

The effect of surface fluorination on the wettability of high density polyethylene

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Abstract

High-density polyethylene (HDPE) samples have been fluorinated and oxyfluorinated for different times. Dynamic contact angle analysis was used to determine the effect of fluorine gas mixtures on the surface of HDPE. The total surface tension of HDPE increased drastically with the length of oxyfluorination treatment, but levelled off after longer treatments. Fluorination resulted in a marked decrease in the total surface tension of HDPE. During fluorination, the dispersive component of the surface tension decreased progressively with fluorination time, while the polar component increased initially but decreased again with longer fluorination treatments. This indicates that short fluorination times lead to increased wettability by polar liquids, while longer fluorination times have the opposite effect. Fluorinated and oxyfluorinated surfaces were exposed to elevated temperatures. Whereas it was found that fluorinated surfaces changed measurably, oxyfluorinated surfaces changed dramatically upon heating at 100 °C. Photoacoustic FT-IR spectroscopy indicated that this was probably due to migration of surface polar groups into the bulk of the polymer, rather than chemical change.

Keywords: Surface inversion; High-density polyethylene; Fluorination; Oxyfluorination; Dynamic contact angle analysis; Wettability

1. Introduction

Polyethylene is well established as the largest tonnage plastic material; this is due to its features of low cost, good mechanical properties, chemical resistance and processability. However, two major disadvantages of polyethylene are the high permeation rate of non-polar hydrocarbon liquids through the polymer and the difficulty of adhesion to its surface. These two factors limit the use of polyethylene in many applications.

Solvent permeation in polymers is a stepwise process which consists of four steps [1]:

1. Wetting of the surface by the permeating liquid.
2. Dissolving of the liquid into the polymer.
3. Diffusion of the liquid through the polymer.
4. Desorption of the liquid from the outer surface.

The permeability rate of liquids through polymeric containers is therefore a function of many parameters. A variety of techniques can be used to increase the barrier properties of polymers.

Solubility parameters of polymers can be related to the wetting or spreading of a solvent on a polymer surface. Hansen showed that the spreading or wetting of a solvent on a polymer surface is analogous to dissolving and that this relationship can be used to assign solubility parameters to polymer surfaces [2]. Hildebrand and Scott derived the following empirical relationship between solubility parameter and surface tension [3]:

$$\delta = 4.1(\gamma/V^{0.33})^{0.43} \quad (1)$$

Brewis and Briggs have stated that it is necessary, but not sufficient, that there should be good contact between an adhesive (wetting phase) and the substrate [4]. Like other polyolefins, high-density polyethylene is characterized by a low surface tension (and therefore low wettability) and an absence of sufficient chemical functionality. It therefore requires a pretreatment in order to create a surface with a satisfactory level of adhesion, for purposes such as printing, bonding, painting, coating and metallizing.

It is clear that wettability affects both adhesion and permeation. A knowledge of the surface tensions and wetting characteristics of polymers is therefore vital in order to predict the behaviour of polymers in many industrial applications.

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Over recent years, surface fluorination has proved to be an effective pretreatment technique for increasing both the adhesion [5] and barrier properties [6] of polyethylene. During surface fluorination, hydrocarbon polymer materials are exposed to diluted fluorine gas mixtures. Fluorine gas reacts with hydrocarbon polymers via a free-radical chain reaction mechanism, resulting in the formation of a partially fluorinated surface layer [7]. The thickness of this layer is controlled by fluorine gas diffusion through the sample. Surface fluorination changes the surface properties of hydrocarbon polymers drastically, while the bulk properties remain largely unchanged.

The basic parameter for a liquid wetting a solid is the contact angle. For a sessile drop, this is defined by the tangent to the liquid at the air/liquid/solid line of contact and a line through the base of the liquid drop where it contacts the solid [8]. Zisman discovered that the contact angle of a liquid on a solid reflects the chemical constitution of the solid surface [8]. An empirical relationship was observed between the cosine of the contact angle and the surface tensions of the wetting liquids for a given solid organic surface. Extrapolation of the line to $\cos \theta = 1$ ($\theta = 0$) defines a critical surface tension γ_c . The significance of this parameter is that liquids with surface tensions greater than γ_c will not spread on the solid and liquids with surface tensions less than γ_c will spread spontaneously. Zisman also related γ_c to the surface chemical constitution of various organic solids and observed that γ_c decreased with increased fluorination.

Although useful, Zisman's theory had some drawbacks [9]. It is based on an empirical relationship with no theoretical basis to date. Zisman plots tend to be curved and often yield critical surface tensions which are much lower than surface tensions determined by other methods. Originally defined for a homologous series of n-alkanes, γ_c is difficult to determine when polar and/or hydrogen-bonding liquids are used. Therefore, other methods which take into account the polarity of surfaces and the different intermolecular forces which exist at surfaces are important. Fowkes suggested that the total free energy at a surface is the sum of the contributions of different intermolecular forces such as dispersion, polar and hydrogen bonding. Owens and Wendt, and Wu used this basis to develop the geometric-mean method and the harmonic-mean method, respectively, to determine the surface tensions of solids [10]. Wu suggested that surface tensions of low energy solids obtained by the geometric-mean method are often much too low, while results obtained with the Harmonic-mean method compare well with values obtained by using other techniques [11].

Schonhorn and Hansen observed a reduction in surface tension after surface fluorination of polyethylene [12]. However, the surface that they obtained was highly amenable to conventional adhesive bonding even though the wettability of the surface was similar to polytetrafluoroethylene. Brewis and Briggs exposed polyethylene to fluorine/nitrogen and fluorine/nitrogen/oxygen mixtures and observed a slight reduction in the surface tension of polyethylene upon suffi-

cient introduction of fluorine atoms [4]. They attributed any increases in surface tension, relative to untreated polyethylene, to the introduction of oxygen-containing functionalities. Hayes measured advancing contact angles on surface fluorinated polyethylene and, using Zisman's method, observed that the surface tension of fluorinated polyethylene decreased towards polar and non-polar liquids, but increased towards liquids with an ability to form hydrogen bonds [13]. Commercial fluorine contains oxygen as an impurity and he attributed this phenomenon to oxidation accompanying fluorination.

In the present study, the effect of fluorination on the wettability of high-density polyethylene has been determined by measuring dynamic contact angles.

It has been reported in the literature that polyethylene surfaces functionalized with carboxylic acid groups (by means of a chromic acid treatment) will be reconstructed to the original polyethylene surface on heating above 35 °C [14]. It was thought that this effect is related to the migration of –COOH groups into the bulk of the polymer, the driving forces being the lowering of the surface tension as well as an increased entropy of mixing (passive diffusion). An opposing force to this migration arises from the fact that, enthalpically, functional groups are more stable at a solid–vapour interface. Because oxyfluorinated samples (treated with mixtures of fluorine and oxygen) also contain –COOH groups (after hydrolysis), it was decided to determine whether a similar effect would be observed upon heating. This was undertaken mainly because surfaces prepared for improved adhesion or permeation properties might be exposed to high temperatures during testing, in which case an effect such as that described above will influence test results. To determine whether –CF functionalities would also undergo a similar effect, fluorinated samples were tested as well.

2. Experimental details

2.1. Materials

High-density polyethylene film [density 0.950 g cm⁻³ and melt flow index 1.5 g (10 min)⁻¹] was obtained from Plastomark. Water and methylene iodide, two convenient test liquids for surface tension determinations, were used in this study. The surface tensions (γ_T) of these purified liquids and their dispersion (γ_d) and polar (γ_p) components (harmonic-mean values) are listed in Table 1.

Table 1
Surface tensions and their components for liquids tested [9]

Liquid	γ_T	γ_d	γ_p
Water	72.8	22.1	50.7
Methylene iodide	50.8	44.1	6.7

Table 2
The effect of velocity on dynamic contact angles

Velocity ($\mu\text{m s}^{-1}$)	θ_a ($^\circ$)	θ_r ($^\circ$)
20	106	75
50	109	78
150	112	78
265	118	80

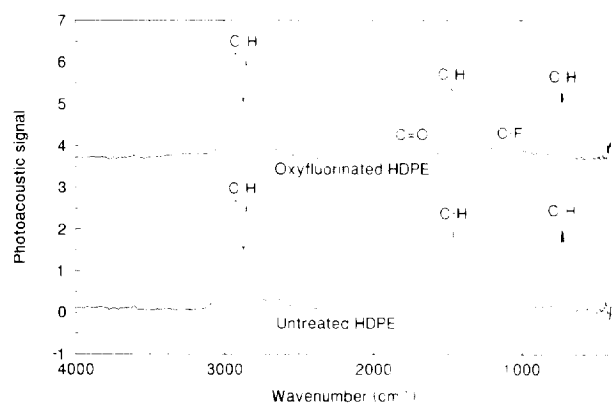


Fig. 1. Photoacoustic FT-IR spectrum of untreated and oxyfluorinated HDPE.

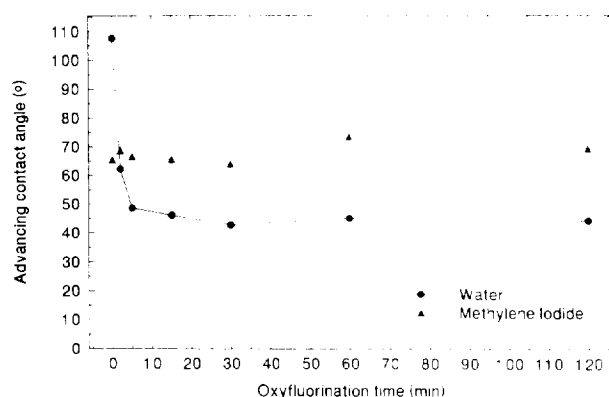


Fig. 2. Contact angles of water and methylene iodide on oxyfluorinated HDPE as a function of treatment time.

2.2. Fluorination

Polyethylene samples, $2 \times 1 \text{ cm}^2$ dimensions, were placed in the fluorination reactor and the system evacuated. The reactor chamber was purged with nitrogen to remove all traces of oxygen and water from the system. Diluted fluorine (10% in nitrogen or oxygen) was introduced into the reactor chamber and a constant flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$ was maintained. The reaction temperature was kept constant at $30 \text{ }^\circ\text{C}$.

2.3. Contact angle measurements

Advancing and receding contact angles were measured with a Cahn Dynamic Contact Angle Analyzer (DCA 322) using the Wilhelmy plate technique. Experiments were carried out at $25 \text{ }^\circ\text{C}$.

2.4. Surface characterization

The surface of the fluorinated polyethylene was characterized using infrared spectroscopy and neutron activation analysis (NAA). Infrared spectra were recorded on an FT-IR spectrophotometer equipped with a photoacoustic accessory. Neutron activation analysis is based on the measurement of γ -rays emitted by radionuclides which are formed by the irradiation of stable nuclides with neutrons. γ -Rays were detected with a Ge(Li) detector.

3. Results and discussion

3.1. Velocity dependence of the dynamic contact angles

During the determination of dynamic contact angles the system is in motion and contact angle values are velocity-dependent, because of the tendency of the three-phase contact line to resist movement. However, a number of authors have observed velocity-independent behaviour at low velocities [15] and an onset of a velocity-dependent regime only at high velocities (typically at values higher than $100 \mu\text{m s}^{-1}$) [16].

Dynamic contact angles of water on HDPE as a function of velocity are listed in Table 2. It is clear that over this broad velocity range, higher advancing contact angles (θ_a) were obtained at higher velocities while the receding contact angles (θ_r) seemed to be velocity-independent. In this study, a velocity of $50 \mu\text{m s}^{-1}$ was used as a compromise between achieving realistic measurement times and accuracy.

3.2. Effect of fluorine/oxygen treatment on the wettability of polyethylene

Photoacoustic FT-IR spectra of untreated and oxyfluorinated HDPE are presented in Fig. 1. Oxygen is incorporated into the surface during oxyfluorination and is observed as $-\text{COF}$ groups. In the presence of atmospheric moisture or water, these groups hydrolyze to the corresponding acid groups (1750 cm^{-1}).

Water contact angles of the hydrolyzed samples, as a function of oxyfluorination time, are presented in Fig. 2. Fluorination of HDPE in the presence of oxygen increased the wettability by water considerably. During the initial period of fluorination, a very steep decrease in contact angle was observed. Thereafter, the contact angle decreased further with time, but the effect was not nearly as pronounced as during the first period. These results are of commercial importance, since in such applications one has to evaluate the benefit of improved wettability against the cost of the fluorination process.

Surface tensions of HDPE as a function of oxyfluorination time are shown in Fig. 3. The total surface tension increased from 30 to 55 dyn cm^{-1} over a period of 120 min. The dispersive component of the surface tension was diminished

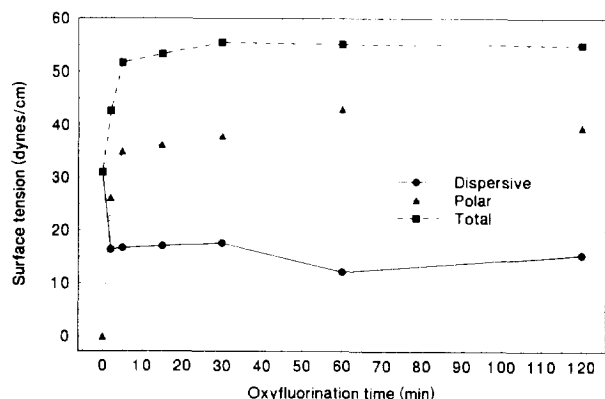


Fig. 3. Surface tension of oxyfluorinated HDPE as a function of treatment time.

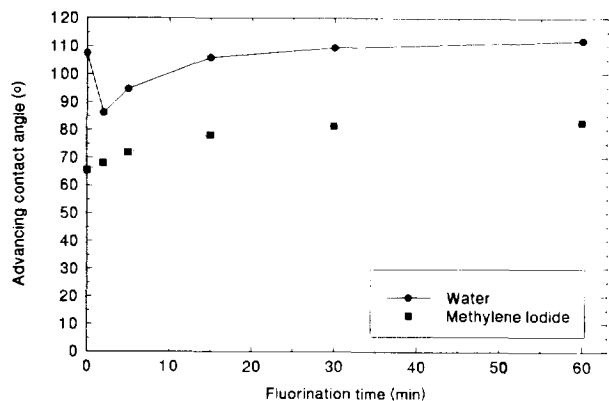


Fig. 4. Contact angles of water and methylene iodide on fluorinated HDPE as a function of treatment time.

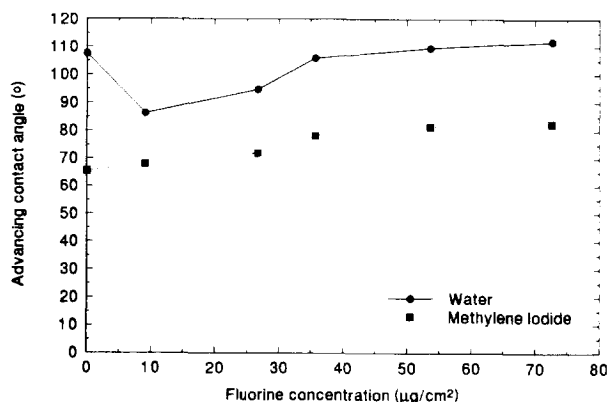


Fig. 5. Contact angles of water and methylene iodide on fluorinated HDPE as a function of surface fluorine concentration.

during oxyfluorination while, at the same time, the polar component increased drastically from zero to 40 dyn cm^{-1} .

3.3. Effect of fluorine/nitrogen treatment on the wettability of polyethylene

The effect of fluorination time on the water contact angle of polyethylene is shown in Fig. 4. Short fluorination times increased the surface hydrophilicity of polyethylene considerably. With increased fluorination times, the contact angle passed through a minimum value and increased once more,

reaching higher values than that of untreated polyethylene after long exposure times. The variation in contact angle as a function of the amount of fluorine incorporated during fluorination (as determined by NAA) is presented in Fig. 5.

Photoacoustic FT-IR spectra of untreated and fluorinated polyethylene are shown in Fig. 6. Although it has been reported that commercial fluorine is known to contain trace amounts of oxygen and various studies have indicated that oxidation accompanies fluorination [13], no evidence of oxygen-containing functionalities was observed. The possible introduction of oxygen might explain the increased wettability but cannot account for the turning point in the graph, since it has been reported that the acid fluoride groups which are formed during oxyfluorination are stable, even up to 1 atm. pure fluorine.

Zisman et al. studied the wetting characteristics of partially fluorinated solids [17] and observed that although CFH surfaces have lower surface free energies than hydrocarbon surfaces (as shown by the behaviour of non-hydrogen bonding liquids such as the alkanes), water contact angles on these surfaces were lower than those on hydrocarbon surfaces (see also Table 3). These workers attributed the lower contact angles of the partially fluorinated surfaces to hydrogen bonding between the solids and water.

The variation of the total surface tension as well as its dispersive and polar components is shown in Fig. 7. Surface fluorination of polyethylene resulted in a marked decrease in the dispersive component of the surface tension, while the polar component increased initially and decreased again with longer fluorination times. The net result was a decrease in

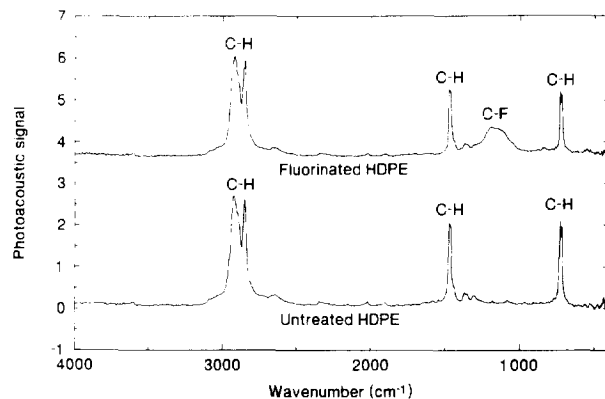


Fig. 6. Photoacoustic FT-IR spectrum of untreated and fluorinated HDPE.

Table 3
Equilibrium water contact angles of some low-surface-energy polymers [18]

Polymer	Water contact angle (°)
Polyethylene	102
Poly(vinyl fluoride)	80
Poly(vinylidene fluoride)	82
Polytrifluoroethylene	92
Polytetrafluoroethylene	108

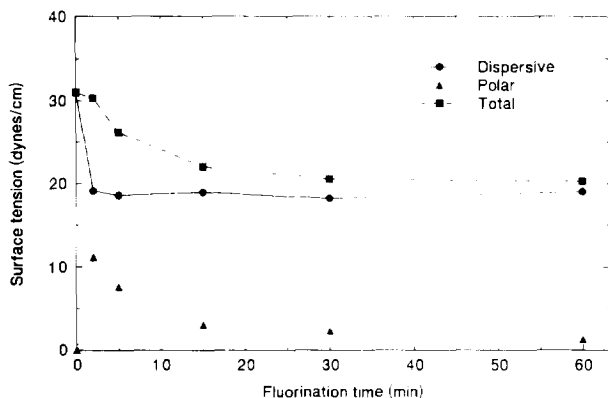
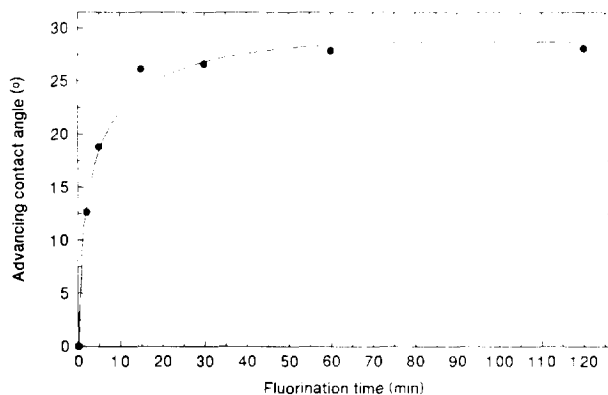


Fig. 7. Surface tension of fluorinated HDPE as a function of treatment time.

Fig. 8. Contact angle of *o*-xylene on fluorinated HDPE as a function of treatment time.

total surface tension from 30 dyn cm⁻¹ for untreated polyethylene to values as low as 20 dyn cm⁻¹ after 1 h of fluorine treatment.

Several studies have revealed that the permeation rate of non-polar liquids such as xylene or toluene through HDPE containers can be markedly reduced by exposing the container surfaces to elemental fluorine [19]. The effect that the decreased surface tension of fluorinated HDPE (which is obtained by fluorinating in the absence of oxygen) has on its wettability by *o*-xylene is shown in Fig. 8. The *o*-xylene contact angle on HDPE is increased from zero (complete wetting) to almost 30°.

3.4. Effect of temperature treatment

Samples fluorinated for 2 h were heated at 30 °C, 50 °C and 100 °C, respectively, for 60 min. Samples oxyfluorinated for 2 h were heated at 30 °C, 50 °C and 100 °C, respectively, for 30 min. The contact angles of water and methylene iodide were then determined and the surface tensions were calculated. The results are given in Table 4.

As noted above, fluorination leads to a decrease in the dispersive component of the surface tension, coupled with an initial slight increase in the polar component, which decreases again after 120 min fluorination time. The result is a net reduction in the total surface tension. Heating these samples at 30 °C and 50 °C had little effect, but heating at 100 °C resulted in a slight increase in the polar component indicating that there might be a mechanism which causes surfaces to change to ones yielding surface energies similar to less fluorinated samples. This mechanism might be the migration of -CF functional groups into the bulk of the polymer, thereby exposing some -CH groups. The driving force behind this migration cannot be the decrease in the total surface tension, because the surface tension is lower than that of polyethylene, and from Table 4 it can be seen that there is a slight increase in the total surface tension on heating. Reports in the literature indicate that modified polyethylene surfaces with surface tensions lower than polyethylene reconstruct much slower than those with higher surface tensions [14]. It can therefore be deduced that an increase in entropy is the sole driving force for the migration of functional groups into the bulk and that the low surface tension actually impedes this movement.

Oxyfluorination leads to a decrease in the dispersive component of the surface tension, coupled with a large increase in the polar component, with a large net increase in the total surface tension. Heating to 30 °C and 50 °C did not have any effect, but heating to 100 °C effected a large decrease in the polar component with a very slight increase in the dispersive component, resulting in the total surface tension decreasing to almost that of untreated polyethylene. This measured total surface tension is, however, made up of different dispersive and polar components to that of untreated polyethylene which has a zero polar component.

Table 4
Surface tensions of HDPE samples treated at different temperatures

Sample	γ_d (dyn cm ⁻¹)	γ_p (dyn cm ⁻¹)	γ_T (dyn cm ⁻¹)
Untreated HDPE	31.0	0.0	31.0
HDPE fluorinated for 120 min			
no heating	21.3	1.2	22.5
heated at 30 °C	20.8	1.7	22.5
heated at 50 °C	23.1	1.3	24.4
heated at 100 °C	19.8	6.0	25.8
HDPE oxyfluorinated for 120 min			
no heating	15.4	39.6	55.0
heated at 30 °C	17.8	36.6	54.4
heated at 50 °C	15.8	38.4	54.2
heated at 100 °C	18.0	15.6	33.6

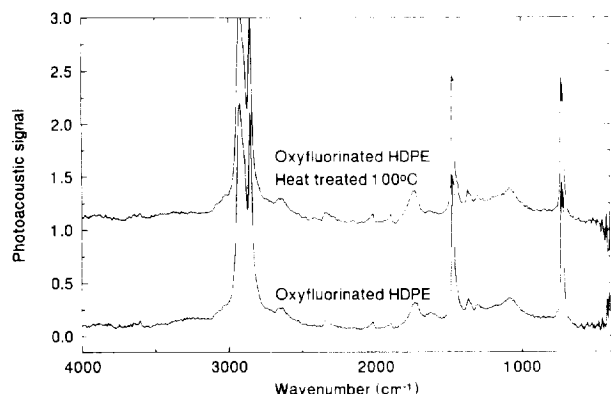


Fig. 9. Photoacoustic FT-IR spectra of oxyfluorinated HDPE before and after heating to 100 °C.

Contact angle studies provide information about the outer 5–10 Å of a solid [14], while photoacoustic infrared spectroscopy samples a much thicker portion ($> 10 \mu\text{m}$). Photoacoustic FT-IR spectra of oxyfluorinated HDPE (120 min) and of the same sample heated for 30 min at 100 °C are presented in Fig. 9. Although the surface tension of the heated sample resembles that of untreated polyethylene, the oxygen functionality was still present. These results suggest that the apparent disappearance of the polar groups from the surface of oxyfluorinated HDPE upon heating resulted from the migration of polar groups into the polymer bulk.

If the observed trend of surface tension change with heating continues at higher temperatures or with longer heating times, it seems feasible that the surface tension may change back to that of polyethylene. However, the observed effect is not as pronounced or rapid as that reported in the literature for chromic acid-treated polyethylene. This may arise from several reasons, including differences in the grade and density of polyethylene used (LDPE was used in the study quoted), different levels of $-\text{COOH}$ functionalization (both with respect to the number of $-\text{COOH}$ groups and depth of functionalization), the presence of $-\text{CF}$ functional groups (which will partly negate the surface tension driving force) and possible crosslinking on the surface during the oxyfluorination process leading to restricted mobility of the polymer chains.

The fact remains that there is a change in the surface tension of oxyfluorinated HDPE with heating, which leads to the

question: is this effect also present at room temperature, albeit very slowly, and what are the implications for the lifetime of oxyfluorinated surfaces? Further research will be needed to quantify this effect.

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