

Microstructure and Surface State of Plasma-treated High-density Polyethylene Elucidated by Energy-tunable Positron Annihilation and Water Contact Angle Measurements

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Positron gamma ray spectroscopy coupled with an energy-tunable positron beam was utilized to the study of the microstructure in polyethylene (PE) modified by the radio-frequency (RF) plasma. The energy dependence of the line-shape S parameter, a measure of the Doppler broadening of the positron radiation, confirmed that the change in the hydrophilic state of the PE surface after plasma modification was due to the altered chemical structure in the near-surface region. Moreover, only a region at a depth shallower than 700 nm was influenced by the plasma modification. The recovery in the surface hydrophobicity after plasma modification was observed through contact angle measurements. The variation of the contact angle of water can be fitted by a two-factor decay model, suggesting that the surface recovery is caused by the diffusion of two different groups.

1. Introduction

Polyethylene (PE) has been used in many technological sectors, such as automotive, medical, aerospace and electronics fields [1]. Although PE has the excellent volumetric property, the low surface energy and the poor adhesivity often prevent its further applications to bonding, printing, and laminating processes [2, 3]. In order to improve the surface property, various methods have been used, e.g. plasma techniques [4, 5], chemical surface etching [6], and casting chemical solution [7]. Environment-friendly technologies for modifying the surface property of the materials are in great demand, instead of the complex and/or hazardous technologies with expensive and toxic reagents. To avoid various chemical pollutants, plasma treatment is an extremely attractive way to improve the surface property of polymers. Moreover, that modification only takes place on the surface without changing the chemical structure in the bulk. [8] Therefore, plasma modification is a potential treatment applicable to surface modification in industry.

The mechanism of plasma modification is complicated, since radical reactions, ion etching, crosslinking, and chain scission may occur at the same time during the process. Many researches focusing on the mechanism have been performed in this field. Hegemann *et al.* utilized a radio-frequency (RF) plasma to modify a series polyolefins in different atmospheres, reporting improved friction for those modified polymers [9]. Guruvenket *et al.* have studied PS and PE modified by an electron cyclotron resonance (ECR) plasma in argon and oxygen gases, and their results indicated that both the microwave power and treatment time influenced the resultant surface state [10]. Nishijima *et al.* employed a positron beam for the study of PE films treated by an ECR plasma and proved

that polar groups such as hydroxyl and carbonyl are introduced onto the surface [11]. In comparison the ECR plasma, the RF plasma provides better uniformity of the plasma-processed surface as the sample size increases [12]. However, so far there has been little research examining the actual depth from the surface influenced by the RF plasma treatment, whereas evaluating the effectiveness is of importance for the product design in industry.

The positron annihilation technique with a variable-energy positron beam can probe the nanostructure of materials with depth-selectivity. By varying the incident positron energy over a wide range, one can obtain the depth profile of the positron annihilation parameters for the investigation of the surfaces and the interface for various thin films [13–15]. In the present work, the near surface region of high-density PE (HDPE) was altered by argon plasma. The depth influenced by plasma was characterized by a variable energy positron beam. The hydrophobicity recovery was examined by the water contact angle measurements.

2. Experiments

2.1 Materials

HDPE for the present work was purchased from Daqing Petroleum Chemical Plant (PE-LA-500012, Daqing, China). The testing materials were prepared by using a microinjection molding machine (Thermo Electron Corp.). The injection time was 30 seconds, the injection pressure was 0.55 MPa, the injection temperature was 190 °C, and the molding temperature was 40 °C. The prepared samples were cut out from the molded polymer in the form of 2-mm thick rectangle shape (10 mm × 50 mm).

2.2 Plasma surface treatment

The surface treatment was performed in a RF-plasma reactor (YZD08-2A) purchased from Tangshan Yanzhao technical institute. The RF discharge was excited at 40 kHz with plain parallel electrodes placed about 50 mm distance. The sample was placed on one electrodes. The treatment for each sample was carried out for 5 min with an RF power of 80 W and an operating Ar pressure of ~80 Pa.

2.3 Positron annihilation technique

Positron annihilation γ -ray spectra for the HDPE samples were measured with a ^{22}Na -based, magnetically-guided positron beam. The line-shape S parameter was determined as the ratio of the counts appearing in the central region (510.3 keV–511.7 keV) to the total counts of the 511 keV annihilation photo peak (506.8 keV–515.2 keV) for each spectrum recorded with a high-purity Ge detector. The mean positron implantation depth, z [nm], is estimated by the following formula [13],

$$z = \frac{40}{\rho} E^{1.6} \quad (1)$$

where E is the incident positron energy in keV and ρ is the density in $\text{g}\cdot\text{cm}^{-3}$.

2.4 Water contact angle measurement

The hydrophilic state on the sample surface was characterized by the water contact angle. The static contact angle of distilled water on the sample surface in air was obtained at room temperature by using a contact angle measuring device (SL2006) from Shanghai Kino Tech Corp. The water contact angles were calculated by a circle fitting to a sessile drop with a volume of 1 μl . For each surface the contact angle measurements were repeated at five different sites.

3. Results and Discussion

Figure 1 shows the variation of the S parameter for the three samples (untreated HDPE, HDPE aged 3 days and HDPE aged 33 days) as a function of E . The upper horizontal axis shows the mean

implantation depth calculated using Eq. (1). In comparison with the untreated sample, the $S(E)$ curves for the treated ones exhibit a distinct decrease in the S values in the energy range less than 6 keV corresponding to $z \sim 700$ nm. As E increases from 0.1 keV, the respective S for all the samples increases and approaches a saturated value of ~ 0.53 at $E > 6$ keV.

For polyolefin systems, S is generally related to the Ps formation probability and the momentum of the electrons belonging to the constituents of the polymer chains. Both of these two parameters are significantly influenced by the chemical structure of the material. According to the spur reaction model [16], Ps formation is partially inhibited by positron trapping and annihilation with polar groups in the matrix giving rise to a reduction of the S parameter. In light of this, the lower S in the near-surface region for the present modified samples suggests the introduction of polar groups into the surface region. Moreover, in comparison with the untreated sample, S for the treated ones is significantly reduced in the range at $E < 6$ keV, corresponding to a mean implantation depth of < 700 nm. This confirms that the chemical structure of the treated sample in the near surface region is different from that for the untreated one, namely, only the region shallower than 700 nm is influenced by the plasma modification.

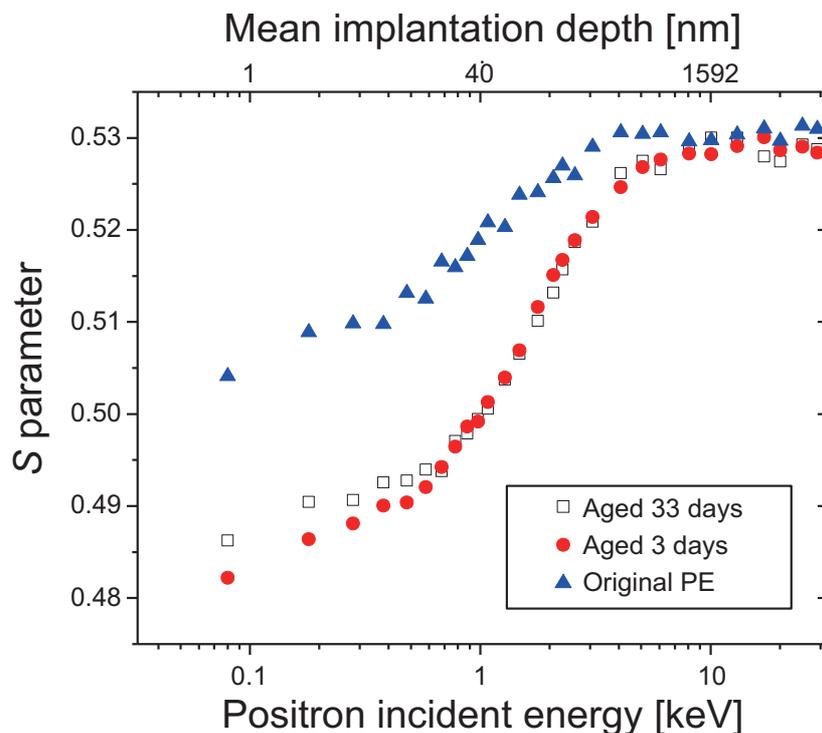


Fig. 1. Variations of S parameter for the samples (original HDPE, aged 3-day HDPE, and aged 33-day HDPE) as a function of positron incident energy.

In order to examine the hydrophobic recovery on the surface of HDPE after the plasma treatment, the water contact angle for the modified HDPE was observed as a function of ageing time as presented in Fig. 2. As one can see, the contact angle for the sample just after the modification is reduced to 22 degrees from 90 degrees of the untreated HDPE, denoted by the dashed line in Fig. 2. This suggests that the hydrophobicity of the sample surface is decreased by plasma treatment. As the ageing time increases to 10 hours, the contact angle increases dramatically from 22 degrees to 85 degrees. Above 10 hours, it approaches an almost constant value around 87 degrees, close to that of untreated HDPE.

The contact angle measurement is only sensitive to the surface. In this method, the change in orientation of the polar groups on the surface can be detected. If the orientation of the groups changes from the upper side to the inner side, the distance between these two positions will be less than several nanometers, and the positron beam cannot distinguish this difference.

The hydrophobic state on the surface of HDPE is determined by the methylene groups in the polymer chains. The exposure of HDPE to the argon plasma, containing energetic neutrals, ions and electrons, may cause hydrogen atoms to detach along with chain scission and consequently formation of free radicals near the surface, followed by the generation of crosslinking and unsaturated groups [10]. This process results in lowering the molecular weight of the polymer chains near the surface, leading to the removal of them from the matrix as well as the activation of the surface, and also helps to improve the crosslinking density. For the present modification procedure, the treated samples were taken out from the chamber and were placed in air. Therefore the surface of the treated sample was exposed to oxygen molecules in the air, so that the activated species, that is, the free radicals on the surface may react with the oxygen to form functional groups [17]. As a result, hydrophilic groups such as hydroxyl and carboxyl groups are introduced into the sample surface [11]. Hence the sharp decrease of the contact angle for HDPE after the plasma modification in Fig. 2 is reasonably ascribed to the generation of polar groups on the surface.

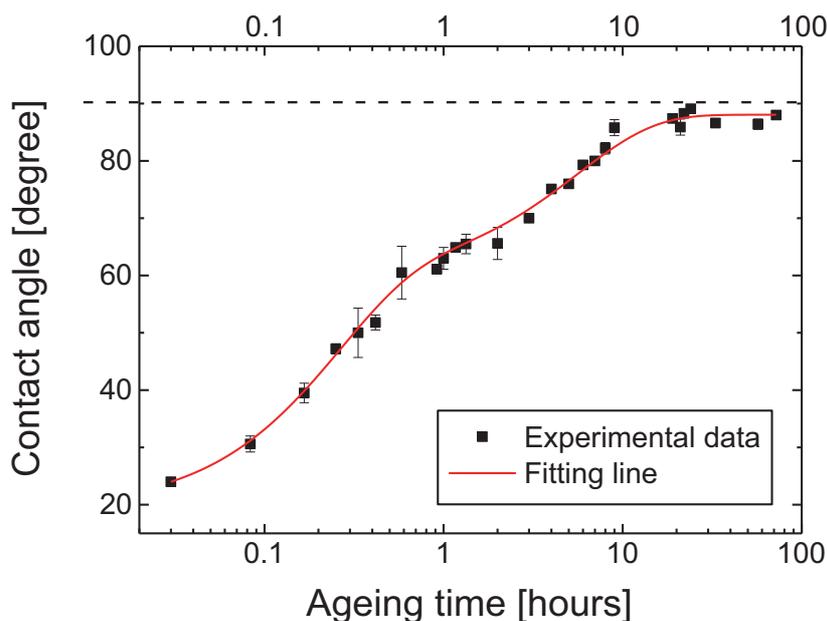


Fig. 2. Variations of the water contact angle for HDPE modified by plasma as a function of ageing time. The solid line is the fitting results, and the dash line represents the contact angle of original HDPE surface.

The increase of the contact angle during the ageing process may be due to the rearrangement of the hydrophilic carboxyl and hydroxyl groups. Most of these polar groups change their orientation towards the bulk to reduce the surface energy, leading to a reduction of the hydrophilic nature of the treated surface. Moreover, the change of orientation for the polar groups on the surface is much faster than the relaxation of chain segments in the polymer bulk. Generally the former is in the time scale of hours, and the latter is in months.

Since argon plasma is utilized in this paper, two different polar groups, carboxyl and hydroxyl groups, are most likely grafted on the surface. For the smaller groups, the change in orientation is

easier than the larger groups in polymers. In this case, we assume a two-factor decay model, taking into account the motion due to the two types of the hydrophilic groups, in order to fit the experimental results of Fig. 2. The fitting line is shown in Fig. 2, and the fitting results were as follows:

$$\theta = 88.1 - 40.6 \exp\left(-\frac{t}{0.25}\right) - 28.2 \exp\left(-\frac{t}{5.6}\right) \quad (2)$$

where θ is the contact angle and t is the ageing time. The above forum indicates that the contact angle of the modified sample should be around 88 degrees for long enough ageing time. The parameters, 0.25 and 5.6 of the second and third damping factors on the right side may be related to the movement of the hydroxyl and carboxyl groups.

4. Conclusion

The microstructure and surface hydrophobic recovery of HDPE modified by RF plasma treatment have been elucidated by means of energy-tunable positron gamma ray spectroscopy as well as water contact angle measurements. The positron results confirmed that only the region shallower than 700 nm is influenced by the plasma modification. The ageing-time dependence of the contact angle was well fitted by a two-factor decay model, suggesting that the surface recovery might be caused by the diffusion of two different groups.

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