



# Adhesion enhancement of polyethylene modified by capacitively coupled radio frequency plasma polymerization of ethanol



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## ABSTRACT

The plasma polymerization of ethanol monomer was carried out under the capacitively coupled radio frequency plasma (CCP) of a radio frequency (RF) power of 100 W at different power to flow rate (P/F) ratios of 0.7, 1.0 and 2.7 W/sccm. The influence of the P/F ratios on deposition rate, chemical composition, surface morphology, and wettability were studied for the plasma polymer films of ethanol monomer on the pristine low density polyethylene (LDPE) surfaces and the surfaces under the oxygen CCP pretreatment of a RF power of 200 W for an exposure time of 1 and 5 min. The deposition rate of the plasma polymer films gradually increased with the P/F ratios. The retention of the hydroxyl groups decreased and the contents of the ketone, carboxylic acid, ester, ether, and epoxide groups increased in the plasma polymer films with the increased P/F ratios. The conformal deposition of the plasma polymer films to the LDPE surfaces was found on the pristine surfaces with the sub-micrometer asperities and the surfaces under oxygen CCP pretreatment with the nanotextures. The dynamic contact angle of the plasma polymer films increased with the P/F ratios on the LDPE surfaces with the sub-micrometer asperities. The plasma polymer films showed the decrease of the dynamic contact angle with the P/F ratios on the surfaces with the nanonodules and the nanopillar array. The significant improvement of the adhesion was achieved for LDPE samples with the nanonodules and the nanopillar array under the surface modification of the oxygen CCP pretreatment followed by the deposition of the plasma polymer films of ethanol monomer due to the cooperation adhesion mechanisms of the mechanical interlocking and the chemical bonding.

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## 1. Introduction

Plasma polymerization is nowadays considered as a promising and versatile technique allowing the deposition of plasma polymer films with functional properties on surfaces without affecting the intrinsic properties of the substrates [1,2]. A number of studies have shown that the improved adhesion properties of the polymers were achieved by depositing the plasma polymer films composing of various functional groups including: amino [3], carboxyl acid [4], epoxide [5–8] etc. It is suggested that the surface functionalization in the plasma polymerization could offer the excellent adhesion through chemical bonding and intermolecular interaction between the plasma polymer films and the adhesives. The interfacial property between the plasma polymer films and the substrates also is another key point for the adhesion of the polymers modified by the plasma polymerization. The plasma pretreatment of the substrate surfaces was a convenient method utilized in the subsequent plasma polymerization of the precursor molecule to exclude adhesive failures in the interface between the substrate and the depositing films [6–8]. There are two essential processes on the surface of the polymers during plasma treatment [9]. One process is plasma

functionalization, i.e. formation of functional groups reacting chemically with activated gaseous species from plasma on the surface. Another process is plasma etching due to degradation of the polymer resulting from bombardment of ions and electrons from plasma to change the surface morphology. The formation of the plasma functional sites allowed for chemical bonding and interaction to offer the excellent adhesion performance between the substrate and the depositing films [6–8]. The roughing of the surfaces could be beneficial to increasing the chemical bonding sites and inducing the mechanical interlocking adhesion enhancement [10]. However the effect of the surface morphology in the plasma pretreatment and the subsequent plasma polymerization on the adhesion performance of polymers was scarcely reported.

Alcohols were one of the most common monomers of the plasma polymerization to fabricate functional surfaces. It is well-known that the chemical structure of the plasma polymers was controlled by process parameters, such as plasma power (P), monomer flow rate (F), reactor pressure, duty cycle, monomer structure, and reactor geometry. Fally et al. [11] studied the plasma polymerization of the monomers with different degrees of unsaturation, propanol, allyl alcohol and propargyl alcohol, under the continuous-wave conditions. It was found that the retention of the hydroxyl functional groups in the plasma polymer films increased as the plasma power reduced during the plasma polymerization. The allyl alcohol led to the formation of the films with a lower degree of the

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crosslinking and higher hydroxyl content than 1-propanol and propargyl alcohol. Rinsch et al. [12] employed a variable duty cycle pulsed plasma polymerization to control the chemistry during plasma deposition using allyl alcohol as monomer. The hydroxyl functionality of the monomer was increasingly retained in the plasma generated thin films as the radio frequency duty cycle was lowered. When the plasma power to monomer flow rate (P/F) ratio decreased, there was a low conversion rate from the hydroxyl groups to other oxygen functionalities and a decrease of the cross-linking and/or the branching of the plasma polymers [13,14]. Friedrich et al. [15] investigated the plasma copolymerization of allyl alcohol and ethylene or butadiene with the various compositions of comonomer mixtures. The plasma polymer films with controlled amounts of hydroxyl functionalities were prepared and the number of the hydroxyl groups increased with the higher concentrations of allyl alcohol in the comonomer mixture. The hydroxyl functional surfaces could be used as adhesion-promoting interlayers between thermally- evaporated aluminum and polypropylene.

Ethanol is a good candidate for plasma polymerization since it is stable, relatively low molecular weight liquid at room temperature with relatively high vapor pressures and a saturated organic compound providing good model compounds of primary hydroxyl functionality. The plasma polymerization of the ethanol as monomer and the influence of the parameters on the chemical functionality in the plasma polymer films were notably absent in detail [16]. In this work, a capacitively coupled radio frequency plasma (CCP) of ethanol monomer was used to deposit the plasma polymer films. The influence of the combined parameter P/F ratio on deposition rate, chemical composition, surface morphology, and wettability of plasma polymer films was studied. The plasma polymer films as adhesion-promoting layers of the low density polyethylene (LDPE) and the effect of the oxygen plasma pretreatment were investigated.

## 2. Experimental

The LDPE substrates were cleaned with acetone and ethanol in ultrasonic bath for 15 min, washed repeatedly with deionized water and dried in an oven at a temperature of 70 °C for 12 h, and finally stored in a drying desiccator for use.

The radio frequency (RF) plasma under the CCP mode at a RF of 13.56 MHz produced in a cylindrical stainless steel chamber with a diameter of 300 mm and a height of 280 mm. Two parallel plate electrodes were placed with a separation of 110 mm. The upper plate electrode was a grounded electrode of 200 mm in diameter and the lower one is a powered electrode of 200 mm in diameter to a RF generator through the matchbox. The CCP reactor, which is described elsewhere [9], was pumped down to a base pressure of  $2 \times 10^{-3}$  Pa by a mechanical/turbine molecular pump package. The ethanol vapor was introduced by controlling the opening of needle valves, while the reactor was kept pumping. The plasma polymer films were deposited under a RF power of 100 W. The monomer flow rates were 36, 101, and 143 sccm at the pressure of 30, 60, and 90 Pa, respectively, calculated from the initial rate of the pressure increase when the pump was disconnected [17]. The depositing times were in the range of 10–60 min and the plasma polymer films for the depositing time of 30 min were investigated for most experimental analysis. The oxygen CCP pretreatment of the LDPE surfaces was under the RF power of 200 W for exposure times of 1 and 5 min.

The thickness of the plasma polymer films was measured by using a Surfcoorder ET-4000M profilometer with a 2  $\mu\text{m}$ -radius pinhead. The attenuated total-reflectance Fourier transform infrared (ATR-FTIR) spectroscopy of the plasma polymer films on the surface of a freshly pressed KBr disk was measured on a Nicolet AVATAR360 IR spectroscope in the range of 700–4000  $\text{cm}^{-1}$ . The surface chemical composition of plasma polymer films was analyzed by X-ray photoelectron spectra (XPS) using an ESCA LAB250 equipment utilizing an unmonochromatized  $\text{AlK}\alpha$  ( $h\nu = 1486.6$  eV) with a power of 300 W.

The X-ray beam with a circular cross-section area was irradiated onto the surface of LDPE samples at an incident angle of 45° with respect to the surface plane. The photoelectrons were detected at a take off angle of 45°. XPS binding energies were calibrated relative to the  $\text{Ag3d}_{5/2}$  electron level at 368.1 eV and the  $\text{Cu2p}_{3/2}$  electron level at 932.3 eV. Charge compensation was achieved using an additional electron gun. Binding energies of the elements of C1s and O1s were referenced to a binding energy of C1s at 285.0 eV, recorded from graphite. The energy resolution of the XPS spectra was about 1.0 eV. The XPS spectra were fitted by a convoluted Gaussian–Lorentzian lineshape after removing the Shirley background [18]. The surface microstructure was observed using a ZEISS SUPRA-55 VP field emission scanning electron microscope (FE-SEM). Dynamic contact angle was measured using a Data Physics OCA20 contact angle analyzer using a water droplet of volume 4  $\mu\text{L}$ . The mean value was calculated from at least four different positions. Adhesive properties were measured for the tensile samples by a WDW-3010 tensile tester. Tensile samples were made by lapping together two LDPE sheets in the presence of a mixture of epoxy resin and curing agent with volume ratio of 4:1 under a constant load of 10 N at room temperature for a lamination time up to 24 h. The lap-shear adhesion strength was measured at a speed of 2  $\text{mm min}^{-1}$  using the samples with a size of  $1 \times 5$   $\text{cm}^2$ . The 180°-peel adhesion strength was measured at a speed of 10  $\text{mm min}^{-1}$  using the samples with the size of  $2 \times 10$   $\text{cm}^2$ . The mean value of adhesion strength was calculated from at least three measurements.

## 3. Results and discussion

### 3.1. Film deposition rate

The deposition rate of the plasma polymer films of ethanol monomer under the CCP of the RF power of 100 W exhibited a gradual increase with the P/F ratios. The plasma polymers film at a P/F ratio of 0.7 W/sccm showed a deposition rate of 5.6  $\text{nm min}^{-1}$ . The deposition rate of the plasma polymer film increased to 7.3  $\text{nm min}^{-1}$  at a P/F ratio of 1.0 W/sccm and then to 11.7  $\text{nm min}^{-1}$  at 2.7 W/sccm. The thickness of the plasma polymer films at P/F ratios of 0.7, 1.0 and 2.7 W/sccm for the deposited time of 30 min was 168, 220 and 350 nm, respectively. The plasma polymer films of ethanol monomer under the CCP of the RF power of 100 W showed higher deposition rate than other saturated alcohols, such as 1-propanol [11] and isopropanol [19]. Noticeably, the deposition rate at a high P/F ratio of 2.7 W/sccm was comparable to the unsaturated alcohols, such as allyl alcohol and propargyl alcohol [11], although the saturated monomers were expected to have a slower deposition rate than the unsaturated ones.

### 3.2. Film chemical analysis

Fig. 1 shows the ATR-FTIR spectra of the plasma polymer films of ethanol monomer under the CCP of the RF power of 100 W at P/F ratios of 0.7, 1.0 and 2.7 W/sccm in the wavenumber region from 700 to 4000  $\text{cm}^{-1}$ . The broad peak about 3455  $\text{cm}^{-1}$  belonged to O–H stretching band indicating a great amount of hydroxyl groups in the plasma polymer films. The peaks at 2960, 2931, 2873  $\text{cm}^{-1}$  and 1457, 1376  $\text{cm}^{-1}$  corresponded to the C–H stretching band and the C–H bending band, respectively. The peaks at 1708 and 1632  $\text{cm}^{-1}$  corresponding to the C=O and O–C=O stretching band, respectively, showed weak intensity in the plasma polymer films at P/F ratios of 0.7 W/sccm. The obvious increase of the peak intensity was observed with the increase of the P/F ratios from 0.7 to 2.7 W/sccm. The intense peak at 1054  $\text{cm}^{-1}$  was ascribed to the C–O stretching band of alcohol in the plasma polymer films at P/F ratios of 0.7 and 1.0 W/sccm. The weak peaks corresponding to the C–O–C breathing band of the ether and epoxide groups appeared at 1170  $\text{cm}^{-1}$  and 1255  $\text{cm}^{-1}$ , respectively, in the plasma polymer films at P/F ratios of 1.0 W/sccm and became very strong at 2.7 W/sccm. The peak at 890  $\text{cm}^{-1}$  could be due to the

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