Fast plasma assisted treatment of solid-state micro-sized particulate material

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Abstract: The plasma assisted improvement of wettability and flowability of different fine powders is described. The plasma down stream reactor designed for an adequate treatment of particulates allows efficient treatment. It is discussed that the fastness of the processes described is due to the homogenous dispersion of particulates in the reactor. This enables intense particle-plasma interaction. The treatment time lies in the range of a tenth of a second instead of hours compared to conventional processes. Concerning the improvement of wettability of hot-melt adhesives, stable aqueous dispersions are obtained even more than 2 years after treatment. Furthermore, the flowability of lactose powder was improved by a factor up to 3.

Keywords: Powder; surface treatment; plasma down stream reactor (PDR); water contact angle (WCA); flowability, flow factor.

1. Introduction

Today, the plasma treatment of polymer is commonly regarded to improve adhesion of subsequently attached materials. Furthermore, 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 [1].

Commercially available ordinary reactors are suitable to treat (preferably flat) objects with macroscopic surface dimensions. However, they are not at all for micro-sized 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 above-mentioned process properties. Two designs are to be mentioned here: the drum-reactor using baffles, mostly applied in industries, and the fluidized bed reactor often used to conduct fundamental studies [2].

Thus, agitation of the powder bulk is a key factor in determining the residence time distribution the micro-particles. In 1996, Wei and Zhu [3] have already shown that a so-called down stream reactor is 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 [2], 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 [4].

At the example of such powders treated in a plasma down-stream reactor (PDR) for the purpose of improving their wettability, and by an out-look on the treat-
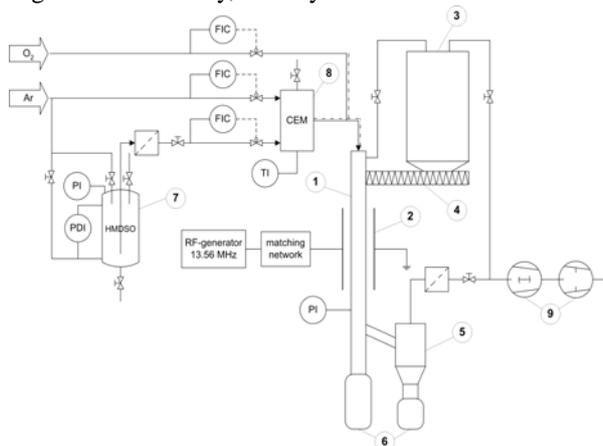
Fig. 1 Schematic of the PDR: (1) glass tube, (2) electrodes, (3) solid storage container, (4) metering screw, (5) cyclone, (6) solid collecting vessels, (7) monomer tank, (8) temperature controlled evaporator mixer , (9) vacuum pump unit, FIC - flow indicator controller, PDI - pressure differential indicator, PI - pressure indicator, TI - temperature indicator.

ment of temperature sensitive lactose powder, in the same set-up, in order to increase its flowability, the benefits of this approach will be shown.

2. Experimental

The PDR used is schematically shown in **Figure 1**. Its core piece is a cylindrical glass tube (1) of $\varnothing 4 \text{ cm} \times 50 \text{ cm}$, 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 sup-

plied by the metering screw (4) is evenly dispersed in the gas stream to the entire cross section of the tube [2]. By this means, optimal exposure of the specific surface of the particulate material to the plasma is achieved. Varying the rotation frequency of the metering screw enables to set the mass of powder $\dot{m} = dm/dt$ (**Tabel 1**) conveyed from the storage container (3) - through the plasma - to the collecting vessels (6).

Table 1 Properties of the HDPE, CoPA and two qualities of lactose. Conditions of the plasma treatment.

	HDPE	CoPA	Lactose	
particle size, x_{50} [µm]	55.6	48.5	6.7	71
specific density [kg/m³]	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 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 flowablity 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.

All powders have been characterized by means of a tensiometer (Krüss, 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 [5] based on Washburn's theory [6] was applied. The capillarity constant of the solid powder bulk was determined by the test liquid n-hexane (Fluka, N° 52770, > 98%). Beside water and hexane, diiodomethane (Fluka, N° 66880, > 98%) was used to subsequently determine the surface energy of the powders of HDPE and CoPA.

Therefore, Young's equation [7] for the total surface energy at the solid

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

is combined with the approximation of the solid-liquid tension

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

by Owens and Wendt [8]. Accordingly, the polar part σ_s^p and the disperse part σ_s^d of the total surface energy of the particulate material measured were derived.

In the case of lactose, the contact angle measurements turned out to be more complicated than in the case of HDPE and CoPA. At first, 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 θ > 90°. Therefore, diiodomethane was substituted by propanol.

Furthermore, an experimental procedure for a 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.
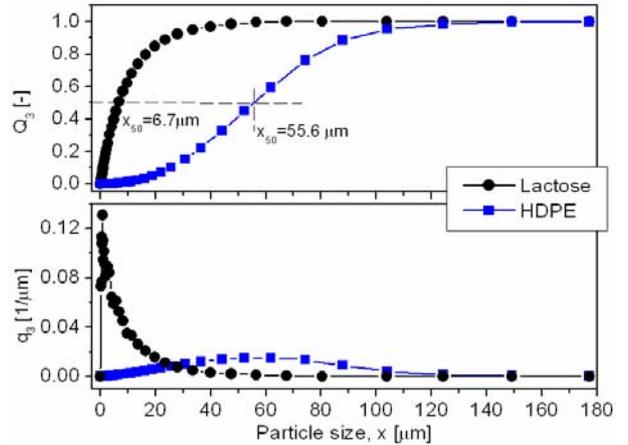
Fig. 2 Cumulative and differential particle size distribution, Q_3 and q_3 exemplarily shown for the powder of HDPE and the finer lactose powder.

The flow behavior of the particulate material was studied for the lactose qualities, only, because the HDPE and CoPA powders with relatively large particle sizes (**Table 1**) revealed sufficient flowablity for the aspired process of wettablity improvement.
A measure for the flowablity of a powder can be given by the flow factor

$$ff_c = \sigma_1 / \sigma_c \qquad (3)$$

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 [9] coined the fol-

lowing 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 [4] (Schulze Schüttgutmesstechnik, Germany, RST-XS) at a pre-shear stress of 5000 Pa.

The powders to be treated were additionally characterized by means of a laser diffraction system (Sympatec, Helos). The cumulative and the differential particle size distributions, Q_3 and q_3, concerning the powder mass allow determining the characteristic particle size x_{50}, see **Figure 2**.

3. Results and discussion

3.1 Wettability of the HDPE and CoPA powders

The WCA is an adequate quantity to study the wettability, i.e. the likeness of a powder forming an aqueous dispersion. Preliminary tests on different external plasma parameters as RF power, gas flow, etc. showed that the most affecting parameter is the ratio [O_2]/[Ar].
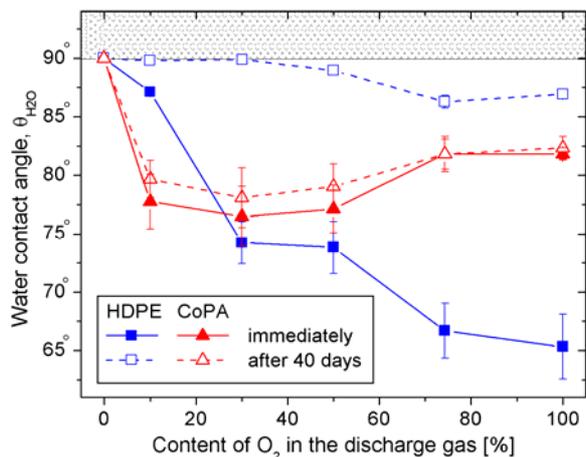
Fig. 3 WCA for HDPE and CoPA powders immediately after being treated in the PDR at different O_2 contents (solid symbols) and 40 days after treatment (open symbols).

In **Figure 3**, 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. This behavior is stronger for HDPE, which is *per se* free of oxygen [10].

Here, the production of oxygen 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 approxi-

mately the same. Treated at the same conditions, XPS measurements reveled an increase by approximately $\Delta([O]/[C]) = 0.16$, which add up to [O]/[C] = 0.27 for CoPA since its innate ratio is ~0.11 [11].

At first sight, this promising result, however, appears

Fig. 4 Comparison of untreated (left) and 0.12 s plasma-treated (right) HDPE powder, while testing their dispersibility in water.

affected by some kind of hydrophobic recovery (aging) of the powders after treatment (**Figure 3**).

This is especially articulated for HDPE. Here, over 7 days after treatment, the [O]/[C] ratio was found to decay by approx. 0.05 for O_2 contents of the plasma higher 10% [10]. For 40 days after treatment, however, the decay in [O]/[C] seemed to have stopped. Thus, aging was no longer making progress.

For CoPA, the decay in [O]/[C] was found to be not as important as for HDPE [11]. Consequently, almost the same WCAs were obtained when analyzing the powder samples after 40 days (**Figure 3**). The decrease in [O]/[C] witnessed by XPS due to the aging of HDPE could be attributed to the diffusion of oxygen contain-
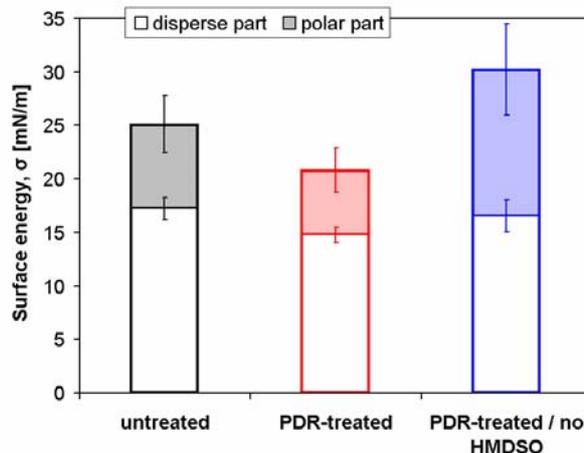
Fig. 5 Comparison of surface energies and their dispers and polar parts for lactose ($x_{50} = 71$ µm) analysed before treatment, after treatment in the PDR with HMDSO admixed to O_2/Ar and treated by O_2/Ar plasma only.

ing 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 dispersions pro-

duced are still fully intact, even now more than 2 years later (**Figure 4**). 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 $\tau = 0.12$ s. This is especially noteworthy, since the wettability improvement, obtained by the PDR, is comparable to long-time achievements (1 h) by other workers [12].

3.2 Flowability of the lactose powder

The idea of flowability enhancement by PECVD in the PDR is illustrated in more detail in [13] and [14]. By admixing HMDSO to the RF plasma in O_2 and Ar at relatively high pressure compared to thin-film PECVD, the creation of SiO_x agglomerates in the range of a few nanometers (below 3 nm) is favored. In the same time, the nanoparticles are assumed to attach to the surface of the lactose substrate particles, acting as spacers evoking a decrease of the Van der Waals forces (VdW) between the particles of the powder treated.
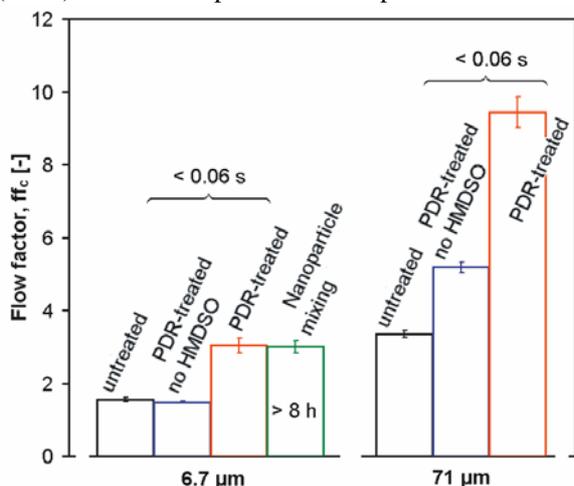
Fig. 6 Flowabilities of lactose (6.7 µm) and lactose (71 µm) analyzed concerning their flow factors: before treatment, after treatment in the PDR with HMDSO admixed to O_2/Ar , treated by O_2/Ar plasma only. PDR-treatment time (0.07 s) and ff_c improvement compared to conventional mixing process with silicate nanoparticles for more than 8 h [15].

Considering the inter-particulate forces acting, we have found the VdW to dominate [14]. According to Hamaker [16], 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 assumed attachement of SiO_x nanoparticles was found to slightly decrease the surface energy σ of lactose treated (**Figure 5**), while lactose treated without HMDSO in the PDR revealed the opposite behavior. Hamaker's constant is likely to decrease if the dispers part of σ of the particulates 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 (**Figure 6**). 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 attachement of charges. The resulting electrostatic repulsion would add to the increase of flowablity.

4. Conclusions

The plasma assisted improvement of wettability and flowability of different powderous materials is described, showing the possibility of fast, i.e. efficient treatment by choosing a reactor design being adequate to the treatment of powders in terms of homogenous dispersion, i.e. mixing of the powder within the plasma. The time savings possible (tenth of a second instead of hours) by a PDR treatment must be emphasized.

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