

# Oxygen Barrier Coating Deposited by Novel Plasma-enhanced Chemical Vapor Deposition

Juan Jiang,<sup>1,2,3</sup> Maike Benter,<sup>1</sup> Rafael Taboryski,<sup>2</sup> Klaus Bechgaard<sup>3</sup>

<sup>1</sup>Nanon AS, Brøndby, Denmark

<sup>2</sup>Department of Micro and Nanotechnology, Technical University of Denmark – DTU, Denmark

<sup>3</sup>Department of Chemistry, University of Copenhagen, Denmark

Received 28 October 2008; accepted 4 February 2009

DOI 10.1002/app.30222

Published online 26 October 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** We report the use of a novel plasma-enhanced chemical vapor deposition chamber with coaxial electrode geometry for the SiO<sub>x</sub> deposition. This novel plasma setup exploits the diffusion of electrons through the inner most electrode to the interior samples space as the major energy source. This configuration enables a gentle treatment of sensitive materials like low-density polyethylene foils and biodegradable materials. SiO<sub>x</sub> coatings deposited in the novel setup were compared with other state of the art plasma coatings and were found to possess equally good or better barrier properties. The barrier effect of single-layer coatings deposited under

different reaction conditions was studied. The coating thickness and the carbon content in the coatings were found to be the critical parameters for the barrier property. The novel barrier coating was applied on different polymeric materials, and it increased the barrier property of the modified low-density polyethylene, polyethylene terephthalate, and polylactide by 96.48%, 99.69%, and 99.25%, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2767–2772, 2010

**Key words:** barrier; coatings; gas permeation; plasma polymerization; polyethylene

## INTRODUCTION

Low-density polyethylene (LDPE) is the most widely used food packaging material due to its easy processing possibilities. However, for long shelf-life packaging, the usage of LDPE is limited due to its poor barrier property toward oxygen.<sup>1–4</sup> The permeability of LDPE film is normally  $\sim 2500 \times 10^{16} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$ . Good oxygen-barrier materials like polyamide 6 (PA6), poly(vinylchloride), and poly(ethylene terephthalate) (PET) have permeability typically around  $5\text{--}30 \times 10^{16} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$ . Other high oxygen-barrier materials like poly(vinylidene chloride) and poly(ethylene vinyl alcohol) (EVOH) have permeability ranging from 0.05 to  $7 \times 10^{16} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$ .<sup>5</sup> However, some of these good and high oxygen-barrier materials like EVOH and PA have limited water vapor barrier properties compared with LDPE. Other materials like poly(vinylchloride) and poly(vinylidene chloride) contain chloride. In comparison, LDPE is an economical and environmental friendly material; therefore, different techniques have been applied to improve the oxygen barrier properties of the LDPE films in the interest of expanding its packaging applications.<sup>6,7</sup> Various

techniques, including producing films by co-extrusion and blend blow-moulding high oxygen-barrier material with LDPE,<sup>8–11</sup> layered films with high barrier materials,<sup>5,12</sup> and surface depositions with high barrier coatings like metallization and silicon oxide (SiO<sub>x</sub>) coating.<sup>13,14</sup> However, surface modification with high-barrier coatings generally provide higher barrier properties than other methods.<sup>5</sup>

There have been concerns about the environmental and health issues with the metallization and wet coating process. Plasma techniques were then introduced for the application of coatings due to their clean and solvent-free processes. Plasma-enhanced chemical vapor deposition (PECVD) of SiO<sub>x</sub> films on polymers has been studied as barrier coatings in the past few decades.<sup>15–17</sup> SiO<sub>x</sub> films have excellent barrier properties toward oxygen, water vapor, and aromatic gases, high transparency and microwave ability.<sup>18–24</sup> However, most of the studies were carried out on polymer substrates with higher glass transition temperatures, like PET or polyethyleneterephthalate.<sup>25–27</sup> The lack of applications of SiO<sub>x</sub> coating on semicrystalline polymers like LDPE is due to the stress yield between the coating and the substrate.<sup>28–30</sup>

The rigid nature of SiO<sub>x</sub> barrier films often leads to cracking and adhesion problems, and therefore affects the barrier properties of the modified foils. The mechanical integrity of the composition

Correspondence to: J. Jiang (asininefish@hotmail.com).

structure depends on the coating defects, cohesive strength, internal stress state, interfacial interaction, and adhesion to the substrates. The thickness of a  $\text{SiO}_x$  barrier coating on polymeric materials typically ranges from 10 to 100 nm.<sup>5,31–35</sup>

The Airco Coating Technology has been one of the early investigators on improving barrier properties of polyethylene foil and reported 28 times barrier improvement in early 90s.<sup>23</sup> Recently, researchers reported a 40% decrease or 18.6 times reduction in the oxygen transmission rate (OTR) of LDPE foil by PECVD of  $\text{SiO}_x$  coating.<sup>36,37</sup> The improvement of these treatment are however still limited and cannot be used as good barrier coatings. The major problem with plasma deposition on LDPE is that the material is sensitive to high temperature, UV light, and ion bombardment.

Here, we present a novel plasma system to deposit  $\text{SiO}_x$  coating on LDPE. The electrons in this plasma system have lower energy than in radio frequency system; therefore, it allows a better preservation of the LDPE during the deposition. The hypothesis for the plasma generation in this setup is that the major acceleration of the electrons occurs inbetween the electrodes, where it has the highest intensity and energy. The electrons used for treating the substrates are diffused through the mesh into the deposition area to ionize molecules or atoms. Within the large volume of the inner electrode, the electrons and ions take less effect of the voltage of the electric field; therefore, the discharge has less ion bombardment on the substrate and more homogeneous.<sup>38</sup> Thus, we are expecting better barrier performance from the  $\text{SiO}_x$  coating deposited in this system. Because of the increasing interest in biodegradable material for packaging applications, we have also deposited the barrier coatings on polylactide (PLA) foils.

## EXPERIMENTAL

### Materials

Hexamethyldisiloxane (98%) was used as received as precursors (ABCR, Germany). Oxygen ( $\text{O}_2$ ) and argon (Ar) (99.9%) were used as carrier gas (Air Liquid, Denmark). The LDPE foil, 26  $\mu\text{m}$ , was provided by Ulfoss Plastic, Denmark. The 12- $\mu\text{m}$  thick PET, 12- $\mu\text{m}$  commercial PET +  $\text{AlO}_x$ , and 12- $\mu\text{m}$  commercial PET +  $\text{SiO}_x$  foils were all from Danapak, Denmark.

The 110- $\mu\text{m}$  PLA foils were obtained from a development project for biodegradable packaging materials at RISØ-DTU, Denmark.

The 90- $\mu\text{m}$  commercial seven-layered barrier foils were made of polypropylene, polyethylene, PA, and EVOH and was from Sanko, Turkey.

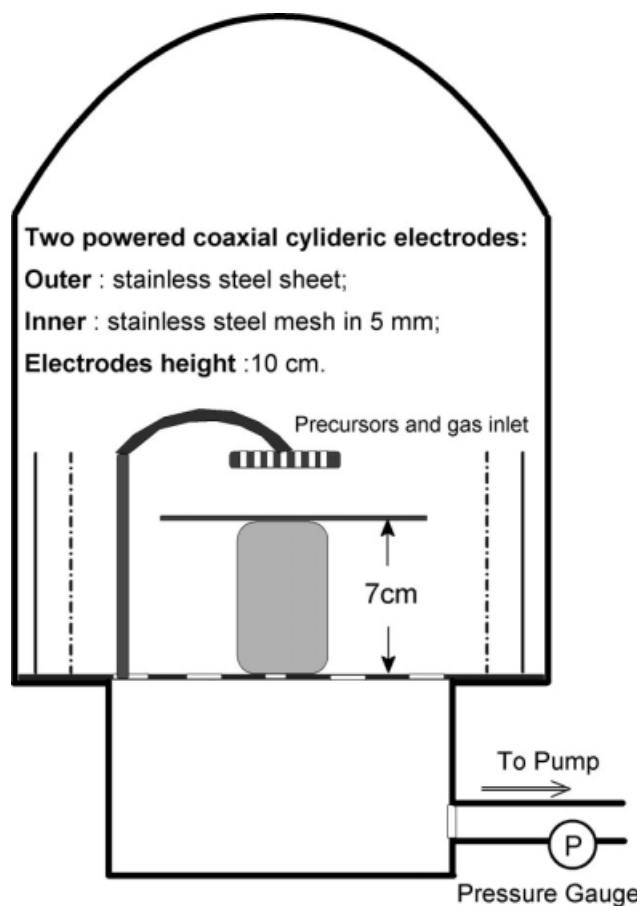


Figure 1 Conceptual drawing of plasma setup.

### Low-pressure PECVD treatment

The deposition setup consisted of a glass bell jar with two concentric cylinder stainless steel electrodes, as shown in Figure 1. The outer electrode was made of a stainless steel sheet with diameter 23 cm, and a concentric inner electrode with diameter 20 cm was made of stainless steel mesh with a square grid size of 5 mm. To generate a plasma, both electrodes were powered by an alternating current power supply (Vetaphone 20–40 kHz, output power 50–500 W). There was a 180 degree phase shift between the power inputs to the two electrodes. No extra heating or cooling units were placed inside the reaction chamber.

The deposition of the  $\text{SiO}_x$  coating was carried out at a constant precursor flow 4 mL/min. The flow rates of the carrier gases  $\text{O}_2$  were varied from 5 to 20 mL/min. The reaction pressure, controlled by a valve between the chamber and the pump, was varied between 10 and 40 Pa. The reaction time was varied between 1 and 5 min to keep the coating thickness below 100 nm.

The  $\text{SiO}_x$  coating was deposited on LDPE foils under different reaction conditions: various monomers to oxygen ratios, deposition times, pressures,

**TABLE I**  
Comparison of Permeability of Treated and Untreated Foils

Materials	Permeability ( $\times 10^{-16}$ cm <sup>3</sup> cm/cm <sup>2</sup> s Pa)	
	Without SiO <sub>x</sub> coating	With novel SiO <sub>x</sub> coating
Danapak PET	12.84 ± 0.64	0.04 ± 0.01
Ulfoss LDPE 12,821	1496.69 ± 74.84	52.64 ± 3.60
PLA	162.10 ± 18.85	1.21 ± 0.21

and deposition powers. The optimal reaction conditions were obtained with a ratio of monomer to oxygen flow at  $\sim 1 : 4$ , reaction pressure at 10 Pa, power at 80 W, and reaction time of 3 min. The coating deposited under this condition is referred to as the novel SiO<sub>x</sub> coating throughout this article. The thickness of the novel SiO<sub>x</sub> coating is around 40 nm. Three types of polymeric foils were tested with and without the novel SiO<sub>x</sub> coating: the PET, LDPE, and PLA.

The substrates, LDPE, PET, and PLA foils were cut into 12 × 12 cm<sup>2</sup> and placed perpendicularly to the outlet of the gas flow. The distance between the gas outlet and the substrate was kept at around 3 cm.

The SiO<sub>x</sub> coating was deposited on LDPE foils under different reaction conditions. Three major serials of reaction conditions have been tested: different reaction pressures, different reaction times, and different reaction powers. Samples from each reaction condition were then tested 3 to 4 times for the oxygen gas transmission rate. The relation between the OTR and the reaction condition was then plotted in the figures with corresponding error bars.

### Permeability measurement

The OTRs of the modified foils were measured on a permeability tester (BTY-B1P, Labthink). The test area of the foil was 9 cm in diameter. The instrument was made according to the differential pressure method (ISO 2556). The systematic uncertainty was 5%. The permeability of the materials was then calculated as shown in eq. (1), based on the thickness and the measured OTR.

$$P = OTR \cdot d \quad (1)$$

where  $P$  is the permeability coefficient (cm<sup>3</sup> cm/cm<sup>2</sup> s Pa), OTR is the oxygen transmission rate (cm<sup>3</sup>/m<sup>2</sup> 24 h 1 atm),  $d$  is the thickness of specimen (μm). The right hand side of the equation should be multiplied by a numerical unit conversion factor of 1.1423 × 10<sup>-18</sup> m<sup>2</sup> 24 hr 1 atm/cm μm s Pa to express the  $P$ , OTR, and  $d$  in the commonly used units shown above.

All the OTR measurements were carried out at room temperature (at  $\sim 25^\circ\text{C}$ ) and relative humidity (at  $\sim 50\%$ ).

### X-ray photoelectron spectroscopy analysis

The X-ray photoelectron spectroscopy measurements were made on a Thermo K-alpha with Al monochromatic X-rays (12 kV, 20 mA, the spot size of 400 × 400 μm<sup>2</sup>) source. The analyzer was placed at a 90° take off angle, yielding a sampling depth of approximately 8 nm. Broad spectrum survey scans (binding energy range -20–1300 eV) were made at low resolution (pass energy, 200 eV).

## RESULTS AND DISCUSSION

### The performance of the novel SiO<sub>x</sub> coating

The OTR was measured on the three SiO<sub>x</sub> coating modified foils, and the permeability was calculated for the respective thickness of the foil and is listed in Table I in the column to the left. The permeability of modified foils is listed in Table I in the column to the right.

The permeability of the modified foils was dramatically reduced by the novel SiO<sub>x</sub> coatings. The improvement of the barrier properties was 99.69, 96.48, and 99.25% on modified PET, LDPE, and PLA foils, respectively.

To compare the material properties according to the same standard, the permeability of the commercially available foils were measured on the same gas transmission instrument. The permeability of the foils and the corresponding thickness are listed in Table II. The permeability of the novel SiO<sub>x</sub> coating-modified PET foils is competitive to the commercially available SiO<sub>x</sub>-coated PET foils.

**TABLE II**  
Comparison of Permeability on Commercial Barrier Foils and the Novel SiO<sub>x</sub> Modified Foils

Materials	Thickness (μm)	Permeability ( $\times 10^{-16}$ cm <sup>3</sup> cm/cm <sup>2</sup> s Pa)
7 layers barrier foil from Sanko: PP, PE, PA, EVOH	90	44.82 ± 2.24
Danapak commercial PET + AlO <sub>x</sub>	12	0.17 ± 0.009
Danapak commercial PET + SiO <sub>x</sub>	12	0.03 ± 0.007
Danapak PET + novel SiO <sub>x</sub> coating	12	0.04 ± 0.01
PLA + novel SiO <sub>x</sub> coating	110	1.21 ± 0.19
Ulfoss LDPE 12,821 + novel SiO <sub>x</sub> coating	26	52.64 ± 3.60

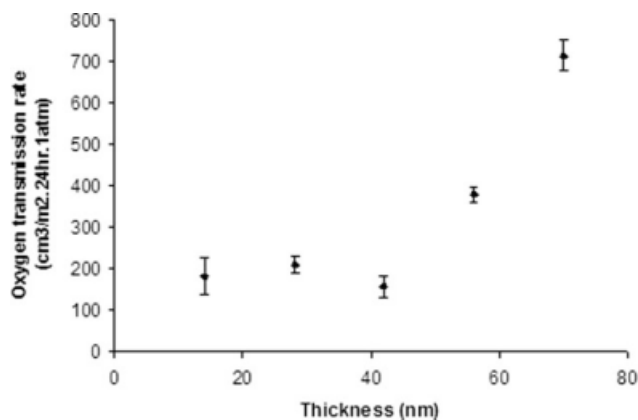


Figure 2 OTR vs. SiO<sub>x</sub> coating thickness.

As for modified LDPE foils, the permeability is around  $52 \times 10^{16} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$ , which is not competitive with modified PET foils at  $0.03 \times 10^{16} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$ . However, in comparison with seven-layered commercial barrier foils, the modified LDPE foils reached same level of barrier property with only one third of the material thickness. PECVD in many aspects is also superior to the layering technique. It only requires one process and there are no problems with delaminating as is the case for multilayered materials. We can also see that the PET foils modified with novel SiO<sub>x</sub> reaches the same barrier property level as the commercial SiO<sub>x</sub>-coating-modified PET foils. Furthermore, the permeability of the novel SiO<sub>x</sub>-coating-modified PLA foils has also reached the high barrier property area at around  $1 \times 10^{16} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$ .

#### The OTRs of the LDPE modified with SiO<sub>x</sub> coating at different conditions

In a previous study of this plasma setup,<sup>38</sup> we have found a linear relationship between the SiO<sub>x</sub> coating thickness and the deposition time, within a reaction time of 20 min. The effect of deposition time on the

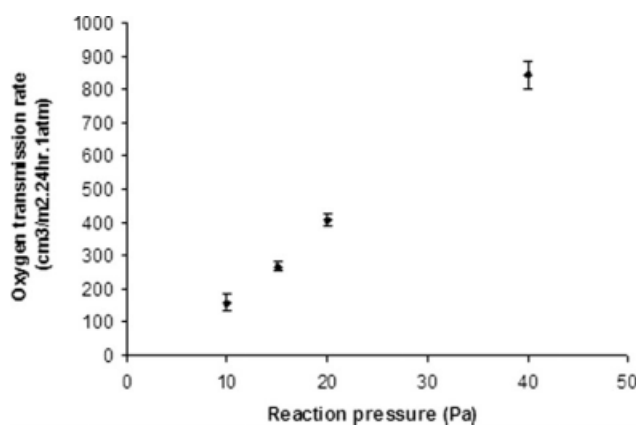


Figure 3 OTR vs. deposition pressure.

TABLE III  
The Thickness and the Element Composition  
in Reaction Pressure Series

Reaction pressure (Pa)	10	15	20	40
OTRs (cm <sup>3</sup> /m <sup>2</sup> 1atm 24 h)	157.45	267.25	405.59	841.85
Thickness (nm)	42	45	23	5
Carbon content in SiO <sub>x</sub> (%)	8.83	15.02	15.62	11.14
Si content in SiO <sub>x</sub> (%)	34.91	32.82	32.39	31.72
O content in SiO <sub>x</sub> (%)	56.26	52.17	51.99	57.14

OTR is directly proportional to the effect of the coating thickness. Therefore, we converted the deposition time to coating thickness and plotted its relation to the OTR in Figure 2.

The growth rate of the coating at the reaction condition was 14 nm/min, the corresponding thickness in the Figure 2 is 14, 28, 42, 56, and 70 nm. When the coating thickness was less than 40 nm, the OTRs of modified foils were not affected. When the coating thickness was bigger than 40 nm, the OTR increased with the increasing thickness. The thickness effect on the OTR matches the literature findings on the PET film as well. The thinner the coating is, the more flexible it is with less cracks. Thicker coating results in more cracking and consequently reduces the barrier effect of the SiO<sub>x</sub> coating.

A similar phenomenon was seen in the series with reaction pressure. Figure 3 shows the relation between the OTR and reaction pressure. The increasing reaction pressures caused nearly linear increase in the OTR. The reaction pressure effect on the OTR is a combination of coating thickness and carbon content in the coating. The reaction pressure dependence on the thickness and the carbon content are listed in Table III.

Although the thickness of coating at 10 and 15 Pa was around 40 nm, the OTR at 15 Pa was much higher due to the high carbon content. However, coating at 20 Pa has the similar carbon content as that at 15 Pa, the OTR increased because the thickness of the coating has decreased to 24 nm. For

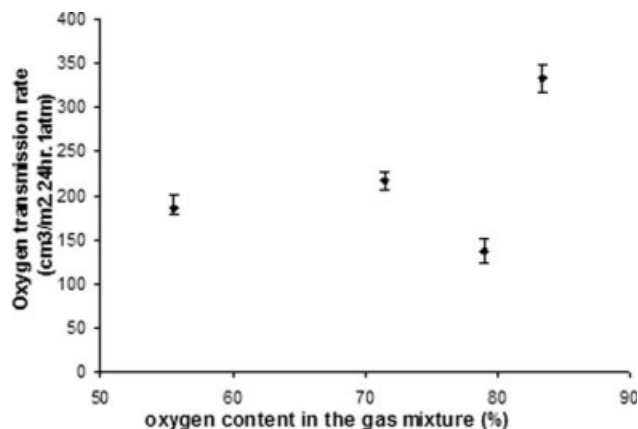


Figure 4 OTR vs. different oxygen content.

**TABLE IV**  
**The Thickness and Carbon Content from Different Oxygen Content Series**

Oxygen content (%)	55.5	71.4	78.9	83.3
OTRs (cm <sup>3</sup> /m <sup>2</sup> 1atm 24 h)	185.78 ± 4.90	216.65 ± 6.38	136.47 ± 13.69	333.26 ± 15.04
Thickness (nm)	50	45	42	36
Carbon content in SiO <sub>x</sub> (%)	7.15	5.10	8.83	6.91
Si content in SiO <sub>x</sub> (%)	35.37	36.23	34.91	35.95
O content in SiO <sub>x</sub> (%)	57.48	58.67	56.26	57.14

optimal barrier coating, the thickness of coating should be around 40 nm and the carbon content should be around less than 15%.

To further approve the effect of the carbon content on the OTR, a series of samples with SiO<sub>x</sub> coatings deposited with different oxygen content in the gas mixtures were made. The oxygen content in the gas mixture was ranging from 55.5, 71.4, 78.9, to 83.3%. Figure 4 shows the relation between OTR and the oxygen content. In Table IV, the carbon content of the coating for the X-ray photoelectron spectroscopy analysis is listed.

We can see from Figure 4 that the oxygen content does not significantly affect the barrier performance of the SiO<sub>x</sub> coating, especially when the oxygen content is below 80%. The coating thicknesses from this series were similar and around 40 nm, and the carbon content in the coating were all below 9%.

When the oxygen content went above 83.3%, the OTR observed experimentally was higher although the coating was at optimal condition. However, the high OTR was not directly related to the barrier performance of the SiO<sub>x</sub> itself. The modified samples were observed to have flaking of coating when applying force, which indicated poor adhesion of the coating to the substrate. This was caused by the high oxygen content in the gas mixture, which resulted in a high etching rate at the beginning of the reaction. Although in theory, high oxygen rate should reduce the carbon content in SiO<sub>x</sub> coatings and thereby increase the barrier property of the coating, high oxygen content (>83.3%) is not applicable here due to the etching of the LDPE substrate.

## CONCLUSIONS

A novel SiO<sub>x</sub> coating process in a low-frequency diffusion plasma system was tested. The tested coating process resulted in good adhesion to the substrate. We found that for a coating thickness of roughly 40 nm, the optimal carbon content in the coating should be less than 9%.

The improvement of the barrier property of the modified LDPE foils was 96.48%, which is better than the recently reported 40% decrease or 18.6 times decrease in the OTR.<sup>36,37</sup> However, the permeability of the modified LDPE was 52.64 ± 3.60 × 10<sup>-16</sup> cm<sup>3</sup> cm/cm<sup>2</sup> s Pa, which is still not suffi-

cient for the food packaging applications. The novel SiO<sub>x</sub> barrier coating could be deposited on various polymeric foils including plasma sensitive materials, which improves the barrier performance of the modified PET and PLA by 99.69 and 99.25%, respectively. The coating was found to be comparable with the current commercially available SiO<sub>x</sub> barrier coatings on PET foils. The limitation of the barrier performance on the LDPE foils was due to the slip and anti-block agent added in the LDPE, which leads to more defects in the SiO<sub>x</sub> coating.<sup>39</sup> The barrier performance could be improved by cleaning the substrate, yet this was not practical for the industrial applications.<sup>40</sup>

## References

- Joles, D. W.; Collier Cameron, A.; Shirazi, A.; Petracek, P. D.; Beaudry, R. M. *J Am Soc Hortic Sci* 1994, 119, 540.
- Charara, Z. N.; Williams, J. W.; Schmist, R. H.; Marshall, M. R. *J Food Sci* 1992, 57, 963.
- Nielsen, T. J.; Jagerstad, I. M.; Oste, R. E.; Wesslen, B. O. *J Food Sci* 1992, 57, 490.
- Ares, G.; Parentelli, C.; G'ambaro, A.; Lareo, C.; Lema, P. *Postharvest Biol Technol* 2006, 41, 191.
- Leterrier, Y. *Prog Mater Sci* 2003, 48, 1.
- Subramanian, P. M. *Polym Eng Sci* 1985, 25, 483.
- Subramanian, P. M. *Am Chem Soc Polym Prepr* 1989, 30, 28.
- Cui, X.; Wang, X. *J Appl Polym Sci* 2006, 101, 3791.
- Siddaramaiah; Guruprasad, K. H.; Nagaralli, R. T.; Somashekarappa, H.; Guru Row, T. N.; Somashekar, R. *J Appl Polym Sci* 2006, 100, 2781.
- Shah, R. K.; Krishnaswamy, R. K.; Takahashi, S.; Paul, D. R. *Polymer* 2006, 47, 6187.
- George, J.; Kumar, R.; Jayaprahash, C.; Ramakrishna, A.; Sabapathy, S. N.; Bawa, A. S. *J Appl Polym Sci* 2006, 102, 4514.
- Nir, M. M.; Ram, A.; Miltz, J. *Polym Eng Sci* 1995, 35, 1878.
- Ringenbach, A.; Jugnet, Y.; Duc, T. M. *J Adhes Sci Technol* 1995, 9, 1209.
- Inagaki, N.; Tasaka, S.; Masumoto, M. *Macromolecules* 1996, 29, 1642.
- Inoue, Y.; Takai, O. *Plasma Sources Sci Technol* 1996, 5, 339.
- Alexander, M. A.; R. D. Short, F. R.; Jones, W.; Michaeli, C. *J Blomfield Appl Surf Sci* 1999, 137, 179.
- Wang, B.; Tropsha, Y.; Montgomery, D. B.; Vogler, E. A.; Spontak, R. J. *J Mater Sci Lett* 1999, 18, 311.
- Lange, J.; Wyser, Y. *Technol Sci* 2003, 16, 149.
- Fracassi, F.; d'Agostino, R.; Favia, P. *J Electrochem Soc* 1992, 139, 2636.
- Lamendola, R.; d'Agostino, R. *Pure Appl Chem* 1998, 70, 1203.
- Creatore, M.; Palumbo, F.; d'Agostino, R. *Plasma Polym* 2002, 7, 291.
- Hegemann, D.; Vohrer, U.; Oehr, C.; Riedel, R. *Surf Coat Technol* 1999, 116, 1033.

23. Felts, J. T.; Grubb, A. D. *J Vac Sci Technol A Vacuum Surf Foils* 1992, 10, 1675.
24. Inagaki, N.; Tasaka, S.; Hiramatsu, H. *J Appl Polym Sci* 1999, 71, 2091.
25. Roberts, A. P.; Henry, B. M.; Sutton, A. P.; Grovenor, C. R. M.; Briggs, G. A. D.; Miyamoto, T.; Kano, M.; Tsukahara, Y.; Yanaka, M. *J Membr Sci* 2002, 208, 75.
26. Wu, D. S.; Lo, W. C.; Chiang, C. C.; Lin, H. B.; Chang, L. S.; Horng, R. H.; Huang, C. L.; Gao, Y. J. *Surf Coat Technol* 2005, 197, 253.
27. Inagaki, N.; Cech, V.; Narushima, K.; Takechi, Y. *J Appl Polym Sci* 2007, 104, 915.
28. Marais, S.; Hirata, Y.; Cabot, C.; Morin-Grognet, S.; Garda, M.-R.; Atmani, H.; Poncin-Epaillard, F. *Surf Coat Technol* 2006, 201, 868.
29. Rochat, G.; Leterrier, Y.; Fayet, P.; Manson, J.-A. E. *Thin Solid Foils* 2005, 484, 94.
30. Schwarzer, N. *Surf Coat Technol* 2000, 133, 397.
31. Phillips, J. C. *J Vac Sci Technol* 2000, 18, 1794.
32. Bieder, A.; Gondoin, V.; Leterrier, Y.; Tornare, G.; Rudolf von Rohr, P. h.; Manson, J.-A. E. *Thin Solid Foils* 2007, 515, 5430.
33. Schmachtenberg, E.; Reny Costa, F.; Göbel, S. *J Appl Polym Sci* 2006, 99, 1485.
34. Leterrier, Y.; Wyser, Y.; Manson, J.-A. E. *J Adhes Sci Technol* 2001, 15, 841.
35. Gupta, A.; Parsons, G. N. *J Vac Sci Technol* 2000, 18, 1764.
36. Sentek, J.; Kus, M.; Schimdt-szalowski, K. *Przem Chem* 2006, 85, 258.
37. Kim, K. S.; Cho, D. L. *Polymer-Korea* 2008, 32, 38.
38. Jiang, J.; Benter, M.; West, K.; Bechgaard, K. *Proceeding at 18<sup>th</sup> International Symposium of Plasma Chemistry*; 2007.
39. Patel, P.; Savargaonkar, N. *Plastics Engineering, Society of Plastics Engineers, Inc*, 2007.
40. Personal communication with Professor d'Agostino, Department of Chemistry, University of Bari: Italy, Oct., 2008.