Journal of Optoelectronics and Advanced Materials Vol. 7, No. 1, February 2005, p. 249 - 252

SOFT PLASMA TREATMENT OF POLYMER SURFACES

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The effect of Ar, Ar/H_2O and Ar/C_2H_5OH soft plasma treatments on the surface free energy of poly(methyl metacrylate) (PMMA) and polycarbonate (PC) has been studied. The plasma gas was excited by a 13.56 MHz radio frequency (RF) generator, in a GENUS 8720 plasma enhanced chemical vapour deposition facility. Changes in the surface free energy of the polymers were followed as a function of the plasma treatment time. Bickerman’s method for precise measurements of contact angles of very small liquid sessile drops in contact with substrates was used to determinate the polar and dispersion components of the polymer free surface energy, on the basis of the theory of Owens, Wendt, Kaelble and Uy. It was found that all RF plasma treatments led to an increase in the polar component of PMMA and PC, mainly due to an increased hydrogen bonding ability. Short (1-5 min) Ar/C_2H_5OH and Ar/H_2O plasma treatments exhibited the same effectiveness, greater than that of pure Ar treatment. It was observed that the introduction of ethanol in plasma gas resulted in more uniform, defect free and undamaged, polymer surfaces compared to those modified with pure Ar or Ar/water plasma gas.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: RF plasma treatment, Surface energy, Polymers, PMMA, PC

1. Introduction

In recent years, optical polymers like PMMA and PC have replaced glass products in many optical applications where low weight, chemical inertness, high impact resistance, flexible formability and relatively low cost are of major importance [1]. The performance of polymers can further be enhanced by applying functional coatings such as protective layers, optical coatings, gas permeation barriers and others. However, the desirable bulk properties of polymers are often compromised by their unfavourable surface characteristics, such as low hardness, low resistance to abrasion and scratching, and low surface energy, which generally leads to low wettability and poor adhesion [1,2].

Low pressure soft plasma treatment has been successfully used as a dry process to alter the surface properties of polymers (for review see [3]). Major contributions to the modification of polymer surface are due to the chemically active species and energetic photons generated by the discharge. These induce the effects of surface cleaning, ablation, crosslinking and surface chemical functionalization [3-5]. The effect of plasma treatment depends on a variety of parameters such as the kind of plasma (DC, radio frequency (RF) or microwave (MW)), the discharge power density, the pressure and flow rate of the gas or gas mixture, as well as the treatment time [6-8].

Different radio frequency glow discharge plasma treatments that influence the polymer surface energy have been described in the literature [9-12]. It has been found that noble gas plasmas (e.g. He or Ar) are effective in creating free radicals, but do not add new chemical functionalities from the gas phase. Typically, a reactive plasma (H_2O or O_2) is used to add a polar functional group which can dramatically increase the surface free energy of the polymer [9, 10]. Hook *et al.* [10] have

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shown that Ar/H_2O RF plasma treatment leads to the incorporation of hydroxyl groups on PMMA surfaces. They recommended a two step mechanism for the structural change on the top surface and within a sublayer up to 20 nm thick. However, in most cases, rough and/or damaged surfaces are produced by these treatments.

The replacement of water with ethanol in the plasma gas provides an attractive possibility to add the hydroxyl functionalities to the substrate surface, but at the same time to treat the surface with ethyl free radicals or ions, which can further modify it.

In the present paper, we study the effect of Ar, Ar/H_2O and Ar/C_2H_5OH RF plasma treatments on the surface free energy of PC and PMMA substrates, in the context of their use as optical elements. The free surface energy is determined from contact angle measurements, using the theory of Owens, Wendt, Kaelble and Uy [13, 14].

2. Experimental details

2.1. Plasma treatment

All samples of commercial optical grade PMMA and PC substrates were carefully cleaned before plasma treatment. The cleaning procedure first involved washing with a 1% detergent solution and then with deionised water in an ultrasonic cleaner. The gas plasma was excited by a 13.56 MHz RF generator, capable of delivering a power output up to 2000 W, in a GENUS 8720 plasma enhanced chemical vapour deposition facility,. During plasma treatment, the substrates were exposed to Ar, Ar/water, and Ar/ethanol vapour mixtures, using an RF power density of 7 mW cm^{-3}, at a pressure of 140 mTorr and a flow rate of 20 sccm. The treatment time was varied between 1 and 30 min. Argon was bubbled through deionised water or ethanol at room temperature, thus saturating the inert gas with water or alcohol vapours.

2.2. Determination of surface energy

Owens and Wendt [13], and independently Kaelble and Uy [14] proved that the total surface energy of a solid, γ_s, can be expressed as the sum of contributions from dispersion γ_s^d and polar γ_s^p force components. These can be determined from the contact angle, θ, data of polar and non-polar liquids with known dispersion γ_{lv}^d and polar γ_{lv}^p parts of their surface energy, via the equation

$$\gamma_{lv}(1+\cos\theta) = 2\sqrt{\gamma_s^d \gamma_{lv}^d} + 2\sqrt{\gamma_s^p \gamma_{lv}^p} \quad . \tag{1}$$

In our study, the contact angles of bidistilled water and methylene iodide were measured by the sessile drop method proposed by Bickerman [15]. He suggested measuring the base diameter, *d*, of several droplets of different volumes, *V*, extrapolating the values of d^3/V to $V = 0$, and calculating θ from the equation

$$\frac{d^3}{V} = \frac{24\sin^3\theta}{\pi\left(2-3\cos\theta+\cos^3\theta\right)} \tag{2}$$

The liquid drops were driven out from a precise micro syringe (type 1701 Varian, 10 µl), supplied with a steel needle. The diameters of the drops waere measured by means of optical microscope provided with a micrometer scale eyepiece. The small diameter of the drops (1-10 µm) allowed many drops to be driven out onto one substrate (6 × 6 cm). Each data point represented an average of 15 single measurements obtained from three different samples. This technique allowed the small contact angles ($\theta < 5°$) to be determined to an accuracy of 1-3 %.

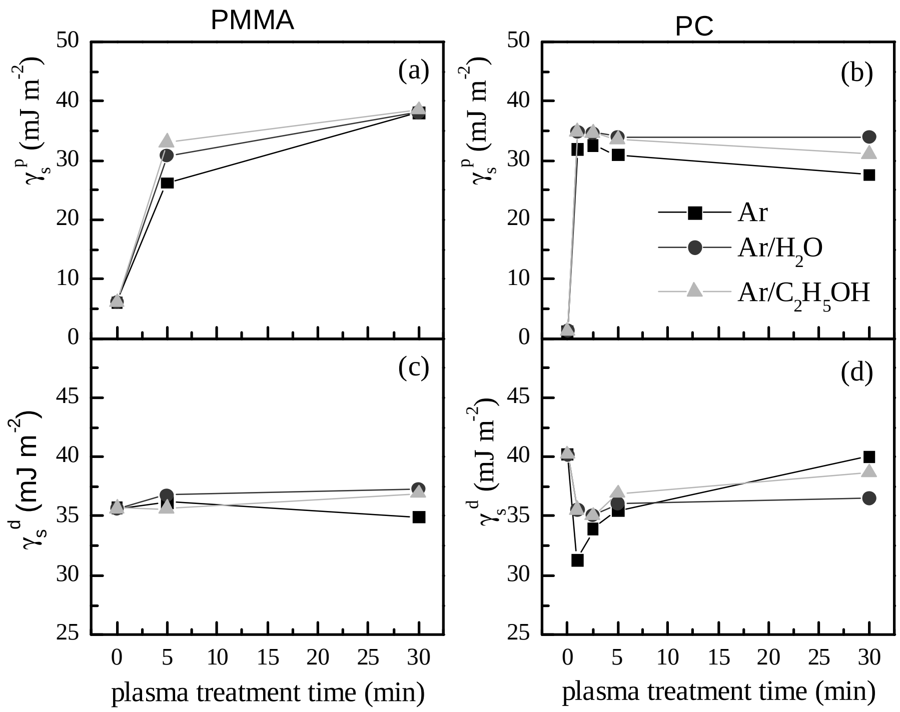

Fig. 1. The polar γ_s^p (a, b) and dispersion γ_s^d (c, d) components in free surface energy of PMMA and PC treated in Ar, Ar/H_20 and Ar/C_2H_5OH plasma vs the time of plasma treatment.

3. Results and discussion

On the basis of the contact angle data, the polar force components of 6.1 and 1.2 mJ m^{-2}, and the dispersion force components of 35.7 and 40.2 mJ m^{-2} were determined for unmodified PMMA and PC respectively. These values agree well with literature data. The low values of the polar components indicate the hydrophobic nature of PMMA and PC substrates. The changes in the polar and dispersion parts of the surface energy of PMMA and PC substrates after Ar, Ar/H_2O and Ar/C_2H_5OH plasma treatments are shown in Fig. 1. For both substrates, the polar component is altered significantly after all RF plasma treatments. In the case of PMMA, γ_s^p increases rapidly with the time of treatment for the first 5 min, and then stabilizes after that period. In the case of PC, γ_s^p increases rapidly for the first 1 min and then remains almost constant. The dispersion component of PMMA changes negligibly, while that of PC decreases slightly for all plasma gases used.

The polar force component arises from the orientation of permanent electric dipoles, which includes dipole-dipole interactions, dipole-induced dipole interactions, hydrogen bonds, π-bonds, charge transfer interactions, etc [13,14]. From the results, it is apparent that the surface free energy (γ_s) of the modified polymer surfaces increases after all RF plasma treatments. This is attributed to the increase in the polar character of the surface after modifications. The great decrease in the water contact angle (i.e. enhanced wettability) observed after all RF plasma modifications indicates that a large incorporation of hydrophilic character capable of hydrogen bonding is added to polymer. Dispersion forces, on the other hand, are related to the internal electron motions, independent of the dipole moments [13, 14]. Thus, the incorporation of hydrophilic character capable of hydrogen bonding to a polymer surface should not have much effect on γ_s^d, which is consistent with the results obtained.

According to Hook *et al.* [10] Ar/H_2O plasma treatment results in surface sputtering (reduction/decarboxylation) and subsequent chemisorption of H_2O and H_2O plasma species to the high energy sites occupying the PMMA surface. It should be noted that the data in the literature about actual hydrolyzing (i.e. attaching covalently an –OH functionality to the hydrophobic polymer surface) of PMMA or PC structure are controversially [2]. Obviously, the data for the surface energy changes only are insufficient, and experiments are now under way in an attempt to clarify the problem by use of IR and X-ray photoelectron spectroscopy.

For both substrates, it was found that increasing the plasma treatment time leads to a rough and etched surface, with signs of patchiness or inhomogeneity. On the other hand, it follows from the results that the organic contaminants and other molecules adsorbed on the surface should have been completely cleaned away after 1-5 min of all RF plasma treatments. As seen from Figs.1a and 1b, short (1-5 min) Ar/C_2H_5OH and Ar/H_2O plasma treatments are more effective for increasing the polar part of surface energy, and hence for improving the wettability, than the pure Ar treatment. On the other hand, the optical microscope study showed that the introduction of ethanol in plasma gas results in more uniform polymer surfaces, without defects or damage (especially for PMMA), as compared to surfaces modified with Ar/water or pure Ar plasma gas. In our opinion, this makes Ar/C_2H_5OH plasma treatment more appropriate for modifying polymers like PMMA and PC, for use in optical applications.

4. Conclusions

On the basis of our contact angle data, it is shown that surface free energy of modified PMMA and PC surfaces increases after Ar, Ar/H_2O and Ar/C_2H_5OH RF plasma treatments. This is attributed to an increase in the polar character of the surface after modifications. This polar character is mainly due to increased hydrogen bonding ability, which is larger after plasma modification with water or ethanol. A short Ar/C_2H_5OH treatment has the same effectiveness as Ar/H_2O treatment, but results in more uniform polymer surfaces, without defects or damage, compared to Ar and Ar/H_2O modified surfaces.

Acknowledgements

This work was accomplished with the financial support of Bulgarian National Science Fund, under contracts No T-1316 and Ф-1208.

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