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Plasma Treatment of Polyethylene Powder Particles in a Hollow Cathode Glow Discharge

Meike Quitzau, Matthias Wolter, Holger Kersten*

A hollow cathode glow discharge mounted in a spiral conveyor has been employed for surface modification of polyethylene (PE) powders. This combination of powder agitation and plasma treatment allows for a homogeneous surface modification for powders as well for foils. In this study, first the results of plasma treatment of PE powders are represented using different process gases (Ar, N₂, CO₂) and different hollow cathode materials like copper and aluminum. The modified PE is analyzed by water contact angle (WCA) measurement to prove changes in wettability and by X-ray photoelectron spectroscopy (XPS) to prove changes in surface composition and to detect formed polar functional groups. Furthermore, the aging of the plasma treated PE material has been investigated.

Introduction

Polyethylene (PE) is widely used in great quantities for the production of foils, insulators, packaging materials, plastic bottles, etc. Unfortunately, untreated PE is hydrophobic due to its unpolar surface. Therefore, it is hard to print or glue PE and hence, the surface has to be modified before converting. The modification of PE can be effected by various chemical, mechanical, or physical methods. One of the most common pre-treatment is the modification by low temperature plasma because only a few monolayers of the polymer surface is modified without affecting the positive bulk properties of the PE material.^[1–3]

Also PE powder particles have been modified by low temperature plasma treatment, i.e., in plasma downer reactors^[1] or in fluidized beds,^[2,3] respectively. However, these experiments need a relatively high gas flow,^[2] very long treatment times up to several hours, and in some devices the powder passes the plasma zone only once.^[1]

In general, the surface of polymers can be modified by several methods like wet chemical processes, graft copolymerization, corona treatment, thermal pre-treatment like flame impingement, or mechanical treatments like blasting or sanding. All these surface treatments stress the

polymer surface rather strong, problems of waste disposal of the partially toxic chemicals occur or the desired surface effect is only moderate. Therefore, plasma treatment is the commonly used process at present.^[4] It is a versatile dry and environment-friendly process which modifies the surface properties almost without changing the intrinsic bulk properties.

Gas phase reactions in a plasma provide several components like atoms, free radicals, ions, electrons, or photons, e.g., the plasma can be a source of chemical highly active species. Depending on the density and energy distribution as well as on the reactivity of the generated species with respect to the polymer surface, different processes like polymerization, functionalization, cross-linking, or etching can take place. As an example of the plasma-surface interaction, Dorai and Kushner^[5] simulated the appearing gas phase and surface kinetics during the corona treatment of polypropylene.

In the present experiment PE powders are modified by means of a dc hollow cathode glow discharge (HCGD) as plasma source which is placed in a spiral conveyor. This rather novel experimental set-up allows for a continuous treatment and homogeneous surface modification of the powder at low gas flow rates and variable treatment times. First results in surface modification of PE powder in the spiral conveyor combined with a HCGD using different process gases (Ar, N₂, CO₂) and two different hollow cathode materials (copper and aluminum) are presented.

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Experimental Part

PE powder (sizes of $320 \pm 180 \mu\text{m}$) which is commonly used as filler material in industry has been modified by plasma treatment in a spiral conveyor which ensures a homogeneous surface modification at a relatively low gas flow where the powder can pass the plasma zone more than one time. The spiral conveyor (Figure 1) consists of a cylindrical stainless steel chamber with a spiral path along the inner wall ending at the top in the center of the vacuum chamber. The set-up is mounted on two vibrational motors. Due to the vibrations of the reactor the powder is agitated 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. After this cycle the powder is conveyed along the spiral path again and the next cycle begins. The plasma chamber is 0.5 m in diameter and height. The hollow cathode consists of a metal cylinder with a length of 20 cm. The cathode material can be varied. In the present experiment copper and aluminum have been used. On both ends of the hollow cylinder two annular anodes are mounted which are at a positive potential (200...400 V). The hollow cathode is at ground potential.

In a HCGD the excitation, dissociation, and ionization are much more efficient compared to other glow discharges. The fast secondary electrons which are released from the cathode surface by ion bombardment are electrostatically confined inside the hollow cathode. They are repelled by the opposite cathode and can oscillate between both cathode surfaces in the negative glow. These "pendular" electrons dissipate most of their energy acquired in the cathode fall by collisions in the plasma. The pendular effect causes increased ionization and dissociation rates as well as a strongly increased current density at constant operating voltage (hollow cathode effect) compared to a linear glow discharge.^[6–10] The

generated active species (radicals, ions, etc.) can be used for the treatment of PE powder as well as PE foils.

The PE substrates were modified by different gases like argon, nitrogen, argon/nitrogen mixture, and carbon dioxide for variable treatment times in the spiral conveyor using two different hollow cathode materials (Cu and Al).

The process gas pressures are between 41 and 51 Pa and the supplied power is 45.5 W. One pass of the falling particles through the plasma zone of the hollow cathode corresponds to an effective treatment time of 200 ms. One entire cycle along the spiral conveyor and the plasma zone takes about 1 min. The number of cycles are in the range of 5–20. Therefore, the effective treatment times are between 1 and 4 s.

The modified PE was analyzed by water contact angle (WCA) measurement and X-ray photoelectron spectroscopy (XPS) to obtain information about changes in wettability and chemical surface composition.

For the XPS measurements the PE powder was stuck on a sample holder by an electrically conductive double-sided adhesive carbon based Leit Tab and analyzed by a VG Microtech spectrometer using an Al K α X-ray source (1486.6 eV). The spectrometer energy scale was calibrated with respect to the C 1s (C–C, C–H) component set at 285 eV. For data fitting CASA XPS software package (Casa Software Ltd., UK) was used. After appropriate Shirley background removal, a Marquardt peak-fitting procedure was applied using Gaussian-Lorentzian curves.

For the WCA measurements the PE powder was stuck by double face adhesive tape on a sample holder. The powder was given on the adhesive tape and excess powder particles were blown off using compressed air. WCA measurements were performed with a camera (four mega pixels) and an image processing system. The reported values correspond to the average of five static contact angles at different positions of the sample.

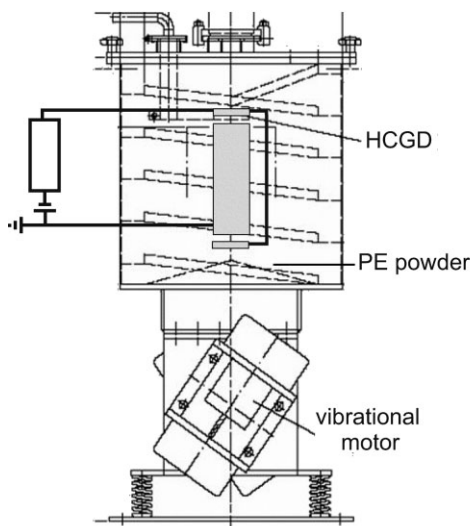


Figure 1. Scheme of the experimental setup of the spiral conveyor for PE powder modification by a HCGD.

Results and Discussion

By the plasma treatment of the PE powder particles, polar functional groups are formed on the surface which can be observed by XPS measurements. A characteristic XPS spectrum of untreated and plasma-treated PE powder by different process gases and copper as cathode material is shown in Figure 2. The spectrum of the untreated PE powder exhibits only the C1s Peak, hydrogen cannot be detected by XPS. After modification by argon plasma the PE surface is only activated but no new functional groups are formed. However, oxygen (O1s) can be recognized on the surface as it is the case for all other tested conditions. These oxygen containing groups like C–O and C=O are formed on the surface by reaction of the unsaturated

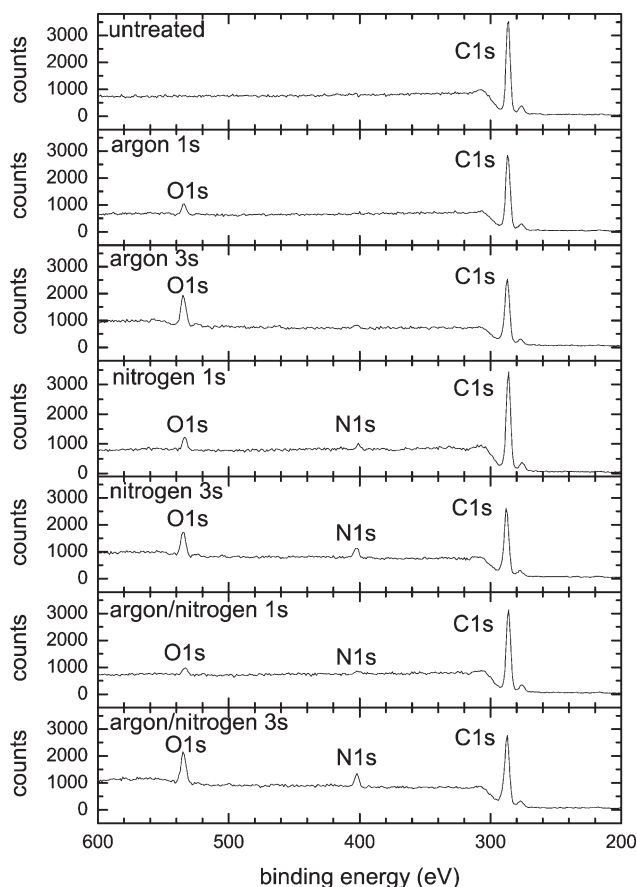


Figure 2. XPS scan of untreated PE powder and after plasma treatment with argon, nitrogen, and argon/nitrogen mixture as process gas and copper as hollow cathode material.

radicals with residual gas and water in the reactor and the environmental oxygen after exposure to air. It is obvious that the oxygen peak increases with treatment time indicating an increase in surface activity by the plasma treatment.

Using nitrogen as process gas, new species in comparison with argon plasma treatment like nitrogen containing polar functional groups (C–N, C=N) are formed on the surface. If a mixture of both gases as process gas is used, also polar nitrogen groups were formed. Under both modification conditions oxygen is detected on the surface as well. When the treatment time of the surface modification is increased, the amount of polar functional groups also increases. This effect can be confirmed by the decrease in C/O and C/N intensity ratios of the detected elements in the XPS fine spectra (Table 1). From the fine scans of carbon 1s, oxygen 1s, and nitrogen 1s several polar functional groups like C–O, C=O, C–N, and C=N can be identified after peak fitting (Table 2).

The XPS spectra show no metal contaminations on the PE surface after plasma treatment, because the discharge power is too small for significant sputtering effects at these

Table 1. Intensity ratios of the different elements calculated from XPS fine spectra. At the untreated PE surface no oxygen was detected.

Process gas	Intensity ratio	Treatment time	
		1 s	3 s
Ar	C/O	8.89	2.29
N	C/O	8.97	3.61
Ar/N	C/N	17.38	3.95
	C/O	12.26	2.92
	C/N	29.02	3.42

Table 2. Polar functional groups formed on the PE surface after plasma modification using different process gases.

Process gas	Polar functional groups			
	C–O	C=O	C–N	C=N
Ar	x	x	–	–
N	x	x	x	x
Ar/N	x	x	x	x

short treatment times. For longer discharge duration of about 20 min sputtering effects can be observed on a used glass sample which has been placed for such a long time in the HCGD discharge.

The polar functional surface groups cause an enhancement in wettability of the PE surface which can be verified by WCA measurements. In Figure 3 the contact angles after different plasma modifications in the HCGD are shown. The

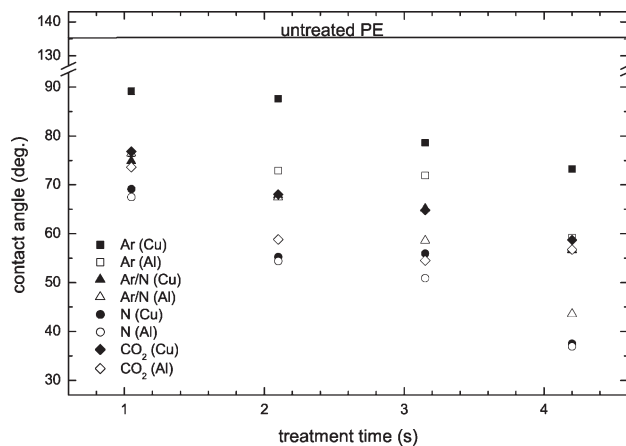


Figure 3. Measured WCAs of plasma modified PE powder using different process gases and hollow cathode materials (filled symbols = copper, unfilled symbols = aluminum) in dependence on effective treatment time.

untreated (hydrophobic) PE powder has a contact angle of 132° . After argon plasma treatment the contact angle decreases from 89° after a treatment time of 1 s to 73° after 4 s plasma treatment. A more pronounced effect can be observed using Ar/N₂ mixture or CO₂ as process gases. In these cases the contact angles decrease after 4 s treatment time to 57° and 59° , respectively. The best enhancement in wettability has been achieved using a pure nitrogen plasma for the modification. The WCA decreases to 38° after a treatment time of 4 s.

However, not only the used process gas affects the enhancement in wettability but also the used hollow cathode material. For example, after a modification with argon plasma, the contact angle decreases to 73° using a copper cathode and to 59° using an aluminum cathode at same discharge conditions. In order to confirm this effect XPS studies of modified PE powder using aluminum as cathode material will be done in the future. The difference in wettability could be referred to the secondary electrons produced during the γ -process depending on the cathode material. The materials possess different secondary electron emission coefficients. The secondary electron emission coefficient of aluminum is different than for copper. This difference could explain that the enhancement in wettability for aluminum as cathode material is more efficient than for copper. The results are the same for PE powder as well as for PE foil materials.

The aging of the plasma modified PE foil was studied, too. In any case the plasma treated PE surface is not stable after exposure to air. The achieved enhancement in wettability after nitrogen plasma treatment in a copper cathode is about 50° directly after plasma treatment and decreases with time (Figure 4). The WCA passes after ca. 4 h into saturation at about 73° , but the aged PE

surface is still more hydrophilic than the untreated surface (132°).

The aging is well known and can be explained by the diffusion of energetically unfavorable groups from the surface and an emergence of the opposite type of groups to the interface in consequence of rotational and translational motions.^[11] The interfacial free energy between the polymer and its environment is minimized by changing the surface composition^[12,13] which can be achieved by the translational and rotational mobility of the polymer chains and chain segments. In a nonpolar environment like air, a polymer minimizes the density of polar groups on the surface^[14] because the unfavorable polar groups diffuse into the polymer bulk and the enhancement in wettability directly after modification decreases and subsequently, the polymer ages.

Conclusion

The plasma treatment of PE powder particles as well as foil material in a spiral conveyor using a hollow cathode discharge as plasma source has been successfully demonstrated. After the plasma modification, polar functional groups can be detected on the powder surface which cause an enhancement in wettability. The plasma treated (hydrophilic) PE powder can be used as filler materials in paints, varnishes, or cosmetics. The enhancement depends on the used process gas, hollow cathode material, and also on the treatment time. The best enhancement has been achieved using nitrogen as process gas and aluminum as hollow cathode material. Additional XPS measurements for aluminum as cathode material should be done in the future. The aging effect was also observed but the modified surface exhibits still better wettability than unmodified PE.

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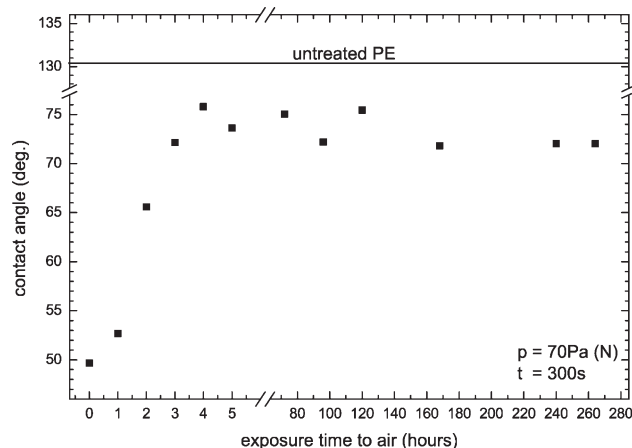


Figure 4. WCAs of modified PE in nitrogen plasma in dependence on the exposure time to air.

- [1] C. Arpagaus, Ph. A. Rossi, R. von Rohr, *Appl. Surf. Sci.* **2005**, 252, 1581.
- [2] N. Inagaki, S. Tasaka, H. Abe, *J. Appl. Polym. Sci.* **1992**, 46, 595.
- [3] C. Vivien, C. Wartelle, B. Mutel, J. Grimblot, *Surf. Interface Anal.* **2002**, 34, 575.
- [4] H. Deutsch, H. Kersten, S. Klagge, A. Deutscher, *Contrib. Plasma Phys.* **1988**, 28, 149.
- [5] R. Dorai, M. J. Kushner, *J. Phys. D: Appl. Phys.* **2003**, 36, 666.
- [6] J.-H. Lee, K.-J. Jeong, *J. Phys. Soc. Jpn.* **2003**, 72, 2530.
- [7] D. J. Sturges, H. J. Oskam, *J. Appl. Polym.* **1964**, 35, 2887.

- [8] M. E. Pillow, *Spectrochim. Acta* **1981**, 36B, 821.
- [9] H. Barankova, L. Bardos, *Surf. Coat. Technol.* **2001**, 146, 468.
- [10] R. R. Arslanbekov, A. A. Kudryavtsev, R. C. Tobin, *Plas. Sour. Sci. Technol.* **1998**, 7, 310.
- [11] R. Chatelier, X. Xie, Th. Gengenbach, H. Griesser, *Langmuir* **1995**, 11, 2576.
- [12] J. D. Andrade, *Polymer Surface Dynamics*, Plenum Press, New York 1988.
- [13] F. Garbassi, M. Morra, E. Occhiello, *Polymer Surface - From Physics to Technology*, Wiley, Chichester **1994**, Chapter 2.
- [14] A. Baszkin, L. Ter-Minassian-Saraga, *Polymer* **1974**, 15, 759.