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Surface modification of low-density polyethylene packaging film via direct fluorination

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ABSTRACT

Low Density Polyethylene (LDPE) films were treated by direct fluorination at different conditions, i.e. static and dynamic ones. Modification of the treated films chemical composition was studied by spectroscopic methods (solid state NMR, XPS and infrared spectroscopy). Surface morphology was investigated by SEM and AFM. Also surface energy measurements and electron paramagnetic resonance (EPR) were carried out. Direct fluorination resulted in printability, barrier properties towards O_2 and tribological properties enhancement. On the contrary, the barrier properties towards water, initially good, were not improved but maintained.

1. Introduction

The presence of fluorine atoms in polymers always results in particular properties, high thermal and chemical stability, hydrophobicity, barriers towards gases, high optical transmittance, printability, low friction coefficient [1–10]. The insertion of fluorine atoms into polymer chains may be performed starting with fluorinated monomers. Nevertheless, practical use of fluoropolymer items is restricted due to their high cost and complexity of synthesis. On the contrary, a treatment with gaseous fluorine of conventional polymer articles is recognized to be one of the well-effective chemical processes to modify and control polymer surface properties. Very often application properties of polymer items are defined mainly by their surface properties. Drawbacks of polymers, i.e., often poor adhesion, printability and barrier properties, low chemical resistance may be corrected by surface fluorination [1–10]. This latter strategy is investigated in the present paper for polymer packaging films. For this case, the weldability is of primary importance. As an example, polytetrafluorethylene (PTFE) wettability is very bad. Direct fluorination is described as a heterogeneous reaction between gaseous molecular fluorine F_2 (undiluted or in a mixture with other gases such as, N_2, Ar, O_2, He) and the polymer surface. Under this process, as a general rule, only the upper surface of the polymer layer is modified [11,12]. Its thickness depends on the treatment conditions. Another important fact is that the bulk properties remain unchanged. In addition, this process allows an application at room temperature because of the reactivity of F_2 and can be considered as a dry technology. A safe and reliable method to neutralize both unused F_2 and the end product of the reaction HF was well developed [13]. All these features are sufficient to consider this technique for wide industrial applications to improve adhesion [8,14,15] and printability properties [16] of a lot of common polymers or to enhance gas separation properties of polymer membranes [2,9,17,18]. Finally, this process is also recognized to reduce friction coefficient, improve

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chemical resistance and antibacterial properties [19]. Reaction of F_2 with a large panel of commercial polymers has been widely investigated and is well understood [3,9].

This work was focused on low density polyethylene (LDPE) films. This polymer exhibits intrinsically very poor printability, wettability and O_2 barrier properties. Industrial film applications are mainly developed in the domains of packaging (food, agriculture…). The desired properties are then printability, permeability towards O_2 and H_2O gas and tribological properties. The main objective is to investigate the possibility of abovementioned target properties enhancement by fluorination simultaneously. A comprehensive physical-chemical characterization was carried out with complementary techniques at different scales: *i*) on the bulk (using solid state Nuclear Magnetic Resonance (NMR), FTIR spectroscopy in transmission mode) and *ii*) on the surface (X-ray Photoelectron Spectroscopy (XPS), and FTIR spectroscopy using Attenuated Total Reflection (ATR) mode, measurements of contact angle and surface energy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Electron Paramagnetic Resonance (EPR)). FT-IR spectra were recorded in order to get preliminary information about the chemical composition of the treated samples. ^{19}F NMR and XPS clarified the C—F bonding and the nature of formed fluorinated groups (CF, CF_2, CF_3…). To complete the results, measurements of surface energy were performed in order to define the polarity of the samples before and after treatment. The behaviour of radicals generated after the fluorination processes was studied by EPR. Finally, the printability, tribological and barriers properties towards O_2 and H_2O gases were investigated and the changes due to fluorination were discussed.

2. Experimental

2.1. Materials

Low density polyethylene films (*Pristine_LDPE*) were developed for packaging applications such as food or agricultural domains and obtained from our partners (*JCE Plasturgie*). The films with 45 μm in thickness were corona treated on one side. All treatments have been performed on the face which was identified as untreated. Polymer films were used as received. Different fluorination processes were applied to treat LDPE films.

2.2. LDPE direct fluorination

Two different routes of the direct fluorination using molecular fluorine F_2 were studied. Both processes have been carried out at room temperature. Fluorine contained less than 0.1 vol% of admixtures (mainly oxygen).

i) Fluorination in *static conditions* was carried out in a closed Nickel reactor with a defined amount of F_2. Prior to the fluorinating mixture insertion the reactor was evacuated to primary vacuum (~10^{-2} mbar) for 1 h. LDPE samples (195 cm^2 in area) were placed inside reaction vessel fabricated from Nickel in an passivated Nickel support. Sample denoted as F_LDPE_SF was then treated by a reactive N_2/F_2 (0.8:0.2, volume ratio) gaseous mixture. The reaction was performed for 24 h to reach the reaction completion. F_2 (g) was diluted to obtain mild treatment conditions. After treatment, the reactor was flushed with nitrogen flow for 1 h to remove unused fluorine and HF products.

ii) Fluorination *in dynamic conditions* using a flux of F_2 gas through the open reactor. LDPE samples (195 cm^2 in area) were placed inside reaction vessel fabricated from Nickel in an alumina cylindrical support. The oven was flushed for 1 h with nitrogen before fluorination. Each sample was then submitted to a fluorinating N_2/F_2 (0.5:0.5, volume ratio) flow for various durations, i.e. from 1 to 280 min. The samples were then denoted F_LDPE_DF*time*, e.g. F_LDPE_DF*280*. The fluorine flow was subsequently stopped, and the reactor oven was flushed with nitrogen for 1 h. The reaction can be expressed as follows (1):

$$(C_2H_4)_n + {}^{E}F_2 \rightarrow (C_2H_xF_y)_n + HF + \text{Volatile Species} \tag{1}$$

^{E}: it is to note that F_2 (g) was always injected in excess into the reactor because of the dynamic flux.

The reactor was flushed with nitrogen flow for 1 h to remove all the volatile species as well as small fragments from the polymer samples.

2.3. Characterization

FTIR spectrometer NICOLET 5700 (Thermo Electron) was used to record IR spectra using both ATR and transmission modes. 100 scans with 4 cm^{-1} resolution were collected to acquire each spectrum between 4000 and 400 cm^{-1}. The single-reflection ATR accessory (Thermo Scientific Smart Orbit) is working with a durable diamond crystal (type IIa Diamond tungsten carbide mounted in stainless steel with a refractive index of 2.4 and an incident angle of 58°) and a swivel pressure tower that ensured consistent pressure from sample to sample. The active sample area was 1.5 mm^2. A wide spectral range (10,000 to below 200 cm^{-1}) and good depth of penetration (DP of 2.03 μm at 1000 cm^{-1}) were then reached. DP was estimated using the following equation:

$$\mathbf{DP} = \frac{\boldsymbol{\lambda}}{\left(2\boldsymbol{\pi}\mathbf{N_C}\left(\sin^2\boldsymbol{\theta} - (\mathbf{N_S}/\mathbf{N_C})\right)^{1/2}\right)}$$

N_C and N_S are the indices of refraction for the crystal and the sample, respectively, θ is the angle of incidence of the light, and λ is the wavelength of the light. For diamond at 1000 cm^{-1}, this leads to a depth of penetration near 2 μm. Previously A.P. Kharitonov et al [4,20] confirmed that the fluorination of LDPE (density 0.92 $g \cdot cm^{-3}$) proceeded as a diffusion-controlled process. It means that the rate of fluorinated layer formation is limited by the rate of fluorine penetration through fluorinated layer to untreated one. Untreated and fluorinated layers are separated by a very thin transient layer where majority of chemical reactions takes place. The thickness of that transient layer is much less that 0.1 μm. The fluorinated layer thickness $\mathbf{d_F}$ (μm) can be calculated by the formula $\mathbf{d_F} = 0.020 \times (\mathbf{p_F})^{0.52} \times \mathbf{t}^{0.5}$, where $\mathbf{p_F}$ is the fluorine partial pressure (bar) and **t** (seconds) is the fluorination duration. The fluorinated layer thicknesses $\mathbf{d_F}$ are equal to 0.11, 0.24, 0.48, 0.83, 1.80 and 4.09 μm for the treatment duration 1, 5, 20, 60, 280 and 1440 min respectively for the case of dynamic conditions. For the case of static conditions the fluorinated layer thicknesses are equal to 0.067, 0.15, 0.30, 0.52, 1.12 and 2.55 μm for the treatment duration 1, 5, 20, 60, 280 and 1440 min respectively.

^{19}F NMR measurements were carried out with a Bruker Avance Spectrometer with working frequency of 282.2 MHz. A Magic Angle Spinning (MAS) probe operating with 2.5 mm rotors was used allowing a 34 kHz spinning rate. For ^{19}F MAS spectra, a simple sequence was used with a single π/2 pulse duration of 4.0 μs. ^{19}F NMR chemical shifts were externally referenced to CF_3COOH and then referenced to $CFCl_3$ ($\delta_{CF3COOH} = -78.5$ ppm vs δ_{CFCl3}).

The X-ray photoelectron spectra (XPS) were recorded using a Thermo K-alpha system with a hemispherical analyser and a microfocussed (analysis area was ca. 200 μm^2) monochromatized radiation Al Kα line (1486.6 eV) operating at 75 W under a residual pressure of 1.10^{-7} mBar. The spectrometer pass energy was set to 200 eV for survey spectrum and to 20 eV for core peak records. Surface charging was minimized using a neutralizer gun which sprayed low energy electrons and Ar^{+} ions over the sample surface. All the binding energies were referenced to the C1s peak at 285.0 eV originated from the surface carbon contamination. The treatment of core peaks was carried out using a nonlinear Shirley-type