Effect of oxygen content on the functionalization of polymer powders using an atmospheric plasma jet in combination with a fluidized bed reactor

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Abstract: Additive manufacturing processes such as laser beam melting (LBM) of polymers have gained more importance for industrial applications [1]. To cover the increased demand, limitations regarding the performance of the used polymer materials have to be overcome. Especially the mechanical stability of the processes parts is weak. By a functionalization of the surface of commercially available polymer particles this problem can be overwhelmed. The proposed solution is a functionalization using an atmospheric plasma jet in combination with a fluidized bed reactor. Consequently, an improvement of adhesion and wettability [2] of the polymer surface without restraining the bulk properties of the powder is achieved. The atmospheric plasma jet process can provide reactive species at moderate temperatures which are suitable for polymer material.

Keywords: Polymer Functionalization, Atmospheric Plasma Jet, Fluidized Bed Reactor, LBM-Process

1. Introduction
Additive manufacturing processes as laser beam melting (LBM) are more and more shifted towards industrial use. However, the named processes still show unsatisfying boundary conditions. One major drawback is limited strength of parts build. To increase the surface energy of polymeric material used in LBM processes a functionalization of the powder is demanded. The temperature sensitivity of the material makes it difficult to use classic chemical pathways as chemical vapor deposition (CVD) which requires temperatures up to 400-500 °C under atmospheric conditions. To overcome these process limitations, an atmospheric plasma jet (APPJ) which can provide reactive chemical species at moderate temperatures [3] is utilized. As operating gas, pressurized air as well as noble gases (e.g. Argon) and inert gases (e.g. Nitrogen) can be used [4, 5]. Depending on the operating gas taken to ignite the plasma jet, different gas phase radicals are generated. Possible gas phase species for a plasma operated with mixtures of Argon and Oxygen are displayed in Figure 1.

![Figure 1. Possible gas phase species for an Ar/O2 Plasma](image)

By a plasma treatment the particle surface is cleaned of residues after the polymerization process and, more important, reactive groups are generated on the particle surface by interactions of the plasma radicals with the active groups of the polymeric chain. The mechanism and possible reaction pathways between plasma radicals and the polymeric structure is not fully understood [6].

2. Experimental Set-Up
Since the operating temperature of common APPJ still exceeds the melting temperatures of standard polymers used in LBM-processes, the plasma is combined with a fluidized bed reactor (FBR) in order to use the excellent heat and mass transfer mechanisms of this reactor type [7]. The specific set-up used in this contribution is shown in Figure 3.

![Figure 2. Set-Up of the fluidized bed reactor equipped with the plasma nozzle](image)

The plasma nozzle is located in the center of the feed zone of the fluidized bed reactor (see Figure 3). To avoid unnecessary contact between the hot plasma jet and the temperature sensitive polymer material, the jet is kept in a housing.
The plasma source was a commercially available system by Plasmatreat, Germany. The plasma was ignited at a frequency of 21kHz with a voltage of 280V. For the experiments shown in this contribution, different mixtures of Argon (Ar, 5.0 Quality, Linde AG) and Oxygen (O₂, 5.0 Quality, Linde AG) are utilized. The temperature of the material can be monitored using three thermocouples. In all experiments the temperature is not affected by the O₂ in the gas mixtures and does not exceed 30°C. As polymer material PA 12 (PA2200; EOS; Germany) as a common polymer used in LBM processes has been investigated. For each experiment around 750ml of polymer powder is processed.

3. Results

To evaluate the effect of the plasma treatment on the surface conditions of the polymer particles, the contact angle as well as the zeta potential was investigated. The contact angle was determined on pellets of the material with a diameter of 13mm, which were compressed with a pressure 2bar. The angles were then measured using an OCA20 by Data Physics using H2O as measuring liquid. The treatment time was 120s for all samples. It is important to say, that the overall treatment time in the FBR is not equal to a direct contact time of the plasma and single particles. The contact time can be calculated by an ideal stirred tank reactor approach to approximately 0.7s. The results for the contact angle measurements are shown in Figure 4.

The results in Figure 4 show that a treatment with pure argon does not have an influence on the contact angle of H₂O. However, treatment of the particles with a plasma ignited with a mixture of 95% Ar and 5% O₂ leads to a significant reduction of the contact angle and thus to a more hydrophilic behavior. An increased amount of oxygen in the gas mixture reduces this effect again. For gas mixtures of 15% and 20% O₂ the initial contact angle of the untreated material can be measured again. The reason for this effect could be an instantaneous combination of created O radicals to stable forms within the plasma which are then no longer available for further reactions with the polymer.

To further investigate the treatment effect, the zeta potential was measured using a Nano ZS by Malvern. These results are shown in Figure 5.

The results of the zeta potential show an increased negative value of the potential with an increased amount of oxygen in the plasma gas. This effect could be attributed to the incorporation of charged molecule in the surface of the particle. In this case, a further decline of the zeta potential is also visible for higher amounts of oxygen in the plasma gas. The mechanisms behind the differences in the two measurement methods are not completely understood and will further be investigated.

4. Conclusion

It is shown, that a combination of a FBR with an atmospheric plasma jet is suitable for the functionalization of polymer particles is possible. Since the Scale-Up mechanisms for fluidized bed systems are well understood, the experimental set-up can be used to produce industrial relevant amounts of powder material for LBM processes. The influence of different gas mixtures ignited in the plasma on contact angle and zeta potential have been investigated. The results indicate that there is an optimum content of O₂ in the gas mixture used for the plasma ignition.

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6. References