Plasma Treatment of Polymer Films by Several Techniques

Manabu Ito, Kazuyoshi Ro, Noritoshi Tomikawa and Haruo Uyama

Technical Research Institute, Toppan Printing Co., Ltd.

4-2-3 Takanodaiminami, Sugito, Saitama 345 Japan

Organosilicons, in particular tetraethoxyorthosilicate (TEOS) and hexamethyldisiloxane (HMDSO) have been plasma-polymerized in radio frequency discharge on polyethylene terephthalate (PET) and polypropylene (PP). Films were formed as function of plasma power, electrode distance, working pressure. For reference, PP and PET were modified by Ar or oxygen plasma. The surface properties of the treated films were analyzed by X-ray photoelectron (XPS) spectroscopy and contact angle measurements. In order to identify the excited species in the discharge, optical emission spectroscopy was carried out. It was concluded that using organosilicons and varying the process parameters, the surface wettability can be controlled to hydrophilic or hydrophobic.

Keywords: plasma polymerization, contact angle, wettability, excited species, OES (Optical Emission Spectroscopy), XPS (X-ray Photoelectron Spectroscopy)

1. Introduction

Plasma polymerization is used to deposit thin polymer films with mechanical, electrical and optical properties covering a various fields. A unique feature of plasma treatment is that the surface structure can be selectively modified for a specific application while the bulk properties of the polymer are unaffected [1]. The technique of plasma polymerization has been found to provide pinhole-free, highly adherent, mechanically intact thin polymer films. During the last years, silico-organic plasma-polymerized thin films have attracted increasing interest for application in such diverse fields as optics [2-5], electronics [6,7] biomedicine and gas barriers [8]. This is mainly owing to the fact that important properties of these films can be varied widely by a suitable choice of source monomer and deposition parameter. Moreover, many siliconorganic monomers are sufficiently volatile, non-toxic and non-flammable, and relatively cheap.

In many cases silico-organic polymer films have to satisfy a long list of requirements with respect to their properties. In order to design a film and its deposition process, a further understanding of the correlations between the monomer and the polymerization conditions used and the resulting film properties is required.

However, plasma chemistry in the gas and at the surface and is complex and the details of deposition mechanism have not yet clear. There are two possible approaches for a better understanding. The first approach is to investigate the excited species in the plasma. The second one is to analyze the composition, structure and surface state of the polymer films.

In this work, the relationship between operational parameters (power supply, distance between electrodes and working pressure), the monomer, the substrate polymer films and analysis of the plasma polymerized films was studied. As starting materials, Tetraethoxyorthosilicate (TEOS) and

Fig.1 Schematic diagram of plasma polymerization system

hexamethyldisiloxane(HMDSO) were used. Polyethyleneterephthalate(PET) and polypropylene(PP) were employed as substrates. For reference, PP and PET were plasma-modified by Ar or oxygen gas.

The surface properties of the polymer films were analyzed by X-ray photoelectron(XPS) spectroscopy and contact angle measurements. Optical emission spectroscopy(OES) was carried out to identify the excited species in the discharge.

2.Experimental detail

2.1.Experimental set-up

Schematic diagram of the vacuum deposition system is shown in Fig.1. This system is a simple capacitively coupled arrangement operating at 13.56MHz and using a stainless steel chamber with internal electrodes(diameter 120mm). The distance between the electrodes can be varied from 10 to 40mm. The upper electrode serves as a shower head injector. The monomers were temperature-controlled and introduced into the system at variable flow rates through needle valve. The flow rates of oxygen and Ar were controlled by mass flow controllers(MFCs). The pumping system is composed of a rotary pump and mechanical booster pump. The working pressure maintained in the discharge is from 0.05 to 0.1Torr; the base vacuum before each run is less than 5×10^{-3} Torr.

The substrate was maintained at ambient temperature during the glow discharge treatment. Table 1 summarizes the plasma-polymerized and plasma-modified parameters used throughout these experiments.

OES was performed with a Sofie DIGISEM monochromator with a focal length of 200 mm and the photons were detected with photomultiplier whose spectral response ranges from 200 to 900 nm. The spectrometer resolution was 0.1nm. The position of the sample was maintained on the axis of the optical probe.

2.2.Material

PET films with an average thickness of 80 μ m were supplied by Teijin and the PP films with an average thickness of 20 μ m were supplied by Tosero. PP and PET were cut into 50mm $\times$ 50mm square pieces. High grade HMDSO and TEOS were purchased from Chisso and used without further purification.

2.3.Film Characterization

2.3.1.XPS analysis

XPS analysis was performed with a Shimadzu ESCA-3200 system. The instrument was equipped with a X-ray source(Mg anode) operating at 5kV and 30mA. The base pressure was 10^{-8} Torr. Peak fitting of the XPS data was done using software supplied by

Table.1 Experimental parameters

	HMDSO	TEOS	O ₂	Ar
RF Power [W]	50 ~ 200		50 ~ 125	
Flow rate [sccm]	—		3 ~ 7	
Working Pressure [Torr]	0.05 ~ 0.1			
Electron Distance [mm]	10 ~ 40			

the manufacturer. Quantification of the XPS data was achieved using peak areas and experimental sensitivity factors.

2.3.2. Contact Angle measurements

The contact angle in air of water were measured at 298K using a Kyowa Kaimen Kagaku contact-angle meter with a goniometer, CA-Z model. Water for the test liquid was distilled in the presence of potassium permanganate. A drop of water pushed out from a microsyringe was transferred to the plasma treated film surface, and the height(h) and the width(w) of the drop on the surface were measured using a telescope with a scale. The advancing angle of the drop was estimated from the equation $\theta/2 = \tan^{-1}(2h/w)$. The reported values correspond to the average of seven measurements of the advancing angle, performed on different parts of the sample.

3. Results and discussions

We will first discuss the non-treated PET or PP film and then discuss the plasma-polymerized films obtained by organosilicons and plasma-modified polymer films by Ar or oxygen. As will become evident, the mechanisms of the plasma treatment are different for the two monomers and two gases investigated. Therefore, it is necessary to discuss them separately.

3.1. Non-treated PET or PP

The results of contact angle measurement are shown in Table.2 and the C1s spectra of PET and PP are shown in Fig. 2 and 3. C1s spectrum for PET contains four distinct peaks: the carbon atoms in the phenyl ring at 285.2eV, the methylene carbon atoms singly bonded to oxygen at 286.8eV, the ester carbon atoms at 289.2eV, and the $\pi \rightarrow \pi^*$ shake-up peak is less than 4% of the total integrated area of the primary peaks. C1s spectrum for PP has only one peak: 285.2eV, due to C-C group.

Fig.2 C1s spectra of PET

Table.2 Contact angle of non-treated PET and PP

	PET	PP
Contact Angle[degree]	77.8	102.5

Fig.3 C1s spectra of OPP

3.2. Plasma polymerized films by HMDSO

Figure 4 depicts the result of contact angle measurement as a function of RF power. The contact angle remained stable with the RF power and the effect of the substrate polymer was not observed.

Fig.4 Contact angle of HMDSO polymerized film

Figure 5 depicts the XPS C1s spectrum of the polymer film polymerized with an RF power 50W. This spectrum indicates Si-C(282.7eV), Si-C-O(284.3eV) and C-C(285.2eV) groups on surface.

Figure 6 shows the contact angle and O/C atomic ratio results as a function of working pressure. As the working pressure increased, that is increase of monomer flow rate, contact angle increased and O/C ratio decreased. This suggests that excess monomer leads to incomplete decomposition of carbon-containing species in the plasma and resulted in high content of hydrophilic functionality, like CH_3 group, into the films.

Fig.5 C1s spectrum of plasma polymerized film

Fig.6 Property of HMDSO polymerized film

3.3. Plasma polymerized films by TEOS

Figure 7 depicts the Si2p spectra of plasma polymerized film on PET. As RF power increased, the Si2p peak shifted to the higher binding energy. This indicates that, with the increase of RF power, Si-O bonding dominates the Si-C bonding in the film.

Fig.7 Si2p spectra of TEOS polymerized film

Figure 8 shows the contact angle results as a function of RF power deposited on PP and PET. Unlike HMDSO case, strong dependence of substrate polymer on contact angle was observed.

The contact angle of TEOS plasma-polymerized films on PET showed approximately 40degrees higher than that on PP.

Fig.8 Contact angle of TEOS polymerized film

3.3.1. Plasma-modified surface by oxygen

Figure 9 displays the contact angle and O/C atomic ratio of the surface of oxygen plasma-modified PP. With the increase of RF power, the contact angle decreased and O/C ratio increased. This suggests that the higher RF power brings about the higher extent of oxygen incorporation into the surface and make the PET film surface hydrophilic.

Fig.9 Property of O₂-plasma modified PP

That is confirmed by C1s spectra of the oxygen plasma-modified PP shown in Fig.10(a,b). With the increase of RF power, the spectra became broad with a skew to the higher binding energy. The broadness of the peak definitely suggests more than one carbon-oxygen species. As shown in Fig.10(b), the spectrum, compared with non-treated PP, reveals the new peaks resulting from plasma oxidation, namely C2 at 285.9eV due to $\text{C}-\text{COO}$ groups, C3 at 286.9eV due to $\text{C}-\text{O}$, C4 at 288.1eV due to $\text{C}=\text{O}$ or $\text{O}-\text{C}-\text{O}$, C5 at 289.4eV due to $\text{O}-\text{C}=\text{O}$. From the OES analysis, strong CO peak was detected in the gas phase. It appears that in an oxygen plasma oxygen incorporation occurs rapidly, but that the oxidized functions are degraded.

Fig.10(a) C1s spectra of O₂ plasma modified OPP

Fig.10(b) C1s spectra of O₂ plasma modified OPP

Figure 11 depicts the contact angle and O/C atomic ratio of the surface of oxygen plasma-modified PET. With the increase RF power, contact angle decreased and O/C ratio increased, as is the same case with PP.

Fig.11 Property of O₂ modified PET

Figure12 displays the C1s spectra of plasma-treated PET by oxygen as a function of RF power. After oxygen-plasma modification, the C-O and O-C=O peaks became broad and newly generated peak (C=O or O-C-O) was detected. The loss of aromaticity in the film could also be monitored by the decrease in the intensity of the $\pi \rightarrow \pi^*$ shake-

up satellite.

Fig.12 C1s spectra of O₂ plasma modified PET

The distinctive trends were not observed among the electrode distance and flow rate of oxygen.

3.3.2. Plasma-modified surface by Ar

Fig.13 Property of Ar plasma-modified PP

Figure 13 shows the contact angle and O/C ratio of the Ar plasma-modified PP. The contact angles decreased compared with the non-treated films. Although argon-plasma treatment does not incorporate new chemical species into polymer, O/C ratio increased and oxygenated functional group was observed after Ar plasma treatment. The grafting of oxygenated functional groups is most probably caused either by the interaction of the activated surface with residual oxygen atoms present in the reactor atmosphere or by oxygen functional groups grafted to the surface during the transfer of the specimens from the plasma reactor to the XPS equipment. The effect of RF power, Ar flow rates and electrode distance were not distinctive in the case of Ar-plasma modification.

3.3.3. Comparison of the film properties

Figure14 shows the C1s spectra of HMDSO or TEOS polymerized films on PET deposited on same conditions. The peak of TEOS shifted slightly to higher binding energy compared with HMDSO peak.

This suggests that Si-C(282.7eV) and Si-C-O(284.3eV) groups exist in the HMDSO films and that O-C related groups in the TEOS films. Si-C related group is attributed Si-CH₃ bond in the HMDSO monomer and O-C related group in the TEOS monomer.

Fig.14 C1s spectra of organosilicon-plasma polymerized film

As seen in 3.2 and 3.3, wettability of TEOS polymerized film can be controlled by varying process parameters, compared with HMDSO. Ar and oxygen plasma treatment can create polar moieties(carboxyl, ether, carbonyl, etc) and make the surface hydrophilic, but by using of organosilicon and varying the process parameters, the surface wettability can controlled to hydrophilic or hydrophobic.

4. Conclusion

XPS analysis and contact angle measurements of the plasma treated films and OES investigation in the discharge has shown the following results:

(1)Ar and oxygen plasma treatment create polar

moieties and made the surface hydrophilic. With the increase of RF power, oxygen plasma made the surface more wettable. Electrode distance and flow rate of Ar and oxygen were not the decisive parameters to determine the surface properties of the treated film.

(2)The films obtained by HMDSO showed higher carbon content and higher contact angle than those of TEOS. Varying the process parameters, the surface wettability can controlled to hydrophilic or hydrophobic.

Acknowledgment

The authors are grateful for the contribution of the following colleagues at Toppan Printing Company: Mr. Ishi and Mr. Ida for their valuable suggestion of the XPS analysis; Mr. Miyama for the fruitful discussion of OES measurement; Mr. Ohata for his XPS measurement.

References

1. N.Inagaki, Plasma surface modification and plasma polymerization, Technomic Publishing Co., Basel, 1996
2. P.K.Tien et.al Appl. Optic. 11,(1972) 637
3. John R. Hollahn et.al Applied Optics 13,(1974) 1844
4. H.-U. Poll et.al Surf.Coat.Technol. 59,(1993) 365
5. C. Rau et.al Thin Solid Films 249,(1994) 28
6. A.Bradely et.al J.Electrochem. Soc.110,(1963) 15
7. N.Inagaki et.al J.Polym.Sci., Polym. Chem. Ed. 21,(1983) 2887
8. E.Sacher et.al J. Appl. Polym. Sci. Appl. Polym. Sci. Symp. 38,(1984)163