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The influence of the structures and compounds of DLC coatings on the barrier properties of PET bottles*

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To reduce the oxygen transmission rate through a polyethylene terephthalate (PET) bottle (an organic plastic) diamond-like carbon (DLC) coatings on the inner surface of the PET bottle were deposited by radio frequency plasma-enhanced chemical vapour deposition (RF-PECVD) technology with C_2H_2 as the source of carbon and Ar as the diluted gas. As the barrier layer to humidity and gas permeation, this paper analyses the DLC film structure, composition, morphology and barrier properties by Fourier transform infrared, atomic force microscopy, scanning electron microscopy and oxygen transmission rate in detail. From the spectrum, it is found that the DLC film mainly consists of sp^3 bonds. The barrier property of the films is significantly relevant to the sp^3 bond concentration in the coating, the film thickness and morphology. Additionally, it is found that DLC film deposited in an inductively coupled plasma enhanced capacitively coupled plasma source shows a compact, homogeneous and crack-free surface, which is beneficial for a good gas barrier property in PET bottles.

Keywords: diamond-like carbon film, barrier properties

PACC: 5250D, 6770

1. Introduction

Glass and metallic containers for beer, beverage and food storage are witnessing rapid replacement by plastic polyethylene terephthalate (PET) bottles because of their lightweight, designable properties, physical toughness, economy and so on. Recently, more than 80% of the total number of beverage containers have been PET bottles.[1] In particular, PET bottles for beer containers, accounting for about 4% of the commercial market at present, are increasing annually by a current amount of 11.5% in the world. However, one of the vital shortcomings obstructing the replacement of metallic or glass containers by plastic ones is that PET bottles demonstrate a low gas barrier property, which causes the sensitive contents of beer to tend to deteriorate by the permeation of gases, in particular the inlet of oxygen gas and outlet of carbon dioxide. Therefore, coated PET to improve the barrier properties has been extensively explored.[2,3] In this campaign, plasma deposition coatings show a perspective technology because of their fast, dry, one-step process. A variety of plasma sources have been developed to deposit barrier layers on plastic film or bottle surfaces such as diamond-like carbon (DLC) and SiOx coatings for the purposes of decreasing the gas and humidity permeation rate.[4−6] Inherently, PET coated by amorphous DLC seems to be a perspective method due to its efficient barrier to oxygen permeation, lack of fragility, easy manipulation and low processing cost as well as excellent recyclability without any pollution.[7]

In this paper, we demonstrate the results of inductively coupled plasma (ICP) enhanced capacitively coupled plasma (CCP) source chemical vapour deposition (CVD) technology as a new plasma source to deposit DLC coatings on PET surfaces. As a comparison, CCP deposition coating is also carried out. We explore the influence of plasma source on the film properties, DLC structure, compound and morphology, which are analysed by Fourier transform infrared (FTIR), atomic force microscopy (AFM) and scanning electron microscopy (SEM). Additionally, the relationship between the surface morphology of DLC films and the oxygen transmission rate (OTR) is also discussed in this paper.

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2. Experimental

DLC films are deposited in single or dual plasma sources, i.e. a CCP source (13.56 MHz) or an ICP (13.56 MHz) enhanced CCP source,[8] respectively, in this experiment. A schematic diagram of the apparatus is illustrated in Fig.1. The powered electrode is a cylindrical rod in the CCP source and three cyclic coils in the ICP source. The PET film substrates (bottles) are placed inside the cyclic coils of the ICP source and covered the cylindrical rod of the CCP source. During deposition, the carbon source acetylene (C_2H_2) and diluted Ar gases flow into the chamber from the bottom, and the discharge parameters, such as the acetylene concentration, the explosion time and total gas pressure, are kept constant at 11%, 20 min and 20 Pa, respectively.

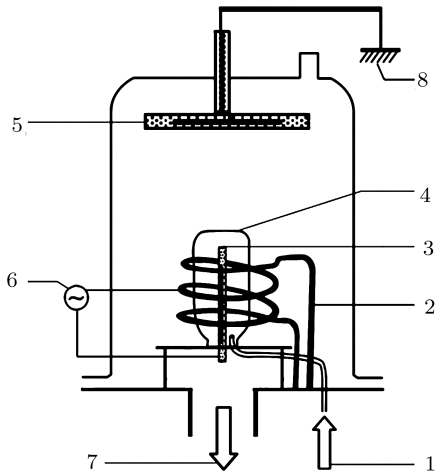


Fig.1. Schematic diagram of the plasma source for DLC deposition (1: gas mixture; 2: ICP plasma coil; 3: CCP plasma electrode; 4: PET bottle (film); 5: grounded electrode; 6: RF power-1; 7: pump; 8: ground).

The OTR is measured with a Model 8001 (Illinois instrument). In the case of OTR measurement, both chambers are purged with dry N_2 gas for 5 h, and all measurements are conducted under ambient conditions ($\sim$ 25 °C, 30%–50% relative humidity).

The morphology of the film is characterized by SEM (HITACHI S-4800) and AFM (CSPM 3000, Ben Yuan, China). The AFM measurements are carried out on an area of 5×5 μm^2 and the tapping mode used can ensure a high resolution measurement without causing any damage or alteration to the thin film surfaces.

The structural components of the coatings are analysed by FTIR spectroscopy. A measurement in the range of 500–4000 cm^{-1} is performed on KBr substrates. A CH stretching peak group around 2920 cm^{-1} is obtained after an interference correction. The shape and amplitude of this peak provide information about the carbon back-bonding (carbon hybridization) in the coatings. The peak is then deconvoluted into individual contributions representing specific stretching vibrations,[9] where five Gaussian peaks are separated based on the vibration frequencies according to Dischler.[10]

3. Results and discussion

Figure 2 displays the typical FTIR spectrum of DLC film deposited in the CCP source. In Fig.2, the obvious absorption peak at around 1400 cm^{-1}, which is assigned to the C–CH_3 group (sp^3) stretching vibration, and the absorption peaks in the range of 3000$\sim$ 2800 cm^{-1} for C–H_n stretching vibrations clearly illustrate that the film consists of a DLC component. Clearly analysing the spectrum, one can note that the DLC film is mostly composed of sp^3 hybridized bonding and has a high bonded hydrogen content.[11,12] Otherwise, owing to C–H stretching vibrations under 3000 cm^{-1}, it is considered that carbon atoms are at a saturation state in the film. The strong absorption peak at 3410$\sim$3300 cm^{-1} is the O–H vibration mode following DLC film post-reaction.

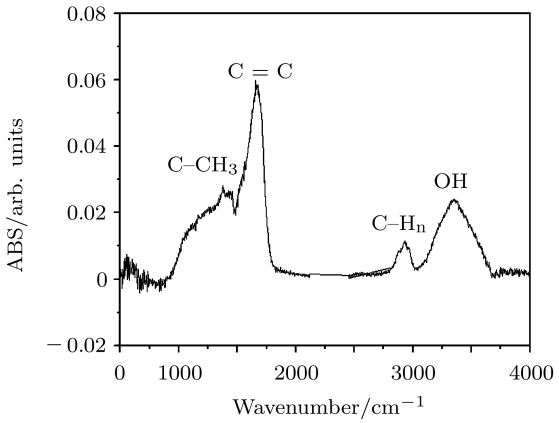


Fig.2. A typical FTIR absorption spectrum of DLC films.

Figure 3 displays the results of fitting peaks in Gaussian mode with different plasma sources, i.e. CCP and ICP enhanced CCP, respectively. The spectrum reveals that the coatings have a typical polymer-like structure: the sp^3 CH_3 bone types at 2875 cm^{-1} and 2970 cm^{-1} strongly dominate the spectrum, but

the clear contribution from sp^2 CH_2 at 2958 cm^{-1} definitely means that it is a polymer-like material based on the description by Dischler.[10] On the other hand, on adding the ICP source a slight increase in the absorption peak intensity for C–H stretching vibrations is observed, and the DLC film has more sp^3 bond content.

The FTIR results are in good agreement with film thickness measurements, i.e. 600 nm for the film thickness in the CCP source and 900 nm in the ICP enhanced CCP source. The high plasma densities in the ICP enhanced CCP source plasma enhanced CVD (PECVD) technique increase the deposition rate and lead to a greater film thickness.

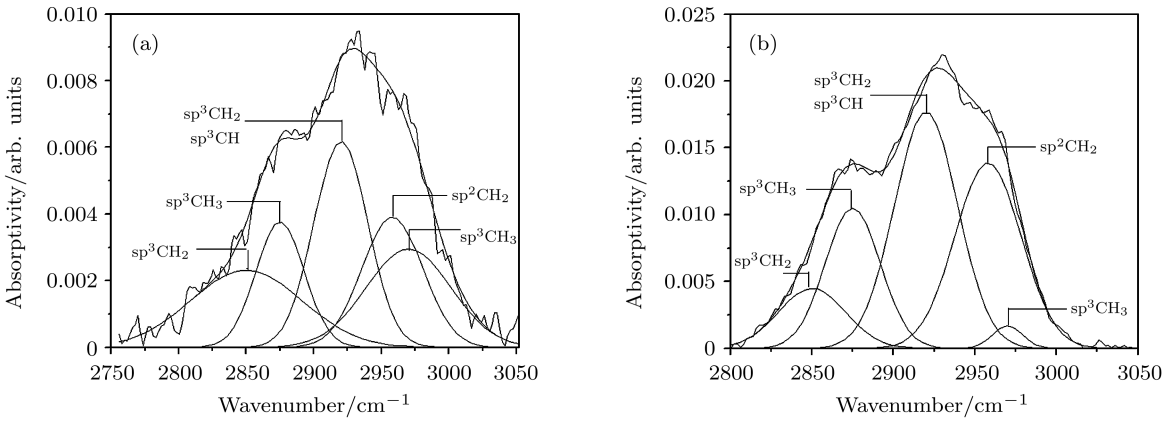


Fig.3. The FTIR of the CH stretching absorption peak from 2750–3050 cm^{-1}: (a) CCP 150 W; (b) CCP 150 W + ICP 100 W.

Figure 4 shows AFM images of the films deposited on p-Si (100) substrates with different plasma sources. In Fig.4(a), one can see that when only the CCP source is employed, the film is composed of uniformly nano-spherical particles and follows the island growth mode. When DLC film is deposited under the ICP enhanced CCP source, in contrast, DLC film is formed with a compact structure (Fig.4(b)); no distinguished growth mode can be recognized from the image. But increasing ablation is obvious in the ICP enhanced CCP source. The root mean square (RMS) roughness of the film is 4.99 nm under conditions of CCP 150 W + ICP 100 W instead of 2.04 nm in CCP 150 W deposited film. Based on other measurements, such as the reference by Kurtosis[13] to a non-dimensional quantity to evaluate the shape of data about a central mean, and the use by Skewness[14] of the symmetry of surface data about a mean data profile, the film roughnesses in the CCP and ICP enhanced CCP sources are listed in Table 1.

Table 1. The surface topography and roughness effect of the plasma source (nm).

sample	RMS	Skewness	Kurtosis
a-CCP150 W	2.04	0.112	4.13
b-CCP150 W + ICP100 W	4.99	0.109	3.17

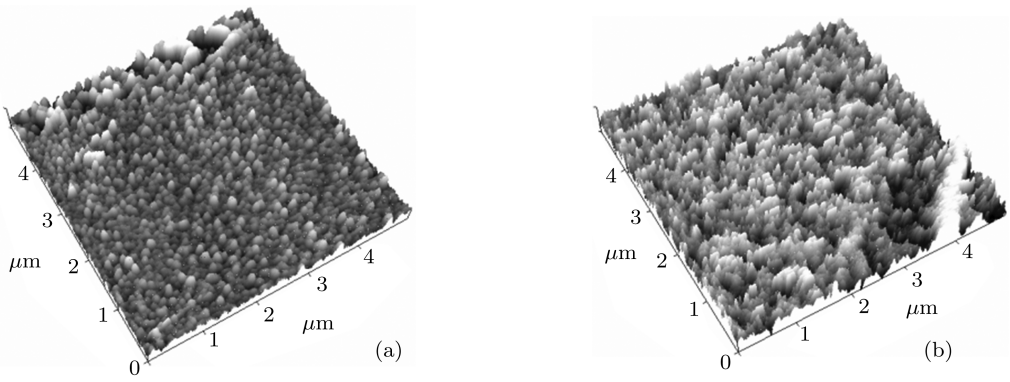


Fig.4. Topographic AFM images of DLC film: (a) CCP 150 W, (b) CCP 150 W + ICP 100 W).

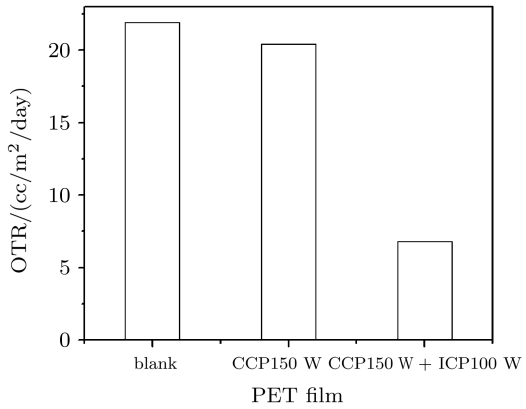


Fig.5. OTR values of PET with DLC coating dependent on the plasma source.

The coated film properties were characterized by OTR measurement. Figure 5 shows the influence of plasma source on the OTR value. It is noticed that for controlling PET film (24 μm) the OTR value is about 22 cc/m^2/day. For DLC coated PETs synthesized in CCP only the OTR is slightly decreased. But for DLC deposited with the ICP enhanced CCP source, it is noticed that the OTR value is decreased by over four times.

Through SEM images figure 6(a) clearly shows that a network-crack structure is formed and spread out over the whole surface in the CCP-deposited DLC coating. In contrast with the enhancement of the ICP plasma source, the cracks completely disappear in Fig.6(b); instead, aggregation of spherical particles is seen on the surface. A possible explanation for the formation of cracks is due to the strong interface force and intrinsic stress between the interface of DLC and PET,[15] and the residual stress is released through surface cracks. Besides, polymeric substrate deformation can also cause cracking of the fragile DLC coating in the plastic surface. Moreover, it is also noticed that micro-cracks are induced when the electron beam is bombarding on the surface during SEM measurement.

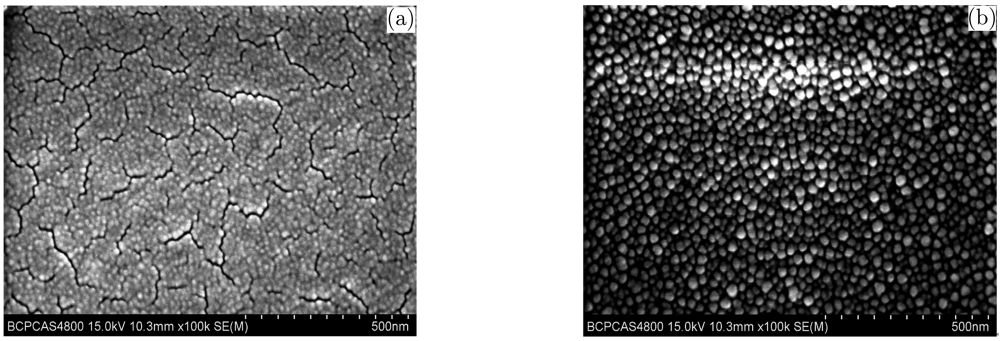


Fig.6. SEM images of DLC film: (a) CCP 150 W, (b) CCP 150 W + ICP 100 W.

Based on SEM images, the OTR value of DLC coated PET bottles depending on CCP and ICP enhanced CCP sources can be explained. The obvious cracks in CCP deposited DLC film definitely cannot block gas permeation, and as a result the OTR is slightly decreased. In the ICP enhanced CCP source the cracks disappear, and the OTR value is obviously improved. But films consisting of aggregated spherical particles also cannot demonstrate a perfect barrier property: the gaps between the spheres are still paths for gas permeation. So the OTR is decreased but not sharply reduced. The relatively compact surface structure in the ICP enhanced CCP source deposited film compared to the CCP deposited cracked film certainly improves the barrier property and decreases the OTR. Therefore, future investigations will be emphasized the decreasing formation of spherical particles and cracks during DLC coating deposition in an ICP enhanced CCP source.

4. Conclusions

The present study on the influence of plasma source on DLC films can be summarized as follows:

(i) FTIR shows that the DLC film coated on the PET bottle surface is mostly composed of sp^3 hybridized bonds.

(ii) SEM images show that the DLC film deposited in the CCP source is composed of a network of micro-cracks, which is assumed to be due to the intrinsic property, and correlated to the intrinsic stress in DLC films and the force between the interface of PET and the DLC coating.

(iii) In the ICP enhanced CCP source, the cracks in the DLC film disappear and the gas barrier property is improved. However, because the coating consists of spherical particles, the OTR is still relatively high.

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