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Surface modification of cyclic olefin copolymer substrate by oxygen plasma treatment

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Abstract

Cyclic olefin copolymer (COC) substrate surface was modified by plasma treatment under oxygen atmosphere. The surface properties were evaluated by contact angle measurement, atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS). It was found that the surface acquired oxygen containing polar functional groups such as C–O, C=O, which increased in number as the plasma treatment time increased. As revealed by AFM profile, these changes were accompanied by a slightly increase in roughness. The adhesive ability between the coating layer (ITO) and the COC surface can be improved after optimum plasma treating procedure, which can be proofed by the optical microscope observation after boiling test.

Keywords: Oxygen plasma treatment; Contact angle; Cyclic olefin copolymer (COC); Indium tin oxide (ITO)

1. Introduction

Recently, many researchers investigated the flexible electronic devices such as FOLEDs, TFTs [1–7]. Cyclic olefin copolymers (COC) used in this study was obtained with metallocene catalysts are engineering thermoplastics with some unique properties, such as high glass transition temperatures in combination with excellent transparency, low dielectric loss, low moisture absorption, and good chemical resistance for high performance optical, medical, electrical, packaging and other applications [8]. In our previous study, we deposited the ITO layer on flexible COC substrate by RF magnetron sputtering inverse target system as transparent anode electrodes in OLEDs devices [9,10]. However, since the hydrophilic property of the sample surface, the adhesive ability between the coating layer and the COC film does not satisfy the requirement for industrial applications. There are many methods can be used to modified the samples surface. Numerous modification processes can be used to modify the plastics surface, which have been described in the literature, e.g. flame treatment [11], UV/ozone treatment [12], corona treatment [13], and various types of plasma treatment [14,15].

In plasma treatment of polymers, the main factors thought to be responsible for the effects on the surface are (a) free radicals present in the plasma, (b) vacuum UV radiation in the chamber, and (c) impingement of ions on the surface. With plasmas derived from simple gases (oxygen, nitrogen, noble gases, etc.) the major modification effect can be described as: (a) ablation or etching, (b) degradation of polymer molecules, (c) cross linking or branching of near-surface molecules, and (d) introduction of new function groups [16]. The etching effect means the polymer surface was ion bombard by plasma. The degradation of polymer molecules of the sample surface was caused by the induced thermal energy during plasma treating. Actually, a simple way to modify the chemical and physical states of the material surface was by plasma treatment without altering the bulk properties. There were no chemical solvents and poison gases have to be used in modified process by plasma treatment, which also fit the green modification process. In order to improve the surface adhesive ability of the COC substrate,

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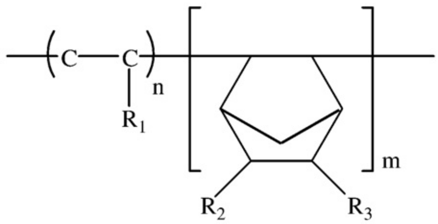

R_1, R_2, R_3: H, C_m H_n

Fig. 1. Chemical structure of the cyclic olefin copolymer.

oxygen plasma treatment was utilized. COC surface was modified by different experimental parameters (RF power and treatment time) by the oxygen plasma processing in this study. Surface roughness and chemical bonding on the COC surface before and after modifying were investigated by atomic force microscope (AFM), and X-ray photoelectron spectroscopy (XPS), respectively. Surface energy of the COC substrate was calculated after contact angles was measured. After the COC surface was modified efficiently, the ITO layer was then sputter-coated on the modified surface. The adhesive ability between the modified surface of COC substrate and the ITO-coated layer was evaluated and examined by boiling water testing method.

2. Experimental

Cyclic olefin copolymer (APEX® COC) was purchased from Mitsui Chemicals, Inc. (JPN) and its chemical structure (see Fig. 1) and characteristics used in this study are described in Table 1. In order to obtain a high optical transparent substrate, the annealing procedure was a necessary process for these materials [9,10]. COC pellets were melted between sheets of aluminum foils as sandwich at 270 °C and then pressed into thin films in a hot press. Here, all samples were annealed at 180 °C for 3 h in a vacuum. Any contaminates were removed from the COC surface by washed them in an ultrasonic bath for 1 min under acetone solvent filled bicker. The plasma reactor, which includes reaction chamber, mechanical and turbomolecular pumps, mass flow controller, radio frequency generator, impedance controller, pressure controller and plasma treatment region. The plasma reactor was operated at radio frequency of 13.56 MHz. 4 cm × 4 cm COC substrates was prepared and placed them on the ground electrode in reactor and modified their surface by oxygen plasma. Oxygen flow rate was fixed at 20 standard cubic cm per min (sccm), and the system pressure was controlled at 500 mTorr during plasma treatment. Two experimental parameters were controlled as follows, (1) the oxygen plasma were operated at RF powers of 25, 50, 75, 100 W, respectively; (2) plasma treatment time of 10 s, 30 s, 60 s, and 120 s.

Table 2
The surface free energy components of the two liquids contact media (unit for γ is mJ/m^2)

Contact media	γ^p	γ^d	Γ
Deionized water	51.0	21.8	72.8
Di-iodomethane	0.0	50.8	50.8

The wetting character of the COC surface was measured by contact angle measuring system (FTA-125) equipped with a charged couple device (CCD) camera and a syringe. The measurements on modified films were carried out within 10 min after the plasma treatment was completed; the contact angle average was calculated from 10 measurements with experimental error of 2–3°. The surface energy of COC substrate can be calculated after contact angles was measured; deionized water and di-iodomethane were used as the testing liquids. According to the 'sessile drop' method [17], 0.2 µl of deionized water and di-iodomethane were dropped on the COC surface separately. Bascially, there are four types of Van der Waals interactions contribute to the surface energy. In particular the polar component results from three different intermolecular forces due to permanent and induced dipoles, and hydrogen-bonding, whereas the dispersion (nonpolar) component of the surface energy is due to instantaneous dipole moments. We calculated the dispersion, γ^d, and polar, γ^p, components of the surface energy from advancing angles using the harmonic-mean method [17]. We used deionized water (polar) and di-iodomethane (nonpolar) as contact liquids, whose surface energy and polarity values are listed in Table 2.

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

$$\gamma_1(1 + \cos\theta_1) = 4\left[\left(\gamma_s^d\gamma_1^d\right)/\left(\gamma_s^d + \gamma_1^d\right) + \left(\gamma_s^p\gamma_1^p\right)/\left(\gamma_s^p + \gamma_1^p\right)\right] \tag{2}$$

$$\gamma_2(1 + \cos\theta_2) = 4\left[\left(\gamma_s^d\gamma_2^d\right)/\left(\gamma_s^d + \gamma_2^d\right) + \left(\gamma_s^p\gamma_2^p\right)/\left(\gamma_s^p + \gamma_2^p\right)\right] \tag{3}$$

where γ, γ^d and γ^p represent the surface free energy, the dispersive term of surface free energy and the polar term of surface free energy, respectively. γ_s is the surface free energy of COC substrate; θ_1 represents the contact angle of deionized water; θ_2 represents the contact angle of di-iodomethane. In addition, γ_1 is the surface free energy of deionized water and γ_2 is the surface energy of di-iodomethane.

In this study, surface roughness of COC substrate was monitored by atomic force microscope (AFM). The average roughness, R_a, of the sample surface was measured. In order to understand plasma treatment effect on the samples surface, the modified COC surface was inspected by X-ray photoelectron

Table 1
Basic properties of COC

Light transmittance (%)	Density (g/cm^3)	T_g (°C)	Refractive index	Birefringence (nm)	Water permeability (g /cm^2-day)	Molecular weight (M_w)
90	1.04	132	1.54	<20	0.09	200,000–250,000