases with increased fluorine content), improved adhesion, and so forth. Among them, ETFE is a particularly interesting thermoplastic, which results from the combination of ethylene and tetrafluoroethylene monomers into a nearly 1:1 alternating structure.\textsuperscript{15} Although isomeric to PVDF (as the homopolymer of CH$_2$CF$_2$), both polymers have drastically different properties. ETFE has high impact resistance (and overall improved mechanical strength), superior radiation resistance, whereas its chemical resistance, weatherability, and electrical properties approach those of fully fluorinated polymers. Despite the presence of ethylene segments in its structure, it does not dissolve in any common solvents. With a relatively high melting temperature (similar to that of FEP in the range 250–280°C), extrusion of ETFE is simplified thanks to its higher shear rate and lower viscosity than both FEP and PFA. For all these reasons, ETFE is a fluoroplastic of choice for industrial applications.

The production of fluoropolymers from the fluorination of hydrogenated polymers is an alternative pioneered by Lagow and Margrave\textsuperscript{17} more than 35 years ago and of recent growing interest.\textsuperscript{18–21} In particular, surface modification of commercially available polymers by direct fluorination to access the unique properties of fluoropolymers has been extensively investigated and reviewed by Kharitonov et al.\textsuperscript{19,20} in the past decade. Still, only a few examples are found in the literature concerning the direct fluorination of hydrogeno-fluoro polymers.\textsuperscript{19,22–25}

In this article, surface modification of ETFE copolymer by direct fluorination has been investigated, and a thorough analysis of the surface composition and resulting properties are provided.

RESULTS AND DISCUSSION

Direct fluorination is a dry method of surface modification, which involves a heterogeneous reaction of gaseous F$_2$ and a solid polymer surface. Although the upper surface of the treated material is modified, the bulk properties remain unchanged. The reaction, which may be conducted at room temperature thanks to the very high reactivity of fluorine, can be applied to a large variety of processed polymers. In this study, 2 mm thick ETFE films were exposed to pure gaseous fluorine (F$_2$) at atmospheric pressure for 20 h either at 95°C (samples referred to as ETFE-f95 herein) or 150°C (samples referred to as ETFE-f150 herein). Calculated weight gain was 2.01% at 95°C and 2.97% at 150°C. The overall aspect of the samples did not show any visible change in both cases. In particular, the surface of the exposed samples presented the original smoothness and relative transparency of ETFE. Neither clouding nor opacification of the resin was observed. A deeper investigation of the surfaces of virgin and modified ETFE was then performed, including spectroscopic, microscopic, thermal and surface characterizations, and the results are discussed below. Comparison with a sample of commercial PTFE is provided when appropriate.

**Solid-State NMR Spectroscopy**

Solid-state NMR spectroscopy allows direct observation of local order around a specific atom and is a technique of choice to check atomic substitutions. Thanks to their high sensitivity, $^1$H and $^{19}$F are particularly interesting nuclei to investigate. The samples were ground into thin powders using a cryogenic grinder prior to analysis. $^1$H NMR analysis led to broad featureless spectra that spread over the whole chemical shift scale (0–15 ppm) and could not be exploited. Because of the large hetero-nuclear $^1$H–$^{19}$F and homo-nuclear $^{19}$F–$^{19}$F dipolar coupling and the anisotropic chemical shift interaction, magic angle spinning at high frequencies was needed to obtain well resolved $^{19}$F NMR spectra to realize an efficient averaging of these interactions. The line position is then given by $\delta_{iso}$ (which is equivalent to the chemical shift in liquid samples) and the spinning sidebands intensities are governed by the anisotropy and asymmetry parameters. The integrated area (including sidebands) is proportional to the number of spins. Figure 1 shows the $^{19}$F NMR spectra of PTFE and ETFE samples recorded at 20 kHz, together with their reconstruction. Relevant parameters are summarized in Table 1. $\delta_{iso}$ and $\eta_{cs}$ were estimated thanks to the spinning sidebands intensities (when too low, $\eta_{cs}$ could not be precisely determined and was approximated to zero).
The spectrum of PTFE was characteristic of a unique anisotropic site with axial symmetry. This allowed identifying $^{19}\text{F}$ nuclei in a $\text{CF}_2\text{–CF}_2$ neighborhood ($\delta_{cs}$ = 122 ppm). A minimum of five lines was necessary to give a good representation of the experimental spectrum of ETFE (Table 1). According to the literature, the main contributions at $\delta_{cs}$ = 116.1 and 122.6 ppm could be assigned to $\text{CF}_2$ fluorine atoms of an alternated E-TFE sequence $\text{CH}_2\text{–CH}_2\text{–CF}_2\text{–CF}_2$ and to inner $\text{CF}_2$ fluorine atoms in a TFE-TFE sequence $\text{CF}_2\text{–CF}_2\text{–CF}_2$, respectively. The presence of the later may be explained by the fact that the degree of monomer alternation never reaches 100%. It is worth noting the slightly higher frequency (and difference in anisotropy and asymmetry parameters) of this signal as compared to that of PTFE despite equivalent neighborhoods, which may be explained by the short length of such sequences in ETFE. The lines at $\delta_{cs}$ = 74.9, 81.7 and 129.4 ppm could be related to $\text{CF}_3$ and $\text{CF}_2$ fluorine atoms in various environments, resulting from added termoners. An extra line at $\delta_{cs}$ = 121.8 ppm corresponding to $^{19}\text{F}$ nuclei in a similar environment to PTFE was included here for consistency with ETFE-$f_{95}$ and ETFE-$f_{150}$ analyses, while being at the limit of detection in this sample.

The central parts of $^{19}\text{F}$ ETFE-$f_{95}$ and ETFE-$f_{150}$ spectra and their reconstruction are given in Figure 2. Both spectra differed from that of ETFE only in the intensity of the line at $\delta_{cs}$ = 121.8 ppm and its spinning sidebands (see Table 2 and arrows in Fig. 2). The isotropic chemical shift value of this line was very close to $\delta_{cs}$ = 122 ppm, suggesting the presence of $\text{CF}_2$ fluorine atoms in a PTFE-like environment in these samples. Furthermore, the $\delta_{cs}$ and $\eta_{cs}$ NMR parameters required for the reconstruction of this line were those of PTFE. The increase of the relative intensity of this line from ETFE-$f_{95}$ to ETFE-$f_{150}$ was in good agreement with the calculated weight gains. This result could be explained by a fluorination of the ETFE surface converting it into a PTFE-like polymeric structure in a high enough ratio to allow detection by solid-state NMR spectroscopy. This analysis also suggested that the bulk material was unaffected by the fluorination treatment as no extra line was needed to reconstruct the spectra and the NMR parameters of the five other lines were unaffected.

### Attenuated Total Reflection Infrared (ATR-IR) and Raman Spectroscopies

Spectroscopic analysis of the surface of ETFE before and after fluorination was performed by ATR-IR (Fig. 3) and Raman (Fig. 4) spectroscopies. Infrared characteristic

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>Intensity (%)</th>
<th>Width (kHz)</th>
<th>$\delta_{cs}$ (ppm)</th>
<th>$\eta_{cs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFE</td>
<td>$-$74.9</td>
<td>2.6</td>
<td>1.6</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-$116.1</td>
<td>83.5</td>
<td>1.8</td>
<td>93</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>$-$121.8</td>
<td>0.2</td>
<td>0.5</td>
<td>68</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$-$122.6</td>
<td>11.5</td>
<td>1.4</td>
<td>80</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>$-$129.4</td>
<td>0.7</td>
<td>0.6</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>Intensity (%)</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFE</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETFE-$f_{95}$</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETFE-$f_{150}$</td>
<td>4.0</td>
<td></td>
<td></td>
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</tbody>
</table>
frequencies of ETFE have been previously assigned in the literature.33,34 CH2 stretching vibrations give rise to very low intensity bands in the 2850–3000 cm−1 range (magnified section of the spectrum in Fig. 3), whereas intense bands in the 650-1400 cm−1 range are assigned to CF2 stretching mode, together with other bands due to deformation motions of CF2, CC, and CH2 groups. The sharp band observed at 1455 cm−1 is assumed to arise from local CH2 scissoring mode. The ATR-IR spectrum of PTFE is dominated by two broad and intense bands at 1146 and 1199 cm−1, which correspond to CF2 symmetric stretching vibrations.35 The spectra recorded for both ETFE-f95 and ETFE-f150 clearly differed from that of ETFE and were instead comparable to the spectrum of PTFE, hence confirming a direct fluorination of CH2 units of ETFE at the surface of the samples.

This observation was further evidenced by Raman spectroscopy. The Raman spectra (Fig. 4) of ETFE and PTFE have little overlap in the spectral region 200-3500 cm−1 and were easily distinguished. In particular, ETFE exhibited two intense bands at about 835 and 2930 cm−1, corresponding to CF2 and CH2 stretches, respectively,21 whereas the corresponding CF2 symmetric stretching modes of PTFE gave rise to an intense band at 732 cm−1.33 Again, the spectra recorded for ETFE-f95 and ETFE-f150 corresponded predominantly to that of PTFE. In the case of ETFE-f95, signals assignable to some residual ETFE could also be observed as well as an additional signal at about 820 cm−1, which could be attributed to CF2 stretching in CH2-(CF2-CF2)n-CH2 segments with n > 2 (partial fluorination).

**Confocal Micro-Raman spectroscopy**

Confocal micro-Raman spectroscopy is a sensitive, non-invasive and non-destructive technique that can be used to directly assess chemical contents in transparent or translucent compounds. Several studies have shown that confocal Raman spectroscopy is an excellent tool for probing bulk
Here, the technique was used to assess fluorination depth. To a first approximation, the confocal point may be equated to a sphere, the diameter of which depends mainly on instrumental parameters. The sample was placed on a motorized stage along three axes and moved by small steps along the \( z \)-axis. A first stage consisted in adjusting and measuring the confocal point diameter, trying to obtain the best compromise between spatial resolution, that is, size of the confocal point and time required to acquire a full set of Raman spectra. Confocal point diameter was finally set to 2.5 \( \mu \text{m} \) with an aperture of confocality hole of 150 \( \mu \text{m} \). Then, a set of spectra was collected under the same conditions, at 2.5 \( \mu \text{m} \) intervals, from \( \sim 25 \mu \text{m} \) above the surface of the sample to 75 \( \mu \text{m} \) toward its core (along the \( z \)-axis in Fig. 5), benefiting from the relative transparency of the polymer. Monitoring the bands at about 732 cm\(^{-1}\) (PTFE CF\(_2\) stretch) and about 835 cm\(^{-1}\) (ETFE CF\(_2\) stretch) allowed us to determine qualitatively a fluorination profile as a function of sample depth. The result is depicted in Figure 6.

Interestingly, some PTFE (that is, a sequence of CF\(_2\)CF\(_2\) units sufficiently long to generate a Raman band characteristic of PTFE) could be detected as far as 35 \( \mu \text{m} \) from the surface in ETFE-\( f95 \) and 50 \( \mu \text{m} \) in ETFE-\( f150 \). In the latter, no signal indicating the presence of ETFE was detected up to \( \sim 25 \mu \text{m} \), whereas coexistence of ETFE and PTFE at the surface of ETFE-\( f95 \) was confirmed.

**Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM-EDS)**

Microscopic analysis of the ETFE film revealed a smooth and homogeneous surface with some linear scratches due to the extrusion process [Fig. 7(A)]. Backscattered electrons (BSE) imaging confirmed the good chemical homogeneity of the alternated copolymer (BSE are directly related to the chemical composition of the sample). Globally, ETFE-\( f95 \) appeared topographically unchanged [Fig. 7(B)], although more pronounced scratches could be observed at the surface. These were more numerous in ETFE-\( f150 \), as depicted in Figure 7C. This may be explained by a “softening” of the surface as it is fluorinated. Figure 8 depicts a sectional view of sample
ETFE-f150 in which a region richer in fluorine, ~40–50 μm wide, was observed as a bright fringe along the surface in the BSE micrograph of the cross section.

Energy dispersive X-ray analysis (EDS) confirmed the fluorination of ETFE at the surface of the sample. The F/C ratio increased from 1.1 for ETFE to 2.0 and 2.1 for ETFE-f95 and ETFE-f150, respectively (Table 3), which is comparable to the theoreitical value of 2 for PTFE.

**X-Ray Photoelectron Spectroscopy (XPS)**

XPS is a suitable method to accurately determine the atomic composition and to investigate the local atomic environment of a material's surface. Atomic composition of the ETFE surface before and after fluorination was estimated from relative intensities of C1s and F1s core level spectra. PTFE was also investigated for comparison purpose. The estimations are summarized in Table 4. XPS confirmed the presence of a PTFE-like layer at the upper surface of ETFE-f95 and ETFE-f150, as clearly identified by the corresponding binding energies and calculated F/C atomic ratios. Two additional C1s components could be detected for ETFE-f95 at 286.7 eV (1.3 at%) and 289.2 eV (2.6 at%). While the former is assigned to some residual ETFE, the latter may correspond to a CHF component resulting from partial fluorination of ETFE.

**TABLE 3** Energy Dispersive X-Ray Analyses of ETFE Before and After Fluorination

<table>
<thead>
<tr>
<th></th>
<th>Atomic %</th>
<th>F/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C</td>
<td>F</td>
</tr>
<tr>
<td>ETFE</td>
<td>47.6</td>
<td>52.4</td>
</tr>
<tr>
<td>ETFE-f95</td>
<td>68.8</td>
<td>33.2</td>
</tr>
<tr>
<td>ETFE-f150</td>
<td>68.0</td>
<td>32.0</td>
</tr>
<tr>
<td>PTFE</td>
<td>68.5</td>
<td>31.5</td>
</tr>
</tbody>
</table>

**TABLE 4** Main XPS Spectral Data and Calculated F/C Ratio for ETFE, ETFE-f95, ETFE-f150, and PTFE

<table>
<thead>
<tr>
<th></th>
<th>C1s #1&lt;sup&gt;a&lt;/sup&gt; BE&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
<th>C1s #2 BE (eV)</th>
<th>C1s #3 BE (eV)</th>
<th>F1s #1 BE (eV)</th>
<th>F1s #2&lt;sup&gt;a&lt;/sup&gt; BE (eV)</th>
<th>Assignment</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>ETFE</td>
<td>286.6</td>
<td>289.2</td>
<td>291.3</td>
<td>688.6</td>
<td>689.4</td>
<td>CH₂CF₂ in ETFE 286.6 eV</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Atomic % 24.2</td>
<td>1.3</td>
<td>2.6</td>
<td>32.2</td>
<td>62.4</td>
<td>CH₂CF₂ in ETFE 291.3 eV</td>
<td>40</td>
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<tr>
<td>C1s #2</td>
<td>BE (eV)</td>
<td>289.2</td>
<td>–</td>
<td>291.4</td>
<td>–</td>
<td>–</td>
<td>CHF(CF₂) in [CF₂CHF]ₙ, 289.0–289.4 eV</td>
</tr>
<tr>
<td>Atomic %</td>
<td>2.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>CH₂CF₂ in ETFE 292–292.6 eV</td>
<td>52–57</td>
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<tr>
<td>C1s #3</td>
<td>BE (eV)</td>
<td>291.3</td>
<td>–</td>
<td>291.4</td>
<td>–</td>
<td>–</td>
<td>CH₂CF₂ in ETFE 286.6 eV</td>
</tr>
<tr>
<td>F1s #1</td>
<td>BE (eV)</td>
<td>688.6</td>
<td>688.5</td>
<td>689.4</td>
<td>–</td>
<td>–</td>
<td>CH₂CF₂ in ETFE 292–292.6 eV</td>
</tr>
<tr>
<td>Atomic %</td>
<td>50.6</td>
<td>–</td>
<td>4.3</td>
<td>–</td>
<td>–</td>
<td>CH₂CF₂ in ETFE 286.6 eV</td>
<td>40</td>
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<tr>
<td>F1s #2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>BE (eV)</td>
<td>689.4</td>
<td>689.4</td>
<td>689.4</td>
<td>–</td>
<td>–</td>
<td>CH₂CF₂ in ETFE 292–292.6 eV</td>
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<tr>
<td>Atomic %</td>
<td>62.4</td>
<td>67.8</td>
<td>67.3</td>
<td>–</td>
<td>–</td>
<td>CH₂CF₂ in ETFE 286.6 eV</td>
<td>40</td>
</tr>
</tbody>
</table>

<sup>a</sup> Values in bold were used as reference for BE calibration.  
<sup>b</sup> BE: binding energy.

**Thermal Properties**

ETFE is a melt processible fluoropolymer with a high melting temperature, which undergoes gross decomposition in a single stage. Thermogravimetric analysis (TGA) was conducted under air atmosphere at a heating rate of 15 °C/min (Fig. 9). In all cases weight loss started at about 380 °C and continued up to about 550 °C, the decomposition profiles following slightly different pathways. Also, it could be concluded that thermal stability of ETFE was preserved, suggesting retention of the global structure of the bulk copolymer after exposure to fluorine. Indeed, a major cleavage of the polymeric chains by F₂ or generated radicals would have resulted in a noticeable decrease of the global thermal stability. Differential scanning calorimetry further confirmed this result. The stacked representation of the DSC curves of ETFE, ETFE-f95, and ETFE-f150 in Figure 10 outlines the great similarity in the thermodynamic properties of the three samples, with a single endotherm centered at 269 °C corresponding to the samples' melting temperature (Table 5).

**Surface Properties**

Dynamic contact angle measurements by expansion and contraction method were carried out for both water and diiodo-methane to assess hydrophobicity and lyophobicity of the surfaces, respectively (Table 6). Advancing and receding contact angles were obtained by increasing or decreasing the liquid drop volume until the three-phase boundary moved over the solid surface. In all cases, higher advancing-receding contact angles were obtained for ETFE-f150 and ETFE-f95 (to a minor extent), which may be explained by a decrease in surface free energy due to fluorination and a slight increase in net liquid/solid contact area due to an increase in nano-micro scale surface roughness. Atomic force microscopy (AFM) was used to assess the surface roughness of the samples. Root mean square roughness, Sₚ, was measured at two different points of the
samples’ surfaces, which were considered as characteristic of the surface state. Results are provided in Table 7 (see also AFM micrographs and depth profiles in supplementary information). ETFE exhibited the smoothest surface and no recurring defect was observed. The three other samples were twice as rough as ETFE with more or less deep scratches covering the surface. This result supported the hypothesis of a roughness increase after fluorination, which contributed to an increase in surface hydrophobicity and lyophobicity.

**Nanoindentation**

Nanoindentation is a very useful technique for the characterization of layered systems because the mechanical response can be assessed at a scale relevant to the layer dimension and because the response of the layer or coating is measured in situ on the test sample. This is crucial as factors such as process-induced microstructuring, residual stress, adhesion and substrate properties are critical in determining the overall system response.44,45 With an elastic modulus (E) ranging between 0.3 and 0.6 GPa, PTFE has a lower stiffness than ETFE (E ≈ 1 GPa).46 This difference in viscoelastic response between PTFE and ETFE was expected to generate a change in stiffness at the extreme surface of the fluorinated samples following the same trend. The elastic moduli of ETFE, ETFE-95, and PTFE samples were obtained from load-displacement loading/unloading curves, using the Oliver and Pharr method,47 which is the most successful and widespread model for nanoindentation data analysis. Hence, the standard way to determine the elastic modulus is by using the initial slope S of the unloading curve:

\[
E_r = \frac{\sqrt{\pi}}{A} \frac{S}{2}
\]

In this equation, \(E_r\) is the reduced modulus given by:

\[
\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_c^2}{E_c}
\]

where \(\nu_i\) and \(E_i\) are the Poisson’s ratio and the elastic modulus of the indenter, whereas \(\nu_c\) and \(E_c\) are the Poisson’s ratio and the elastic modulus of the coating, respectively.

Figure 11 shows load-displacement curves of ETFE, PTFE, and ETFE-95 for a maximum indentation load of 1 mN, corresponding to a maximum penetration depth of about 1 μm. The elastic moduli of PTFE and ETFE were evaluated at 0.50 and 1.37 GPa, respectively (using Poisson’s ratio of 0.46 and 0.4, respectively). The elastic response of ETFE-95 appeared in-between, with a calculated E value of 0.87 GPa. This is in good agreement with a material presenting a soft perfluorinated outer layer on a stiffer ETFE substrate. Penetration was then successively increased with the indentation load (Fig. 12). As a result, E modulus of ETFE-95 gradually increased up to a depth of about 9 μm where the value of the original ETFE sample was recovered (i.e. 1.37 GPa at 156 mN maximum load).

**DISCUSSION**

Thanks to NMR, IR, and Raman spectroscopies characteristic features of PTFE such as anisotropic interactions, molecular vibrations, and resonant frequencies were detected at the surface of ETFE after fluorine exposure. Such spectroscopic data strongly depend on molecular features like atomic composition and structure, and their correspondence with virgin PTFE was quite remarkable. By taking advantage of the relative transparency of ETFE, confocal micro-Raman spectroscopy was used to provide information on fluorination depth. The quality and accuracy of the result were beyond expectations. The value of ~50 μm obtained in the case of ETFE-
150 was nicely corroborated by scanning electron microscopy. BSE imaging highlighted the presence of a brighter fringe (due to the higher content in fluorine) showing a good regularity along the surface and a width ranging between 45 and 50 μm. The results obtained by XPS spectroscopy brought further evidence of the close chemical composition of the surface to virgin PTFE. They also revealed the absence of contaminations such as oxygen, and in the case of ETFE-f95, a partial fluorination (as already suggested by Raman spectroscopy). While surface modification did not affect the bulk properties of the ETFE copolymer such as thermal behavior, new interfacial properties were expected. Surface wettability of modified ETFE reflected well the changes in surface chemistry, with an increase in fluorine content, and surface roughness. Nanoindentation revealed that the PTFE-like layer was thick enough to produce a more ductile mechanical response in the first 9 μm of the layer.

EXPERIMENTAL

ETFE (ET6235Z) and PTFE (TFM 1700) were kindly provided by 3M Dyneon GmdH, Burgkirchen, Germany. The ETFE samples were semi-rigid, translucent 2 mm thick films, while the PTFE samples were rigid, opaque-white 2 mm thick films.

Fluorination of ETFE

Fluorinations were performed in a 5 liter cylindrical nickel reactor in a Thermolyne 79400 tube furnace, at the Laboratoire des Matériaux Inorganiques, Aubière, France. The reactor was passivated at 400 °C under a pure fluorine atmosphere. Small cut-outs (about 2 cm²) were weighed and placed on a microperforated nickel plate. The plate was introduced at the center of the reactor, so that temperature variation at the samples was ±2 °C. The reactor was then heated to 100 °C and vacuumed for 1 hour. Once back at room temperature, vacuum was stopped and pure gaseous fluorine was introduced up to atmospheric pressure, keeping a small vent to maintain a continuous flow of F₂ in the cylinder. The reactor was heated to the desired temperatures (95 °C or 150 °C) for 20 hours. After this time, it was allowed to cool down to room temperature and flushed with nitrogen for 3 hours. The samples were then recovered and weighed, with no further treatment.

Instruments

Solid-state NMR spectra were recorded on a Varian VNMRS 400 Solid spectrometer with a magnetic field strength of 9.4 T. A T3 triple resonance MAS probe with a Vespel stator and Zirconia 3.2 mm o.d. pencil MAS rotor were used. Samples were ground into thin powders prior to analysis using a cryogenic grinder. The experiments were performed at room temperature with a spinning rate of 20 kHz. A single pulse sequence was used with 3 μs π/2 pulse duration and a recycle delay of 5 seconds. 64 transients were acquired. No ¹H decoupling was conducted during acquisition because the

|TABLE 6 Water and Diiodomethane Dynamic Contact Angle Values for ETFE, ETFE-f95, ETFE-f150 and PTFE |
|---|---|---|---|---|---|---|---|
| | Water | ICH₂I | | | | |
| | θₐ | θᵣ | H | θₐ | θᵣ | H |
| ETFE-f95 | 99.2 ± 4.0 | 68.3 ± 4.2 | 31.0 | 73.3 ± 10.7 | 54.5 ± 6.9 | 18.8 |
| ETFE-f150 | 111.5 ± 8.9 | 90.8 ± 3.2 | 20.7 | 92.8 ± 5.0 | 79.0 ± 6.1 | 13.7 |
| ETFE | 96.8 ± 8.0 | 60.3 ± 8.3 | 36.5 | 66.7 ± 2.5 | 52.2 ± 11.2 | 14.6 |
| PTFE | 81.4 ± 3.3 | 50.5 ± 3.3 | 30.9 | 69.4 ± 7.0 | 53.7 ± 6.4 | 15.7 |

θₐ: advancing contact angle
θᵣ: receding contact angle.
H: hysteresis θₐ − θᵣ.

|TABLE 7 Root Mean Square Roughness (Sq) of ETFE, ETFE-f95, ETFE-f150, and PTFE at Two Different Points of the Samples’ Surfaces |
|---|---|---|
| | Point 1 | Point 2 |
| ETFE | 24 | 23 |
| ETFE-f95 | 80 | 56 |
| ETFE-f150 | 56 | 40 |
| PTFE | 137 | 45 |

FIGURE 11 Nanoindentation load-displacement plots of ETFE (dashed line), ETFE-f95 (full line) and PTFE (dotted line) for an indentation with a peak load of 1 mN.
probe was not capable of $^{19}$F/$^1$H double resonance. The isotropic chemical shift $\delta_{iso}$ used for spectrum simulation was defined as

$$\delta_{iso} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz})$$

with $\delta_{ii} = \sigma_{ref} - \sigma_i$ and $\sigma_i$ ($i = x, y, z$) the principal components of the shielding tensor.

$$\delta_{cs} = \delta_{zz} - \delta_{iso} \quad \text{and} \quad \eta_{cs} = \frac{(\delta_{yy} - \delta_{xx})}{\delta_{cs}}$$

represented the anisotropy and asymmetry parameters using the convention $|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$. The $^{19}$F chemical shifts reported herein are relative to CFCl$_3$, referenced via the CF$_2$--CF$_2$ signal of PTFE at -122 ppm. All solid-state NMR spectra were modelled using the Dmfit program.40

Fourier Transform Infrared (FTIR) spectra were recorded with a PerkinElmer Spectrum 100 spectrometer (PerkinElmer Inc., USA) equipped with an attenuated total reflection (ATR) crystal.

Raman spectra were recorded at 298 K with a LabRAM ARA-MIS IR2 confocal micro-Raman spectrometer (Jobin-Yvon S.A., Horiba, France) equipped with a CCD detector cooled by a Peltier effect module. The spectral resolution was ±1 cm$^{-1}$. Raman spectra were obtained by excitation with a 633 nm radiation from a He–Ne laser generating less than 12 mW on the samples. These were mounted on a XYZ motorized stage with 0.1 µm step resolution.

Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) were performed on a Zeiss DSM 962 microscope (Carl Zeiss, Oberkochen, Germany) equipped with a Link Isis X-ray detector.

Surface composition was monitored by XPS on an ESCALAB 250 (Thermo Electron, Thermo Fisher Scientific, WI). The X-ray excitation was provided by a monochromatic Al Kz (1486.6 eV) source. Analyzed surface had a 400-µm diameter. Background signal was removed using the Shirley method.49 Surface atomic concentrations were determined from photoelectron peak areas using the atomic sensitivity factors reported by Scofield. The F1s component of PTFE at 689.4 eV50 and the C1s component of ETFE at 286.6 eV40 were used for calibration of binding energies.

Thermogravimetric analyses were performed on a TA Instruments Q50 thermogravimetric analyzer under air at a constant heating rate of 15 °C/min. Samples were grinded to powders prior to analysis.

Differential scanning calorimetry measurements were performed on a PerkinElmer Pyris 1 DSC apparatus (PerkinElmer, MA) under nitrogen atmosphere. Indium and n-hexane standards were used for temperature and energy calibration. Heating curves were recorded in the temperature range -50 to 300 °C at a heating rate of 20 °C /min. Melting temperatures $T_m$ were determined at the endothermal peaks maximum. Integrations limits for heat of melting ($\Delta H_m$) determination were 200–290 °C. The samples’ degree of crystallinity $X_c$ was estimated according to the equation $X_c (%) = (\Delta H_m / \Delta H_{m100}) \times 100$ where $\Delta H_{m100}$ is the heat of melting for a theoretical 100% crystalline ETFE copolymer with the reported value of 113.4 J/g.51

Contact angles were measured at ambient temperature on an Attension Theta tensiometer (BiolinScientific AB, Sweden) by the sessile drop technique against 20 µL of water purified by a Milli-Q water purification system (Milli-Q, MA) or diiodomethane (from Nacalai Tesque, Japan). Dynamic contact angles and contact angle hystereses were assessed by increasing or decreasing the liquid droplet volume at a constant rate (injection at 2 µL/s and suction at 20 µL/s) until the three-phase boundary moved over the solid surface. Averaged contact angle values were determined from five different points on each sample’s surface.

Atomic force microscopic (AFM) observation was conducted on a SPA 400 (Seiko Instruments, Japan), using an AC mode (tapping mechanism) driven dynamic force microscope in air at room temperature. The samples’ surfaces were scanned at a rate of 5 µm s$^{-1}$ by a silicon nitride integrated tip on a commercial rectangle cantilever (SI-DF20, Seiko Instruments, Japan) with a normal force constant of 16 N m$^{-1}$ at a driving

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**FIGURE 12** (A) Load-displacement curves of ETFE-95 at various indentation loads and (B) evaluated Young Modulus of ETFE-95 as a function of penetration depth.
frequency of 136 kHz in air. The observations were performed at two different points for each sample.

Nanoindentation experiments were performed using CSM Instruments Open Platforms (CSM Instruments, MA). Indentations were conducted using a Berkovich indenter with a pyramidal tip. Indentation sites were selected by optic microscopy (500×). For each sample, three indentation tests were performed with good repeatability (error within about 1%). The load range was varied from 25 to 50 mN (resolution 0.1 μN and 0.1 nm) for the ultra nanoindentation platform and from 50 mN to 30 N (resolution 0.1 mN and 0.3 nm) for the microindentation platform. The force required to indent the material was monitored as a function of penetration depth. The elastic modulus of the samples was derived from the load-displacement loading/unloading curves using the Oliver and Pharr model.47

CONCLUSIONS

Based on a wide range of analytical tools, it may be concluded that the conversion of the surface composition of an ETFE film into PTFE by direct fluorination was successfully achieved at atmospheric pressure at 95 °C or 150 °C. Conversion rate appeared to be temperature dependent, with some residual ETFE remaining at the surface at 95 °C. Confocal micro Raman spectroscopy allowed drawing a qualitative depth profile of fluorination. At 95 °C, the presence of ETFE gradually increased from the surface to the core while that of PTFE decreased up to a depth of about 35 μm where its detection became negligible. However, at 150 °C, no Raman signal of significant intensity corresponding to ETFE was detected up to about 25 μm, whereas the signal of PTFE was present as deep as 50 μm within the sample. As a result, the fluorinated polymer films presented new surface properties, such as wettability or hardness, which were neither that of ETFE nor that of PTFE, whereas the integrity of the bulk material was maintained. No structural degradation of the polymers arising from pure F2 exposure was observed as confirmed by their preserved thermal behavior.

To our knowledge, this work provides the first example of an intimate PTFE-like/ETFE bilayer, which considering the surface properties of both materials may not be obtained satisfactorily by other means as the adhesion capability of PTFE to ETFE is poor. Chemical conversion by direct fluorination provides the great advantage to avoid issues such as layers adhesion, cohesion, peeling, and so forth. It may be involved in coating applications where the use of ETFE will be technically preferred while the surface properties of PTFE will be more suitable for practical applications. For example, with a limiting oxygen index (LOI) of 30%, better flame retardancy of ETFE liners may be obtained by direct fluorination (PTFE LOI> 95%).

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REFERENCES AND NOTES

46 Generally admitted data provided for PTFE and ETFE. The values of E will vary depending on the manufacturer and grade of the polymers.