Fast plasma surface processing of powders

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INTRODUCTION

Motivation

Today, the plasma treatment of polymers is commonly regarded to improve adhesion of subsequently attached materials. Furthermore, plasma cleaning, i.e. oxygen based treatment of metal or ceramic surfaces prior bonding, is already a common processing step in many production lines, e.g. of semiconductor industries (Thornton et al. 1994).
Commercially available reactors are usually suitable to treat (preferably flat) objects with macroscopic surface dimensions. However, they are not for microscopic particulate materials, i.e. powders. This becomes most obvious when considering the insufficiencies in homogeneity and thus efficiency of the desired treatment of a compact powder bulk in such batch reactors.
Agitating the powder bulk, while processing, has shown to improve the desired processing. Here, two designs are to be mentioned: the drum-reactor using baffles, mostly applied in industries, and the fluidized bed reactor often used to conduct fundamental studies (Arpagaus et al. 2005-1).Thus, agitation of the powder bulk is a key factor in determining the residence time distribution the micro-particles. In 1996, Wei and Zhu have already shown that so-called down-stream reactors are superior to other designs in terms of an extremely narrow residence time distribution and of a small mean residence time at all. These parameters, however, exert tremendous influence in view of the aspired homogeneity of the plasma-chemical treatment and its time and energy efficiency, see e.g. Yasuda's parameter. Nevertheless, the beneficial symbiosis of carefully designed reactors, in order to optimize the treatment conditions of particulates (Arpagaus et al. 2005-1), and the benefits of non-thermal plasma-chemistry was rarely achieved.
Powders of the hot-melt adhesives high density polyethylene (HDPE) and Co-polyamide (CoPA) are inherently non-dispersible in water. Required aqueous dispersions or pastes of them, today, are obtained by admixing considerable amount of tensides (Urban and Takamura 2002).
At the example of such powders treated in a plasma down-stream reactor (PDR) for the purpose of improving their wettability, and by an outlook on the treatment of lactose powder, in the same set-up, in order to increase its flowability, the benefits of this approach will be shown.

Precis

This study, partially financed by generous contributions of the Claude & Giuliana Foundation and Novartis Pharma AG, describes plasma assisted improvement of wettability and flowability of different powders, showing the possibility of efficient treatment by choosing a reactor design being adequate in terms of homogenous powder dispersion in the plasma. The time savings possible (tenth of second instead of hours) due to a PDR must be emphasized.

EXPERIMENTAL

The PDR applied (Fig. 1) consist mainly of a cylindrical glass tube (1) of ∅ 4 cm × 50 cm, where at medium height, a low pressure capacitively coupled radio frequency (RF) discharge (13.56 MHz) is ignited. By means of a nozzle in the upper end of the tube, the particulate material supplied by the metering screw (4) is evenly dispersed in the gas stream to the entire cross section of the tube (Arpagaus et al. 2005-1). Optimal exposure of the particulate surfaces to the plasma is achieved. Varying the rotation of the metering screw enables to set the mass of powder dm/dt (Table 1) conveyed from the storage container (3) to the collecting vessels (6).

In the experiments on rendering powders of HDPE and CoPA wettable, mixtures of O_2 and Ar were fed at the top end of the glass tube (1), while in study of improving the flowability of lactose powder, hexamethyldisiloxane (HMDSO) was additionally admixed by means of the evaporation mixer (8). Here, Ar served to supply the mixer with HMDSO from the tank (7) and further to replenish the gas mixture as to keep the mixing ratio q and the total gas flow Q_{tot} (Table 1) constant for all parameter sets. Experiments have been conducted for 1 to 3 min in order to obtain an adequate amount of powder treated for the analytical methods to be applied afterwards.

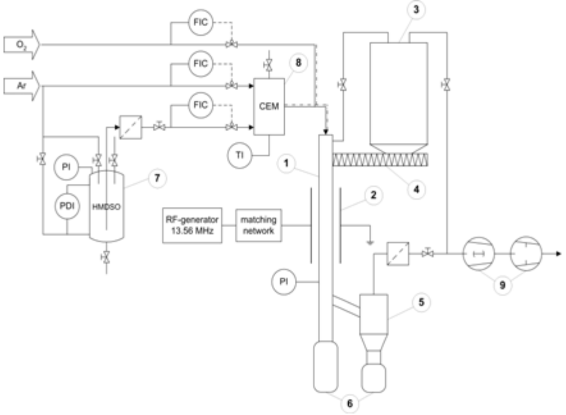

Figure 1. Schematic of the PDR: Descriptive of parts enumerated see in the text.

All powders have been characterized by means of a Krüss tensiometer K100 in order to determine the water contact angle (WCA). To derive the contact angle θ of a test liquid at the surface of particulate material, the capillary penetration method (Buckton 1993) and based on Washburn's theory (1921) was applied. The capillarity constant of the solid powder bulk was determined by the test liquid n-hexane. Water and diiodomethane were used to subsequently determine the surface energy of the powders of HDPE and CoPA. Therefore, Young's equation for the total surface energy at the solid

$$\sigma_s = \sigma_{sl} + \sigma_l \cos(\theta) \tag{1}$$

is combined with the approximation of the solid-liquid tension

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^d \sigma_l^d} - 2\sqrt{\sigma_s^p \sigma_l^p} \tag{2}$$

by Owens and Wendt (1969). Accordingly, the polar part and the disperse part of the total surface energy of the particulate material measured were derived.

Table 1. Properties of the HDPE, CoPA and two qualities of lactose. Plasma treatment conditions.

	HDPE	**CoPA**	**Lactose**	
particle size, x_{50} [µm]	55.6	48.5	6.7	71
specific density [kg/m^3]	950	1100	1525	
powder flow, $\dot{m}$ [kg/h]	5.0	5.0	1.3	2.4
discharge power, P [W]	100	100	100	
Gas pressure, p [mbar]	1.7	1.7	2.0	
total gas flow, Q_{tot} [sccm]	500	500	1183	
$N^*_{HMDSO}/N^*_{O2} = 1/q$	0	0	0.1	
Gas velocity, v_G [m/s]	4.3	4.3	8.7	

In the case of lactose, the contact angle measurements were more complicated than for HDPE and CoPA, because the solubility of the lactose in the test liquids mentioned cannot be neglected.

Therefore, measurements had to be conducted with lactose-saturated test liquids. However, the saturated solutions revealed different surface tensions than the pure liquids and especially the saturated diiodomethane no longer penetrated the solid lactose bulk, indicating a contact angle $\theta > 90°$. Therefore, diiodomethane was substituted by propanol as a test liquid. Furthermore, an experimental procedure for reproducible measurement of the capillarity constant of the lactose powder with a mean particle size of x_{50} = 6.7 µm could not be established. Finally, lactose with x_{50} = 71 µm was chosen as an adequate substitute, assuming though that the tendencies observed are also valid for lactose of a different particle size. Additionally, the plasma effect on the flowability of powder was mainly studied for lactose when admixing HMDSO to the gas (Tab. 1).
The flow behavior is described by the flow factor

$$ff_c = {}^{\sigma_1}\!/_{\sigma_c} \tag{3}$$

Here, σ_1 is the consolidating pressure and σ_c the unconfined yield strength. The higher ff_c, the better a powder flows. Based on ff_c, Schulze (1996) coined the following classification: $ff_c < 1$: not flowing, $1 < ff_c < 2$: very cohesive, $2 < ff_c < 4$: cohesive, $4 < ff_c < 10$: easy flowing, $ff_c > 10$: free flowing. The flow factors reported were determined by a ring shear tester (Schulze Schüttgut-messtechnik, Germany, RST-XS) at a pre-shear stress of 5000 Pa. The powders were antecedently tested by a laser diffraction system (Sympatec, Helos) concerning the cumulative and the differential particle size distributions as to determine the particle size x_{50} (Tab. 1).

RESULTS

Wettability of the HDPE and CoPA powders

The WCA is an adequate quantity to study the wettability. Tests on different external plasma parameters as RF power, gas flow, etc. showed that the most affecting tool is the ratio $[O_2]/[Ar]$.
In Fig. 2, the respective influence of the O_2 content on the WCA for both HDPE and CoPA is shown. Evaluating WCA values of exactly 90° appears questionable since the process of liquid penetrating the powder, on which the analytical method used (Sect. 2) is based, is obviously limited to the very same angle. Thus it belongs to speculations, whether the pure Ar treatment is as well effective or not. Nevertheless, for 10% of O_2, a strong reduction of the WCA is already evident compared to untreated powders. Wettability further improves with increasing O_2 content.

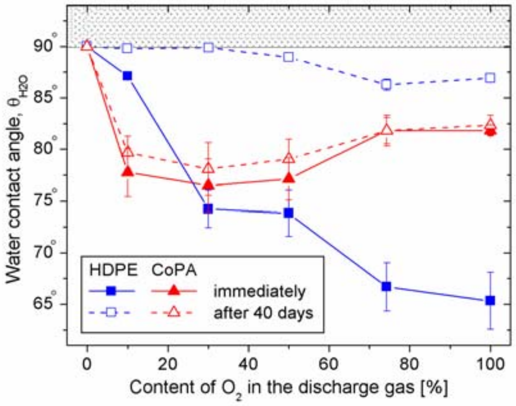

Figure 2. WCA for HDPE and CoPA powders immediately after being treated in the PDR at different O_2 contents (solid symbols) and 40 days after treatment (open symbols)

This behavior is stronger for HDPE, which is free of O (Arpagaus et al. 2005-2). Here, the production of O containing structures at the surface as C-O-C, C=O and O-C=O (evidenced by XPS) appears to be more effective than for CoPA, although the increase in the [O]/[C] ratio is approx. the same. Treated in equal conditions, spectra showed an increase by $\Delta([O]/[C]) \approx 0.16$, adding up to [O]/[C] = 0.27 for CoPA since its innate ratio is ~0.11 (Arpagaus et al. 2005-3). At first sight, these promising results are deteriorated by some kind of hydrophobic recovery of the powders after treatment (Fig. 2) Especially over 7 days after treatment of HDPE, the [O]/[C] ratio was found to decay by approx. 0.05 for O_2 contents of the plasma higher 10% (Arpagaus et al. 2005-2). But, 40 days after treatment, the decay in [O]/[C], i.e. aging, seemed to have stopped. For CoPA, the decay in [O]/[C] is less pronounced (Arpagaus et al. 2005-3). Consequently, almost the same WCAs were obtained when analyzing the powder samples after 40 days (Fig. 2). The decrease in [O]/[C] witnessed by XPS due to the aging of HDPE could be attributed to the diffusion of oxygen containing groups from the surface of an HDPE particulate into its bulk [10]. Obviously this process would be less important for CoPA since the material itself contains oxygen as mentioned before. Thus, the gradient in concentration would be smaller. Nevertheless, also aged powders were found to be dispersible in water if being plasma-treated at O_2 contents > 30% for HDPE and > 10% for CoPA. The aqueous pastes produced are still (2 years later) fully intact. Finally, it must be emphasized that assuming the mean particles velocity being equal to the gas velocity (Table 1), the mean residence time, i.e. the mean treatment time of the particulates is τ = 0.12 s. This is especially noteworthy, since the wettability improvement, obtained by the PDR, is comparable to long-term achievements (1 h) by other workers (Jung et al. 2001).

Wettability of the HDPE and CoPA powders

The idea of flowability enhancement by PECVD in the PDR is illustrated in more detail in (Spillmann et al. 2007). By admixing HMDSO to the plasma in O_2 and Ar at relatively high pressure compared to thin-film PECVD, the creation of agglomerates in the range of a few nanometers (below 3 nm) is favored.

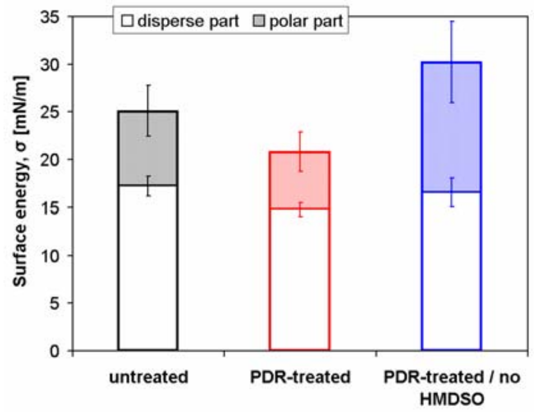

Figure 3. Comparison of surface energies and their disperse and polar parts for lactose (x_{50} = 71 µm) analysed before treatment, after PDR treatment with HMDSO admixed and in O_2/Ar only.

In the same time, the nanoparticles attach to the surface of the particles, here, evoking a decrease of the Van der Waals forces (VdW) between the particles.

Considering the inter-particulate forces acting, we have found the VdW to dominate (Spillmann et al. 2007). According to Hamaker (1937), the VdW between two sphere-like particles is the higher, the larger their radius is. Moreover, it is the smaller, the larger the inter-particulate distance is. Furthermore, it is proportional to the material specific Hamaker constant. The attachment of SiO_x nanoparticles was found to slightly decrease the surface energy of lactose treated (Fig. 3), while lactose treated without HMDSO in the PDR revealed the opposite behavior.

Hamaker's constant is likely to decrease if the disperse part of σ decreases. Being the case for HMDSO treated lactose, the VdW would decrease as well. However, the expected positive effect is much inferior the actual increase in ff_c for lactose treated by HMDSO containing gas mixtures (Fig. 4).

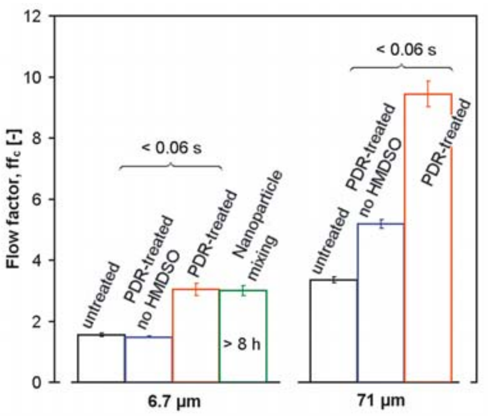

Figure 4. Flow factors of lactose (6.7 µm) and lactose (71 µm) analyzed before treatment, after PDR treatment with HMDSO admixed and treated in O_2/Ar only: Comparison to conventional mixing with silicate nanoparticles for more than 8 h.

Surprisingly, lactose of particle size of 71 µm showed as well a significant increase in its ff_c when being treated without HMDSO admixed. It is speculated that this finding is due to a lasting attachment of charges. The resulting electrostatic repulsion would also enhance flowablity.

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