OLEOPHOBIC AND HYDROPHOBIC FEATURE EXPERIMENTS OF FLUORINATED HIGH DENSITY POLYETHYLENE

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Abstract: The surface performances of directly fluorinated high density polyethylene (HDPE) are studied with Fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM) and contact angle (CA) system. The SEM images show that there is a three-layer structure called the reaction, virgin and boundary layer structure. The depth of fluorinated layer is 5.75 μm with 1 h fluorination time and 7.86 μm with 2 h. The depths are 5.46 μm and 5.07 μm when fluorine density is 2% and 1%, respectively. CA indicates that the HDPE surface property becomes more hydrophobic with the increasing water contact angle from 78.5° to 104.5°. Oleophobic and hydrophobic features of HDPE are identified by comparison of mass change experiments. It is shown that the increment rate of fluorinated HDPE is much lower than that of un-fluorinated HDPE filled in neither distilled water nor jet fuel.

Key words: high density polyethylene; contact angle; surface property; oleophobic and hydrophobic features

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INTRODUCTION

High density polyethylene (HDPE) is one of the most widely used polymers in the industry on account of desired properties, good processability and relatively low cost. However, it has some disadvantages such as poor barrier properties and low chemical resistance [1-3]. Direct fluorination, which can be used to modify the surface properties of polymer, is a heterogeneous reaction of elemental gaseous F_2 and its mixtures (fluorine and nitrogen, argon or helium)[4-7] react with polymer surface.

Unique properties of direct fluorinated polymers are due to the characteristics of the fluorine atom. Fluorine is the most reactive and electronegative of all elements, and its dense electron cloud has very low polarizability[8]. As shown in Table 1, it has very small dissociation energy (153 kJ/mol) and a very high binding energy[9].

Table 1 Binding energy of fluorine

Bond	F—C	F—H	F—S
Binding energy/(kJ • mol^{-1})	490	570	330

When a mixture of fluorine reacts with the polymer surface (fluorine pressure and treatment duration should not exceed certain level), the surface is formed carbon-fluorine bonds which are more stable than carbon-hydrogen bonds by approximately 75 kJ/mol. The strong bonds in fluorocarbons, compared with hydrocarbons, are

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largely responsible for the exceptional thermal and chemical stability. At the same time when the surface is modified by materials with low surface free energy, oil and water-retard surfaces have been produced[10]. These features of elemental fluorine have initiated its wide utilization to enhance various application properties of HDPE: Barrier properties, chemical resistance, adhesion, printability and others[11-15]. Owing to barrier surface layer, environment pollution at diffusion of jet fuel and other fuel through the walls of polymer fuel tanks fall up to several tens of times[16]. Therefore, it has a broad amount of applications, such as oil and gas pipes, barrier membranes, HDPE composites, barrier films and fuel tanks[17-20].

Most experiments on the direct fluorination have focused on the performances of the adhesion, gas separation, and chemical resistance properties[21-23]. However, relatively less attention, as well as experiments in detail, has been paid to oleophobic and hydrophobic properties, especially HDPE′s. Oleophobic and hydrophobic properties can afford the self-cleaning ability of the surface of polymers, combination of oleophobic and hydrophobic coating materials and filter materials[24-25]. In order to research the oleophobic and hydrophobic properties of the surface performances of direct fluorinated HDPE, Fourier transform infrared (FT-IR), scanning electron microscopy (SEM) and contact angle (CA) are applied in the study. At the same time, a series of oil and water-retard experiments are performed.

1 EXPERIMENT

1.1 Materials and preparations

The matrix material used in this experiment is HDPE with density of 0.955 g/cm^3 and an melt flow index (MFI) of 0.35 g/10 min (190 ℃/2.16 kg), obtained from Shanghai Golden Phillips Petrochemical Co. Ltd.

Surface fluorination of HDPE sheets of 50 mm×50 mm×1 mm size is performed in our laboratory. Fluorination is carried out in closed vessels at a total mixture pressure of 95.8 kPa by treating with mixture (F_2+N_2). Different fluorination time (1 and 2 h) and different fluorination concentration (1% and 2%) are applied to the HDPE sheets to investigate an effect of extent of fluorination on their surface properties. Fluorinated HDPE sheets are stored in a silicagel desiccator at room temperature.

1.2 FT-IR study

For structure analysis, FT-IR of the virgin and fluorinated HDPE are studied using a spectrometer THERMO NICOLET 5700. The IR-spectrum is recorded by transmission in a dry air atmosphere between 4 000—400 cm^{-1} with 64 spectral accumulations.

1.3 SEM observation and contact angle measurements

The micro-structural characteristics are carried out with a Jeol JSM-5800LV SEM. Contact angels are measured with measuring system JC2000C1. Measurements are performed by a sessile drop method using the drop shape analyzer (°) at room temperature (20±2 ℃) and averaged. Distilled water droplet is dropped to the sample surface from a distance of 5 mm by the vibrating injector. The diameter of the droplet is about 1 cm. The contact angles of water are measured to observe the ability of water-repellency on the direct fluorinated HDPE surface.

1.4 Mass varying measurements

The mass measurement experiments are operated in a thermostatic tank at 90 ℃, where the temperature is controlled within ±0.5 ℃ throughout a run except for an initial fluctuation. Increment of mass and time are recorded over a period from 1 d to 10 d. Fluorinated and un-fluorinated HDPE sheets with the same amount are each immersed in four cleaned and pre-weighed glass cups. The first and the second cups (referred to as Sample 1 and Sample 2) are filled with distilled water, meanwhile the third and the fourth cups (referred to as Sample 3 and Sample 4) are filled with jet fuel. Table 2 gives selected properties for the jet fuel.

Table 2 Selected properties of tested jet fuel

Property	Jet fuel
Initial density (20 °C)/(kg • m^{-3})	796
Original distillate temperature/°C	40
10% distillate temperature/°C	80
20% distillate temperature/°C	105
50% distillate temperature/°C	145
90% distillate temperature/°C	180
End distillate temperature/°C	251
Residual/(V/V, %)	2.5
Loss/(V/V, %)	1.5

Mass varying experiments are measured using an electronic balance (Shimadzu UX4200S) with an accuracy of 0.1 mg. Temperatures at the experiment location are closed to 20 °C, and there are no velocities over the surface of jet fuel.

2 RESULTS AND DISCUSSION

2.1 Surface performance of direct fluorinated HDPE hollow sphere

FT-IR spectra of the virgin and fluorinated HDPE films are shown in Figs. 1,2.

Fig. 1 shows four typical bands of the virgin HDPE, where 2 916 cm^{-1} is due to —CH_2 dissymmetry stretching vibration, 2 850 cm^{-1} is —CH_2 symmetry stretching vibration, 1 463 cm^{-1} is —CH_2 bending vibration, and the band at 719 cm^{-1} is the —CH_2 rocking vibration.

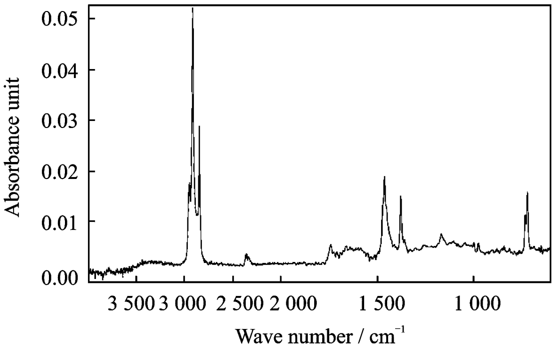


Fig. 1 FT-IR spectra of virgin HDPE film (thickness of film is equal to 20 μm)

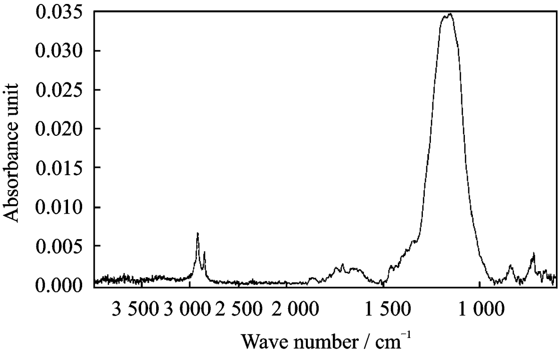


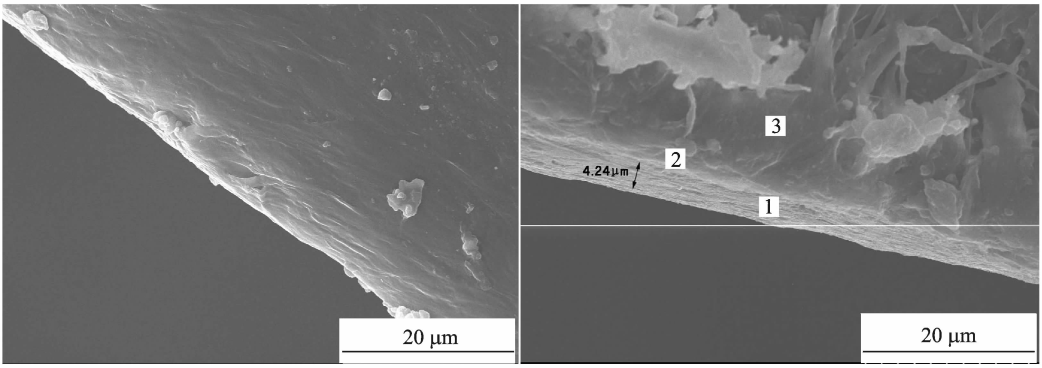
Fig. 2 FT-IR spectra of fluorinated HDPE film (thickness of film is equal to 20 μm)

In the case of fluorinated HDPE, a broad peak appears at 1 200 cm^{-1} in Fig. 2, which is due to the absorption of C—F bond. According to the literature, the frequency at 1 000—1 300 cm^{-1} is a characteristic frequency of the C—F bond.

Kharitonov, et al[26] observed that fluorinated polymer consisted of three-layer structure: Fluorinated layer, unmodified layer (virgin layer), and boundary layer (main chemical conversion processes proceed inside that reaction zone). Fig. 3 shows the SEM image of un-fluorinated and fluorinated HDPE. However, the boundary layer is very narrow, almost invisible, suggesting that HDPE has the high crystal capability.

The SEM images show that the depth of fluorinated layers has remarkable change under the different fluorination time and the density of fluorinate mixtures. Figs. 4(a, b) have the same experiment conditions except that the fluorination time of former is half of that of the latter. As expected, the longer the fluorination time is, the higher the fluorine level is. The depth of fluorinated layer in Fig. 4(a) is 5.75 μm but in Fig. 4(b) is 7.86 μm. The density of fluorinate mixture of Fig. 5(a) is 1% more than that of Fig. 5(b). The depth of fluorinated layer of Fig. 5(a) (5.46 μm) is 0.39 μm thicker than that of Fig. 5(b) (5.07 μm), and there is similar tendency showed in Fig. 4. However, their relationship is not linearity.

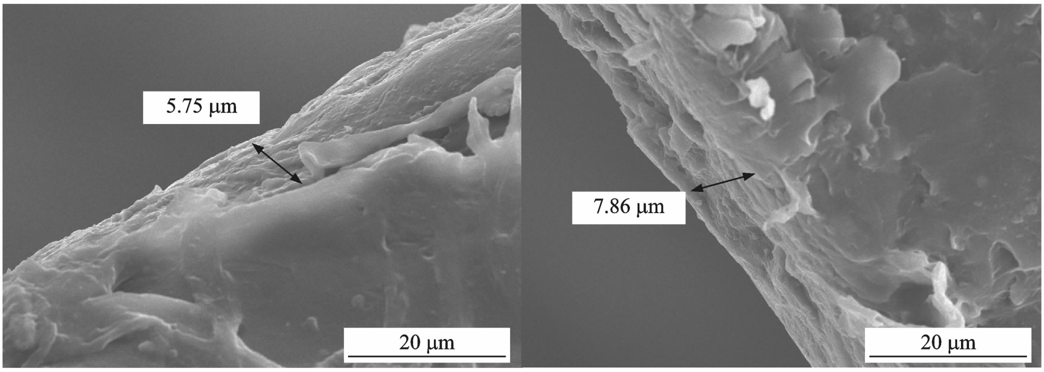
As summarized in Table 3 and showed in Fig . 6 , the wetting behavior of the fluorinated



(a) Un-fluorine treated film (b) Fluorine treated film

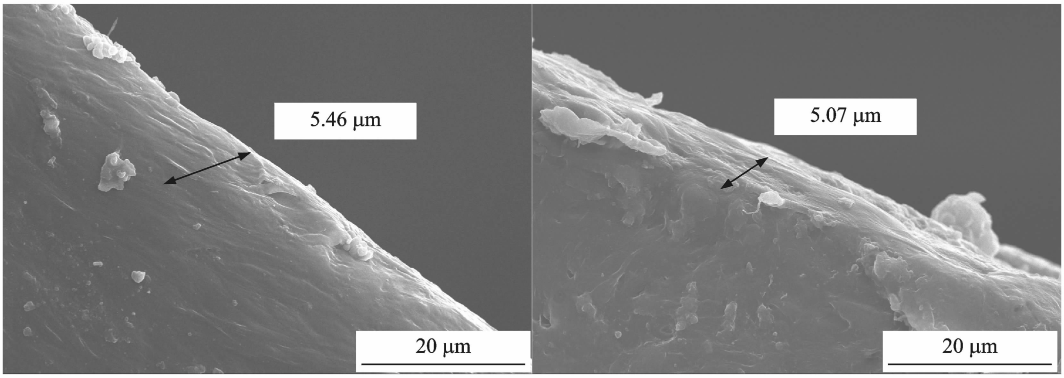
1—Fluorinated layer; 2—Narrow boundary layer; 3—Unmodified layer

Fig. 3 Cross section of un-fluorine and fluorine treated HDPE films



(a) Fluorination time of 1 h (b) Fluorination time of 2 h

Fig. 4 SEM images of different time



(a) Fluorination density of 2% (b) Fluorination density of 1%

Fig. 5 SEM images of different density

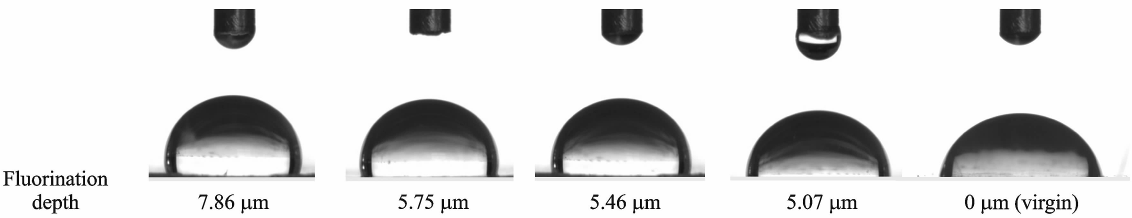


Fig. 6 CA of water

Table 3 CA of water measured by sessile drop method

Fluorination depth/μm	7.86	5.75	5.46	5.07	0.00
CA/(°)	104.5	98.5	93.5	90.0	78.5

HDPE is observed by CA, and CA of water on the surface of HDPE is measured before and after the direct fluorination. The surface of HDPE becomes significantly more hydrophobic, as a result of direct fluorination, as shown by the notable increase of CA of water from 78.5° to 90.0°. At the same time, CA increases from 90.0° to 104.5° as the fluorination depth increases from 5.07 μm to 7.86 μm. This remarkable growth in the surface hydrophobicity is due to the increasing F/C ratio and the absence of hydrophilic ionic C—F bonds. From CAs, the surface tension of direct fluorinated HDPE sharply decreases from over 30 m · $(\mathrm{Nm})^{-1}$ to 19 m · $(\mathrm{Nm})^{-1}$ after fluorination due to the incorporation of fluorine. Fluorinated HDPE layer indeed becomes similar to PTFE which has a surface tension of 18.5 m · $(\mathrm{Nm})^{-1}$.

2.2 Oil and water-retard experiment

Table 4 lists the initial mass and the mass change for four samples immersed in water and jet fuel during 10 d measurements, respectively.

Table 4 Mass change measurements of four samples

Sample	Initial	1 d	2 d	3 d	4 d	5 d	6 d	7 d	8 d	9 d	10 d
1 (Water, fluo)/‰	8.229 2	8.229 6	8.230 1	8.230 5	8.230 8	8.232 6	8.232 7	8.233 8	8.233 0	8.236 4	8.234 6
2 (Water, un-flu)/‰	8.538 8	8.541 7	8.544 7	8.547	8.550 6	8.552 3	8.553 5	8.555 0	8.554 9	8.563 1	8.565 1
3 (Petrol, fluo)/%	7.834 4	8.234 1	8.676 7	8.766 5	8.822 4	8.873 6	8.897 0	8.911 9	8.926 8	8.944 5	8.966 6
4 (Petrol, un-flu)/%	8.729 0	10.064 7	10.177 4	10.239 2	10.256 7	10.239 6	10.248 6	10.221 7	10.194 8	10.164 0	10.176 7

Fig. 7 shows the relationship between the increment rate of fluorinated and un-fluorinated HDPE hollow spheres during 10 d. As previously mentioned, the main difference observed between the fluorinated and un-fluorinated HDPE is the barrier property. The direct fluorination enhances the surface barrier performance of HDPE. Therefore, the increasing rate of Sample 1 (fluorinated HDPE) is much lower than that of Sample 2 (un-fluorinated HDPE).

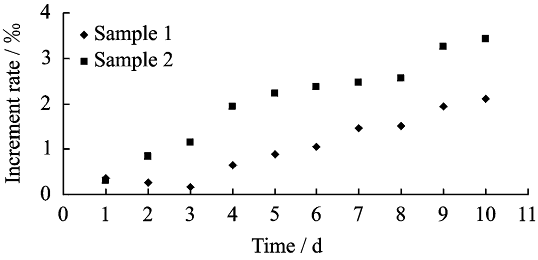


Fig. 7 Comparison of mass change between fluorinated and un-fluorinated HDPE hollow spheres in water

Similar trend is obtained in Fig. 8. Fluorinated HDPE hollow sphere forms a resistant surface to oil according to the fluorination performance. C—F bond has a higher barrier property of impenetrability in fuel, especially in jet fuel. The increasing rate of un-fluorinated HDPE is higher than that of the fluorinated one.

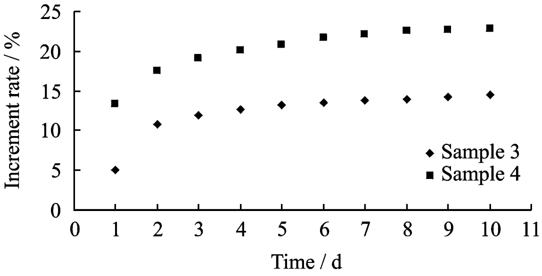


Fig. 8 Comparison of mass change between fluorinated and un-fluorinated HDPE hollow spheres in jet fuel

At the same time, Fig. 8 shows that the cure in the initial two days is sharper than that in the later days. The reason is that a multi-component mixture such as jet fuel is quite different from a pure liquid such as water. The evaporation of water is a constant with respect to time. However, the evaporation of jet fuel is not linear with time. The permeability of a liquid consisting of a mixture of hydrocarbons is very sensitive to increment of mass. With the light compounds are decreased, and the permeability of jet fuel is decreased, too.

3 CONCLUSION

Compared with the modified treatment of surface property mentioned in the previous literatures, the direct fluorination method applied in HDPE is a more effective, simple and convenient modified technology. The different depths of fluorinated layers show that the fluorination level is affected by the fluorination time and the density of fluorinate mixtures. A higher CA obtained on the surface of HDPE indicates that the direct fluorination make it have lower surface energy and more hydrophobic feature. Therefore, direct fluorination decreases water and jet fuel permeating through the surface of HDPE hollow spheres.

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