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# Effect of Oxygen on Surface Properties and Drug Release Behavior of Plasma Polymer of *n*-Butyl Methacrylate

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**Abstract:** The effects of oxygen on the chemical structure, morphology, hydrophilicity and drug release behavior of radio-frequency plasma poly *n*- butyl methacrylate (PPBMA) thin film were carried out for the first time. ATR-FTIR and XPS showed that oxygen had little influence on the chemical structure and composition of PPBMAs, which did not agree with the thought that the presence of oxygen gas would increase the oxidized carbon functionalities in the plasma polymer. SEM and static contact angle measurement indicated that in case of deposition with oxygen, the smoothness and hydrophilicity of PPBMA were dramatically improved. The drug release behavior showed that drug release from the PPBMA coating without oxygen was biphasic patterns, while from PPBMA coating with oxygen was *Higuchi* release. These results were helpful for the design and tailoring of the PPBMA polymer film and other of plasma polymers film, but could provide a new idea for the drug release controlled form.

**Keywords:** Plasma *n*-butyl methacrylate polymer, oxygen, chemical structure, morphology, hydrophilicity.

Plasma polymerization is a thin film deposition process on a wide variety of substrates. Species excited in the plasma undergo condensation reactions, forming polymeric material. Variations of the power, pressure, time and flow rate of monomer can change the characteristics of plasma polymers. Besides, carrier gases, such as Ar, $O_2$, $H_2$, also affect the properties of some plasma polymers. Oxygen, as a reactive carrier gas, even at low fraction, can effectively increase the Si-O bonds content in the organo-silicon plasma polymer and the content of carbonyl and carboxyl functionalities in the plasma olefin polymers [1-4].

Because of unique properties, plasma polymer films have been used in a variety of applications including barrier coatings, protective coatings, selective permeation membrane *et al*.[5]. Plasma poly *n*-butyl methacrylate (PPBMA) polymer film, which deposited from pure BMA monomer, has been successfully used as a barrier coating in the biomedical materials [6,7]. The operating conditions, such as deposition power and duration, are optimized for getting PPBMA with the desired structure and properties. But the information, regarding the effect of carrier gas, including oxygen, is few.

In this experiment, the effects of low level of oxygen addition in the BMA on the

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chemical structure, morphology, hydrophilicity and drug release profile of PPBMA were investigated.

## Experimental

The drug-eluting system used for the release experiment was EVA/ paclitaxel matrix on 316 L stainless steel. This release matrix consisted of two layers. The inner layer was EVA polymer and 10 w % paclitaxel loading, and the outer one was EVA polymer.

316 L stainless steel was located in the center of the RF plasma reaction chamber. The system was pumped down to a base pressure $2.0\times10^{-2}$ Pa. *Prior to* BMA deposition, the samples were subjected to a brief of oxygen plasma (20Pa, 40w, 20s) to clean the surface of substrates. Then, the system was evacuated to background pressure $2.0\times10^{-2}$. Pure BMA monomer or 90 vol % BMA and 10 vol % of oxygen mixture were then introduced. The power kept 40 w, the pressure was 20 Pa and the time was 30 min. The matrices for release study were placed in vials containing 4 mL of pure water and placed in a shaking water bath at 37℃. Aliquots of medium were replaced with the same amount of fresh water at intervals. Paclitaxel concentration was analyzed by HPLC. To evaluate the physicochemical properties of PPBMA, ATR-FTIR, XPS, SEM and static contact angle measurement were applied.

## Results and Discussion

**Figure 1** showed that there were some differences both in terms of intensity and location of absorption band of BMA monomer and its plasma polymers, but there was little difference in absorption band between the PPBMA films deposited with and without oxygen. The C=O stretching band at 1720 cm$^{-1}$ almost disappeared and the C-O-C stretching band at 1295 cm$^{-1}$, 1268 cm$^{-1}$, 1168 cm$^{-1}$ decreased dramatically after polymerization. The band at 1650cm$^{-1}$ C=C stretching vibration, the C-H stretching band of $CH_3$ and $CH_2$ groups at 2963cm$^{-1}$, 2875 cm$^{-1}$ still existed [8]. Besides, a broad and strong absorption bands in the 3500–3100 cm$^{-1}$ region, indicating that a great deal of O-H was produced in the reaction.

**Figure 1** FT-IR spectra of (a) BMA monomer, PBMA coating deposited (b) without oxygen, (c) with oxygen

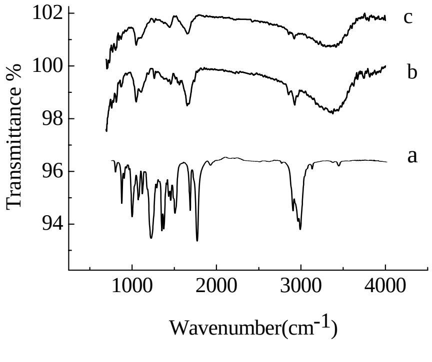
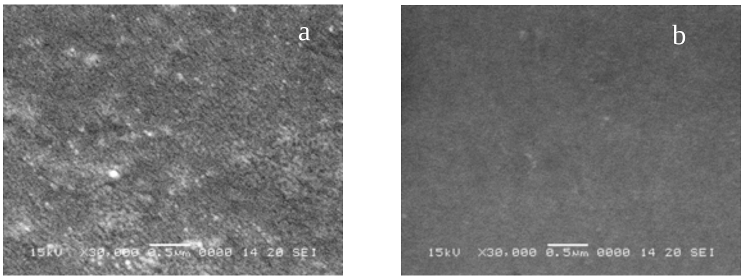


**Table 1** Results of deconvolution of the C1s XPS peak-presence of carbon in various chemical functionalities

| Plasma deposition | Relative fraction, % | | | | | |
|---|---|---|---|---|---|---|
| | 284.2eV | 285.0eV | 285.8 eV | 286.4eV | 287.1eV | 287.8eV |
| | (C-H) | (C-C) | (C=C) | (C-OH) | (C-O-C) | (C=O) |
| Without oxygen | 29.68 | 32.66 | 17.37 | 8.43 | 6.68 | 5.12 |
| With oxygen | 31.85 | 34.55 | 13.88 | 7.58 | 6.53 | 5.79 |

**Figure 2** SEM micrographs of PBMA deposition (a) without oxygen (b) with oxygen



The results of deconvolution of C*1s* XPS peaks (**Table 1**) confirmed that the plasma films had stronger C-H and C-C bands, but less intensive C-O and C=O bands. Oxygen almost did not increase the content of C-O, C=O and –OH bands. This is somewhat unexpected. One would think that the presence of oxygen in the plasma would create more oxygen-bearing groups, *e.g.*, carboxyl and carbonyl functionalities. But the experiment result seems disagree with the hypothesis. This might be correlated with the mechanism of the BMA plasma polymerization.

The plane view SEM images of PPBMA films are shown in **Figure 2**. Dome-like structure of nanometer-sized was observed in (a), but not in (b). The film deposited in the presence of oxygen was uniform and smooth. Reaction in the gas phase led to the production of powders, but at the surface could result in very flat films [9]. In the case of PPBMA deposition without oxygen, polymerization occurred on the substrate and in the plasma volume, resulting in the "dome-like" structure film. Due to the dilution and side reaction effect of oxygen, the reaction occurred mainly on the substrate, resulting in a dense film.

**Figure 3** Static contact angle images of (a) EVA, (b) PBMA deposition without oxygen and (c) with oxygen

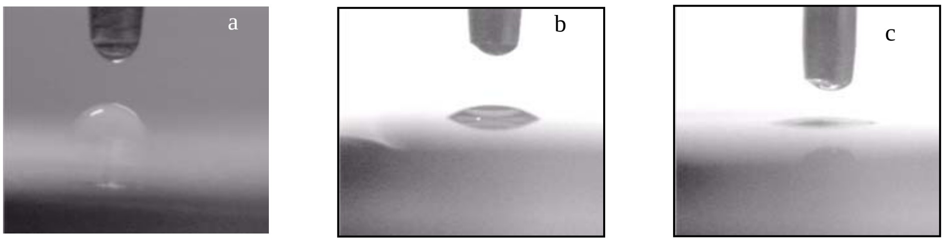
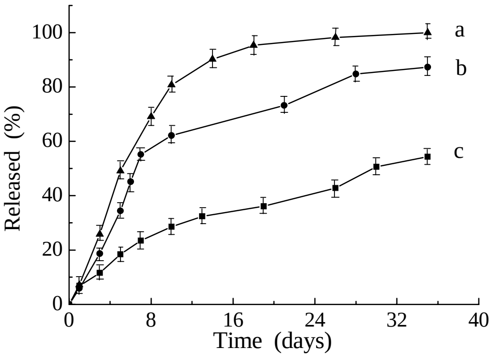


**Figure 4** Paclitaxel release profiles from (a) control, (b) PPBMA barrier coating in case of deposition without oxygen and (c) with oxygen.



Surface wettability was measured by static contact angle (**Figure 3**). For the wettability study, glass substrates were pre-coated with EVA. It can be seen that the static contact angle decreased abruptly after plasma polymerization. In particular, the static contact angle of PPBMA deposited with oxygen was near zero, which was lower than that of PPBMA deposited without oxygen, suggesting that the hydrophilicity of plasma polymer improved when oxygen was introduced.

The release profiles of paclitaxel from 10% drug loading EVA matrices before and after plasma deposition are illustrated in **Figure 4**. Before deposition, paclitaxel released fast and paclitaxel released 100% after 35 days. After the deposition, drug release rate significantly decreased. The PPBMA deposition without oxygen showed an irregular release profile as a function of time. The burst release followed a slow release. This is probably due to the non-homogeneity of the surface morphology. In case of the PPBMA deposition with oxygen, the release rate was the slowest and only 50% of paclitaxel was released after 30 days. The release profile seemed to a typical *Higuchi* release pattern (Released $Q=9.52t^{1/2}-3.02$, $R=0.9944$).

In conclusion, the chemical structure of the PPBMA film was not significantly affected by oxygen. But the smoothness and hydrophilicity increased in the case deposition with oxygen. The drug release from PPBMA coating deposition without the oxygen was a biphasic patterns, and the PPBMA coating deposition with oxygen was dense, the release rate was slow and the release profile was *Higuchi* release.

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