*36th EPS Conference on Plasma Phys. Sofia, June 29 - July 3, 2009 ECA Vol.**33E**, P-1.071 (2009)*

Modification of Polyethylene Powder with an Organic Precursor

M. Quitzau, M. Wolter, H. Kersten

Institute of Experimental and Applied Physics, University of Kiel, Germany

Abstract

Hexamethyldisiloxane (HMDSO) films were deposited on polyethylene (PE, C_2H_4) powder by hollow cathode glow discharge. The reactive species in a HMDSO/Ar plasma were studied by optical emission spectroscopy (OES). The formed Si containing groups on the modified powder surface were analyzed by X-ray photoelectron spectroscopy (XPS)and the wettability depending on the HMDSO fraction was investigated by contact angle measurements.

Introduction

The deposition of thin films by plasma treatment is very efficient to produce polymers with well-defined functional surface properties which are of interest in various technologies. Polymer films produced by plasmas have highly branched and crosslinked chemical structures and are difficult to dissolve in the usual organic solvents [1]. Such films are used as protective coatings for optical components [2], barrier films for food and pharmaceutical packaging [3] or coatings of biocompatible materials [4]. Plasma treatment of polymers can also be used to modify surface morphology and surface energy without effecting the positive bulk properties of the polymer [5, 6, 7]. Polyethylene is widely used in great quantities for the production of foils, insulators, packaging materials, etc. PE powders are used as fillers in dyes or varnish to e.g. matting and enhance the scratch resistance.

Untreated PE is hydrophobic due to its unpolar surface. To enhance the hydrophilicity / adhesion the surface of the PE is commonly modified by plasma treatment whereby certain functional polar groups are generated on the polymer surface depending on the plasma environment. Powder modification becomes more and more important especially in the case of modification of polyolefins [8]. Most of commercially used plasma reactors are only for the treatment of flat objects. Agitation of the powder particles during the exposure to the plasma can achieve a homogeneous surface treatment e.g. by plasma downer [5] or fluidized bed reactors [6, 7]. To reduce the gas flow rates and to enhance the modification time a spiral conveyor combined with a plasma source can be used.

Experimental

To modify the PE surface in the present study a hollow cathode glow discharge (HCGD) in combination with a spiral conveyor is used (fig. 1) which ensures a homogeneous surface modification at a relative low gas flow where the powder can pass the plasma zone several times. The spiral conveyor consists of a cylindrical stainless steel chamber with a spiral path along the inner wall ending at the top in the centre of the vacuum chamber. The whole set-up is mounted on two vibrational motors. Due to the vibrations of the chamber the powder is conveyed from the bottom of the chamber along the spiral path up to the top. Here it falls down through the plasma zone of the HCGD where the modification takes place.

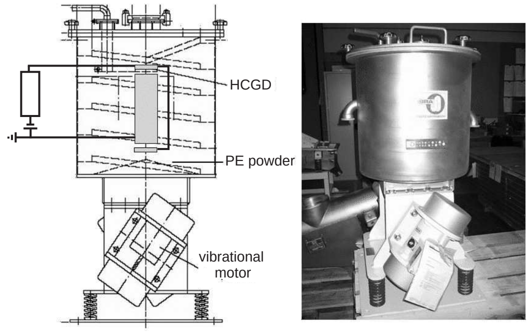

Figure 1: Scheme of the experimental setup of the spiral conveyor for PE powder modification by a hollow cathode glow discharge (HCGD).

In a hollow cathode glow discharge excitation, dissociation and ionization are much more efficient compared to other glow discharges (hollow cathode effect) [9]. The generated active species (radicals, ions, etc.) can be used for the treatment of PE powder as well as PE foils.

For surface treatment of PE powder a mixture of HMDSO and Ar was used as process gas and copper as hollow cathode material. The input power was 45W and the working pressure is kept constant at 50Pa with different mixtures of Ar/HMDSO with a HMDSO-fraction of 0,10...80%. The hollow cathode has a length of 20cm, a diameter of 3.4cm and is centrally mounted in the spiral conveyor.

The active species in the Ar/HMDSO plasma were analyzed by optical emission spectroscopy. The emission spectra were taken in the center of the hollow cathode (2cm) and integrated over the whole length (20cm). The surface composition of the treated and untreated PE powder was analyzed by XPS. The changes in surface energy of the PE were investigated by contact angle measurements using the sessile drop methode with water, glycerine and ethylene glycol as test liquids.

Results and Discussion

Free radicals generated in the plasma can react with other reactive species in the gas phase to produce an amount of new species. A fundamental knowledge of the complex reaction process in plasma is essential for success in plasma organic synthesis. In figure 2 a typical emission spectrum of Ar/HMDSO plasma is shown with 50% HMDSO. It can be clearly seen that the Ar/HMDSO plasma contains of Ar, SiH, SiO, CH, OH, H, H2, N2, O2 species. The lines between 700nm and 850nm can be assigned to Ar. The HMDSO structural formula is $(CH_3)_3$-Si-O-Si-$(CH_3)_3$. The bond energy of SiO (8,3eV) is higher than of SiC (4,6eV) and CH (3,5eV) so that SiC und SiH in the HMDSO monomer are easily broken upon electron impact[10]. The amount of CH, H and H2 fragments are dissociation products of -CH3 functional groups [11]. The weak lines of SiH and SiO fragments at 410-430nm are a direct evidence of the dissociation of Si-O-Si functional groups. The emission line at 309nm indicates the presence of the polar radical OH. In figure 3 the emission spectra of different HMDSO/Ar gas mixtures are shown. In a pure Ar plasma only the Ar lines between 650nm and 850nm can be detected. After adding of HMDSO to Ar plasma new lines between 300nm and 450nm can be observed. These emission lines can be assigned to SiO, SiH, CH and OH and

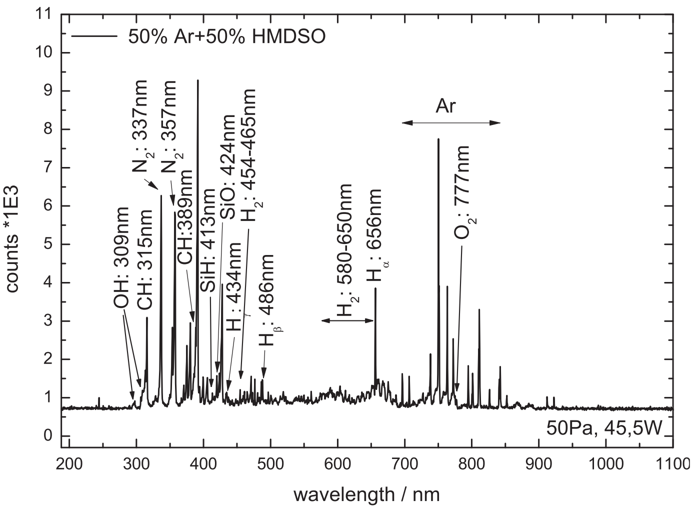

Figure 2: Emission spectrum of Ar/HMDSO plasma.

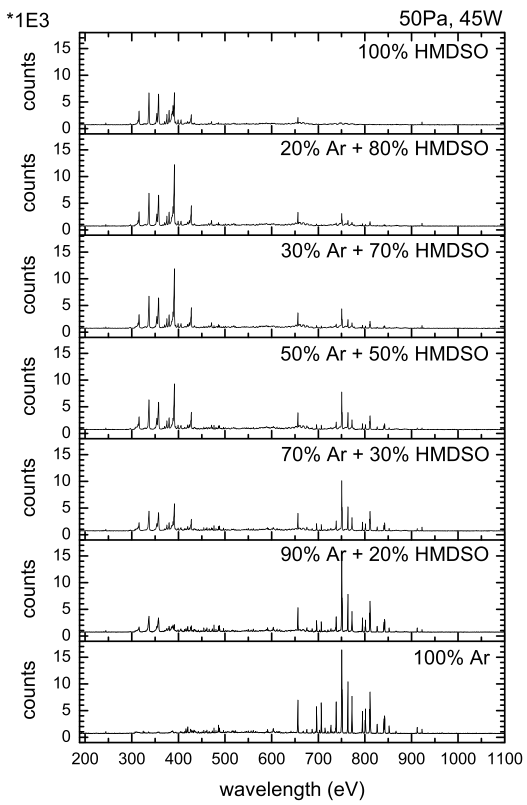

Figure 3: Emission spectra of Ar/HMDSO plasma with different HMDSO-fractions.

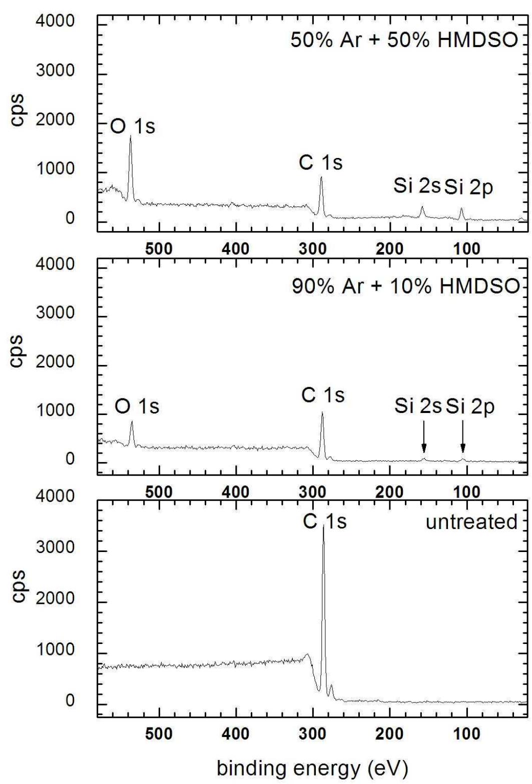

Figure 4: Overview spectra of untreated and plasma treated polyethylen with different HMDSO fractions.

their intensities grow with increasing HMDSO-fraction. This knowlegde is relevant for process control of thin film deposition and for optimization of the process conditions.

After proving the occurrence of HMDSO-fragments in the plasma PE powder was treated to deposit SiO_x films on the surface. This can be analyzed by XPS measurements. In figure 4 the overview scans of pure and plasmatreated PE are shown. In the spectrum of the pure PE only the C 1s-peak can be recognized. After treatment with Ar/HMDSO plasma Si 2p- and O 1s-peaks can additionally be observed which intensities increase and the C 1s-peak decreases with increasing HMDSO fraction due to encapsulation. The formed polar functional groups on the surface are C-O, C=O, Si-O and Si-C. These groups cause a change in wettability of the modified PE powder. That can be confirmed by contact angle measurements, too.

Conclusions

The generated active species in an Ar/HMDSO plasma were studied by OES. In addition to excited Ar different species like SiO and SiH can be observed which originate from the added HMDSO. After the treatment of PE powder with Ar/HMDSO plasma a decrease in the contact angle can be observed with is attributed to the formation of polar functional groups which can be verified by XPS measurements. A dependence on time and HMDSO-fraction of the contact angle is determined. The increasing angle with increasing HMDSO-fraction can be an indication for the encapsulation of the PE powder surface required e.g. for protective or scratch resistent coatings.

References

[1] L. Zuri, M.S. Silverstein and M. Narkis, J. Appl. Polym. Sci. **62**, 2147 (1996)

[2] G. Akovali, M.O. Rzaev, D.G. Mamedor, Eur. Polym. J. **32**, 375 (1996)

[3] F. Benitez, E. Martinez, J. Esteve, J. Thin Solid Films **109**, 377 (2000)

[4] M. Morra, E. Occhiello, F. Garbassi, J. Apll. Polym. Sci. **48**, 1331 (1993)

[5] C. Arpagaus, A. Rossi, Ph. R. von Rohr, Appl. Surf. Sci. **252**, 1581 (2005)

[6] N. Inagaki, S. Tasaka, H. Abe, J. Appl. Polym. Sci. **46**, 595 (1992)

[7] C. Vivien, C. Wartelle, B. Mutel, J. Grimblot, Surf. Interf. Anal. **34**, 575 (2002)

[8] A. Sonnenfeld, A. Spillmann, C. Arpagaus, P.R. von Rohr, Plasma Process. Polym. **6**, 170 (2009)

[9] J.-H. Lee, K.-J. Jeong,, J. Phys. Soc. Japn. **72**, 2530 (2003)

[10] Y. Wang, J. Zhang, X.Y. Shen, Mater. Chem. Phys. **96**, 498 (2006)

[11] V. Léveilléand, S. Clulimbo, Plasma Sources Sci. Technol. **14**, 467 (2005)