Characterization of polymer materials and powders for selective laser melting

K. Wudy, D. Drummer, and M. Drexler

Citation: [AIP Conference Proceedings](#) **1593**, 702 (2014); doi: 10.1063/1.4873875

View online: <http://dx.doi.org/10.1063/1.4873875>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1593?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Simulation of the temperature distribution in the selective beam melting process for polymer material](#)

AIP Conf. Proc. **1593**, 708 (2014); 10.1063/1.4873876

[Rapid additive manufacturing of MR compatible multipinhole collimators with selective laser melting of tungsten powder](#)

Med. Phys. **40**, 012501 (2013); 10.1118/1.4769122

[Comparison of aged polyamide powders for selective laser sintering](#)

AIP Conf. Proc. **1431**, 5 (2012); 10.1063/1.4707544

[Modeling the selective laser melting of polylactide composite materials](#)

J. Laser Appl. **23**, 012005 (2011); 10.2351/1.3538944

[Characterization of Dielectric and Magnetic Properties of Powdered Materials such as Powdered Coal](#)

AIP Conf. Proc. **820**, 461 (2006); 10.1063/1.2184564

Characterization of Polymer Materials and Powders for Selective Laser Melting

K. Wudy^{1*}, D. Drummer¹ and M. Drexler¹

¹*Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nuernberg, Germany –
info@lkt.uni-erlangen.de, wudy@lkt.uni-erlangen.de*

Abstract

Concerning individualization, the requirements to products have increased. The trend towards individualized serial products faces manufacturing techniques with demands of increasing flexibility. Additive manufacturing techniques generate components directly out of a CAD data set while requiring no specific tool or form. Due to this additive manufacturing processes comply, in opposite to conventional techniques, with these increased demands on processing technology. With a variety of available additive manufacturing techniques, some of them have a high potential to generate series products with reproducible properties. Selective laser melting (SLM) of powder materials shows the highest potential for this application. If components made by SLM are desired to be applied in technical series products, their achievable properties play a major part. These properties are mainly determined by the processed materials. The range of present commercially available materials for SLM of polymer powders is limited.

This paper shows interrelations of various material properties to create a basic understanding of sintering processes and additional qualifying new materials. Main properties of polymer materials, with regard to their consolidation are viscosity and surface energy. On the one hand the difference of the surface energy between powder and melt influences, the wetting behavior, and thus the penetration depth. On the other hand, a high surface tension is fundamental for good coalescence of bordering particles. To fulfill these requirements limits of the surface tension will be determined on the basis of a reference material. For these reason methods for determining surface tension of solids, powders and melts are analyzed, to carry out a possible process-related material characterization. Not only an insight into observed SLM phenomena is provided but also hints concerning suitable material selection.

Keywords: selective laser melting of polymers, material characterization, surface tension

INTRODUCTION

Selective laser melting of polymers is an additive manufacturing technique that allows manufacturing of complex parts without any tools or molds. Concerning individualization, the requirements posed to products have increased in recent years. Therefore selective laser melting makes the production of complex geometries possible and reduces additional production steps and assemblies. This is how, as opposed to conventional techniques like injection molding, they comply with the increased demands to processing technology. In particular, Additive manufacturing techniques are established in rapid prototyping. A tendency has recently revealed towards the rapid manufacturing of components for engineering applications. That is why the requirements regarding quality management and process reliability have increased. [1, 2]

In selective laser melting of polymers a powdered material and a CO₂ laser is used, to selectively heat and fuse plastic powder particles into a complete layer. In a first step the powdery good is applied into a building chamber, which is preheated on a temperature between the melting and crystallization temperature of the polymer. Afterwards a CO₂ laser controlled by a scanning system heats selectively the cross section of the generated component to fuse particles together and produce a homogeneous melt. The surrounding powder particles remain loosely in the build chamber,

supporting the molten structure. Then the building chamber is lowered over the thickness of one layer, usually 0.1 mm and a new layer of powder is applied. Step by step, this process is repeated until the component is completed. After production process the whole building chamber with its powder and components is cooled down slowly. A schematic of the selective laser melting process is shown in Figure 1. [1,3]

FIGURE 1: Schematic process cycle of selective laser melting of polymers

If components made by additive manufacturing are due to be applied in serial production, their achievable properties and reproducibility play a major role. To enlarge the process reliability basic understanding of the process is inalienable. There are plenty of material-dependent influencing factors which affect the process of selective laser melting. During of material coating powder properties like particle geometry and particle size distribution play a major role. Whereas the viscosity of the melt, the surface tension of the solid powder and melt are mainly influencing the phase of material consolidation. On the one hand surface tension

of solid and melt influences the wetting behavior and thus the contour accuracy. On the other hand surface tension determines the sinking depth of melt into powder bed and is therefore responsible for the representation of shape details and surface roughness. This paper shows interrelations of the surface tension of the solid materials and of melts to create a basic understanding of sintering processes. [4-6]

In selective laser melting of polymers various phase boundaries occur where interfacial phenomena are important. If the melt meets the powder bed, a phase boundary between the melt and the powdery good arise. This phase boundary is responsible for the contour accuracy as well as surface roughness. In laser melting process a third medium, a gas occurs at the phase boundary. However, the interaction at the interface is strongly influenced by the solid's surface tension. The difference between the surface tension of the solid and melt determines whether wetting can occur or not. The following equilibrium known as Young equilibrium expresses the dependence of the surface tension of melt and solid on the wetting angle. [7-9]

$$\sigma_S - \sigma_{SL} = \sigma_L \cdot \cos\gamma \quad (1)$$

Whereas σ_s stands for the surface tension of the solid powder material and σ_L is the surface tension of the melt. The angle between the solid substrate and the liquid is γ and the resulting interface tension is σ_{SL} . If $\sigma_s - \sigma_{SL}$ is bigger than σ_L or $\cos\gamma$ is one the liquid will wet the solid substrate completely. The equilibrium of a liquid in contact with a solid is shown in Figure 2. [9]

FIGURE 2: Three-phase equilibrium for wetting systems

The spreading pressure (S) characterizes the wetting behavior of a system consist of a solid and a liquid / melt. [9]

$$S = \sigma_S - \sigma_L - \sigma_{SL} \quad (2)$$

If the spreading pressure is greater than or equal to zero, spreading will occur. The greater the spreading pressure is, the better the melt will wet the solid. Thus, wetting is favored by high solid surface tension and low liquid surface tension. Therefore the value of the solid and melt surface tension determines the wetting properties and thus contour accuracy. The surface tension is therefore a necessary criterion for the sintering process. [8, 10]

However, for the process of laser melting is also critical to which extent the melt seeps inside the powder bed. The sinking depth is defined as the depth to which extent the melt sinks into the powder bed. The sinking depth can be expressed mathematically by the following Washburn equation [5, 6]

$$p = h \cdot \rho \cdot g = \frac{2 \cdot \sigma_L \cdot \cos\gamma}{x} \quad (3)$$

where h is the sinking depth, g is the constant of gravitation, ρ is the density of melt and x is the distance between two particles. Girifalco and Good developed the following important relationship between σ_L and σ_S [11]

$$\cos\gamma \approx 2 \cdot \Phi \cdot \left(\frac{\sigma_S}{\sigma_L} \right)^{\frac{1}{2}} - 1 \quad (4)$$

with

$$\Phi \approx \frac{4 \cdot (V_S - V_L)^{1/3}}{(V_S^{1/3} + V_L^{1/3})^2} \quad (5)$$

In this equation V_S and V_L are the molar volume of the solid and melt. The equations 3 and 4 shows, that a high surface tension of the solid particles in combination with a low surface tension of the melt leads to a $\cos\gamma$ greater zero and thus to a high sinking depth. Hence, this is responsible for a high surface roughness and poor surface quality of the generated components.

Statements before lead to the following requirements a material has to fulfill to produce components with high contour accuracy and surface quality.

- To reach a high contour accuracy, the melt has to wet the solid material, that's why a high solid surface tension and low liquid surface tension is needed.
- To avoid absorption of the melt into the powder bed and generate a high surface quality, the surface tension of the solid should be as low as possible.

So there are two contradictory requirements for the surface tension of the material. In subsequent studies, the influence of an increasing surface tension of the solid on the sinking depth and contour accuracy is analyzed. Therefore the laser melting powder was functionalized by plasma treatment to enlarge the surface tension of the powder. Functionalization leads to additional groups, in the case of ambient air as plasma gas oxygen groups, on the powder surface. The plasma treatment does not change the chemical structure of the polymer for which reason the functionalization is reversible in the molten state. Thus, by the plasma treatment, the surface tension of the solid can be changed at constant surface tension of the melt.

Methods to determine surface tension of solids and melt

The surface tension of a solid and melt can be measured in different ways. But only σ_L can be determined with experiments directly. However the knowledge of the characteristics σ_s , σ_{SL} is essential for understand adhesion phenomena in selective laser melting. [9]

The surface tension of solids can in opposite to liquids only determined indirectly. The surface tension of the

solid can be calculated from measurements of the contact angle between the solid and different liquids with the sessile drop method. As liquids different test fluids with known surface tension are used. The test fluid has to have a higher surface tension than the solid to form a measurable contact angle. With the known surface tension of the test fluid and the measured contact angle between solid and fluid the surface tension of the solid can be calculated according to equations of state, e. g. Neumann, Wu as well as Owens and Wendt. [9]

The surface tension of melts or liquids can be determined with the so called punch method. In contrast to the determination of the solid surface tension, the surface tension of the melt is determined directly from the drop geometry. This method utilizes a metal punch, where the test medium is placed on. The liquid or melt wets the surface of the punch to form a drop. By using the Young-Laplace equation the surface tension of the melt can be calculated from drops' geometry with the following equation: [9]

$$\sigma_L \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \rho \cdot g \cdot h \quad (6)$$

where R_1 , R_2 are the radii of the curvature, ρ is the density of the melt, g is the constant of gravity and h is the vertical height of the drop (see figure 3).

FIGURE 3: Determining the surface tension of the melt with the punch method

The measurement of surface tension is influenced by several parameters. These include the measurement system itself, the surface roughness, the ambient conditions as well as the temperature [9]. Therefore estimation of the surface tension from molecular parameters is developed by Sugden and is defined according to the following equation,

$$\sigma = \left(\frac{P_s}{V} \right)^4 \quad (6)$$

where P_s is the parachor, σ is the surface tension and V is the molar volume. The measured surface tension is compared with the calculated by means of the parachor to forego in the future costly measuring methods like determination of the surface tension with the sessile drop method. [11]

EXPERIMENTAL

Material

In selective laser melting Polyamide 12 (PA 12) powder is used commercially. An unmodified PA 12 laser melting powder type PA 2200 from the supplier EOS GmbH, Germany, was chosen determination of the surface tension in melted and powdery state.

Plasma treatment

The powder was treated on an atmospheric pressure plasma jet apparatus with ambient atmosphere. Plasma treatment time was 120 seconds. After plasma treatment the powder material was immediately closed airtight in a specimen cup to avoid contamination.

Surface tension measurement

For the determination of surface tension of the powder, the sessile drop method was used. The determination of the surface tension of solids with the sessile drop method is an indirect method. For the measurements an instrument from the company DataPhysics was used. The surface tension of the solid was calculated according to the equation from Neumann. To generate a homogenous surface the powder was cold compressed to a pellet (diameter: 13 mm) with a pressure of approximately 1500 bar. The contact angles between the pellet surface and the measuring fluid with known surface tension were measured within one day after the plasma treatment. As measuring fluid distilled water was used. With a microliter syringe a 2 μ L drop was put on the pellet. The drop is illuminated from one side by a light source and is observed by a CCD camera system on the other side. Four pellets were produced and on each pellet four drops were placed to measure the contact angle. The surface tension of the solid was measured at 30, 45 and 60 $^{\circ}$ C under nitrogen atmosphere.

The surface tension of the PA 12 melt was determined with the so called punch method. The measurements were conducted on unfunctionalized and functionalized PA 12 powders to analyze whether plasma treatment changes the surface tension. For the measurements a heatable measuring cell with an inert atmosphere was used. The surface tension of the melt was measured at 185, 190, 195, 200, 205, 210, 215 and 220 $^{\circ}$ C under nitrogen atmosphere to avoid degradation of the polymer.

For the calculation of the surface tension according to Sugden using the parachor pressure volume temperature (PVT) measurements are conducted. From these measurements the molar Volume of PA 12 can be calculated. For PVT measurements a cooling rate of 1 K/min and a pressure of 400 as well as 800 bar were used. Then the various pressure curves are extrapolated to 1 bar, to calculate the molar volume as a function of temperature.

Processing Experiments

To analyze the contour accuracy and the sinter depth due to different powder surface tensions constant boundary conditions, e. g. homogenous temperature distribution, are required. Therefore, in small building chambers only one layer is manufactured by selective laser melting. Afterwards produced layers will be analyzed with regard to their contour accuracy and sinter depth by photo-optical methods and transmitted-light microscopy under polarized light. Layers were produced with a selective laser melting machine (supplier: DTM, equipment: Sinterstation 200 type) by a laser power 15 W and scanning speed 1257 mm/sec. In the processing experiments a square with an edge

length of 25 mm was exposed. To analyze the influence of functionalization, layers were generated from powder with and without plasma treatment at a temperature of 23 and 175 °C.

RESULTS AND DISCUSSION

Surface tension

Figure 4 shows the specific volume as well as the calculated surface tension in dependency of the temperature. With increasing temperature the surface tension decreases. In selective laser melting of PA 12 the surface tension of the powder and melt at the building temperature (approx. 175 °C) is of interest. With selective laser melting, melt and solid material both exist over the entire period of building in a so called two-phase mixture area. For the PVT measurements, the material is first melted and then cooled down with a defined cooling rate. In the cooling phase the reduction of the specific volume is measured in dependency of the temperature. Hence, only the surface tension of the melt can be calculated with these measurements at building temperature. In addition, due to the melting of the material, the plasma functionalization is repealed. Therefore the calculation of the surface tension in this case is suitable only for polymer melts.

FIGURE 4: Specific volume and calculated surface tension independency of temperature

In addition to the calculated surface tension in figure 5 the measured surface tension of the powdery material and melt is shown. The surface tension of the melt of the functionalized and unfunctionalized PA 12 powder is on the same level between 35 and 40 mN/m. The calculated surface tensions of the melt are in comparison to the measured values lower. This can be justified by the calculation method as the calculation by means of the group contributions to the parachor gives only an approximation. A still higher accuracy can be reached with the direct measurement of melt's surface tension. The experimental values of the surface tension of the solid compared to calculated values show a large discrepancy between these values. The

measured values are approximately 20 mN/m below the calculated surface tensions. The surface tension of the solid can be measured only indirectly. Due to this the specimen roughness has influence on the determined values. The surfaces of the pellets have a high surface roughness, because as basic material a powdery good is used. With increasing wetting surface the determined surface tension decreases according to [Kop.]. In addition, as mention, the calculated surface tensions exhibit no difference between the pretreated and basic PA 12 powder. Whereas the determined surface tensions with sessile drop method reveal an influence of pretreatment. As expected the values of the surface tension rises with plasma functionalization, due to additional polar groups on the powder surface. To summarize the surface tension measurements and calculations it can be said that in the case of melts the punch method is preferred. In the case of solid's surface tension the sessile drop method is favored due to differentiation of functionalized and unfunctionalized powder is possible.

FIGURE 5: Measured surface tension in dependency of temperature

In selective laser melting surface tension in theory influences both the contour accuracy and the sinking depth. Therefore the PA 12 powder and the plasma treated PA 12 powder were processed with a selective laser melting machine. An increase in the surface tension of the powder in combination with an unchanged surface tension of the melt results in a larger spreading coefficient S according to equation 2. Due to this correlation the melt will wet a larger area of solid surface. Figure 6 indicates this effect. The red squares in figure 6 represent the respective exposed areas. Therefore it is obvious that the pre-treated material is filling always a larger surface area vertical to the scan lines. Due to effects of curling it is not possible to make a statement on the contour accuracy in the direction of the scan lines. With increasing temperature the density of the layers increases as well, because of lower melt viscosity. The investigations reveal that by plasma treatment, the surface tension of

the powder is increased and thus the contour accuracy can be improved slightly. The studies show a clear trend. However analyzes with a higher surface tension difference of the powder, e.g. with different plasma gases must be conducted to verify these results.

FIGURE 6: Photo of a layer manufactured at a powder temperature of 23 and 175 °C (left: PA 12, right: pretreated PA 12)

To determine the sinking depth of the melt into the powder bed the generated layers will be cut and analyzed by polarized light microscopy. Figure 7 shows microscopy of cuts through sintered layer at 23 and 175 °C. As basic powder material PA 12 and plasma pre-treated PA 12 was used. The density of layers manufactured at 23 °C is much lower compared to the layers sintered at 175 °C. Thus it is not possible to determine the sinking depth of the layers with low density. Due to higher surface tension of the pre-treated powder it is expected, that the sinking depth will rise. Results shown in Figure 7 down reveal that with increasing surface tension of the powder the sinking depth raised slightly. The specimen builds with unfunctionalized PA 12 powder exhibit a sharp separation between molded material and powder. Whereas the specimen made of plasma treated PA 12 powder shows a rough break between melt and powder. Some of the particles seem to be embedded from the melt. The increasing surface tension of the powder seems to result in increasing sinking depth, due to capillary effects, which leads to a higher surface roughness and worse surface quality. The shown investigations point out that with increasing surface tension the sinking depth increases. However, this must be verified with further investigations.

Consequently, plasma treatment leads to a higher surface tension of the powder, which influences the contour accuracy in a positive way. But in theory the sinking depth increases with the surface tension as well and the surface quality becomes worse. This trend was indicated by the analysis shown.

FIGURE 7: Cut through a layer manufactured at a powder temperature of 23 and 175 °C (left: PA 12, right: pretreated PA 12)

CONCLUSION

Within the paper it could be shown, that there is a correlation between the calculated and measured surface tensions of the melt. For plasma treated material it is recommended to determine the surface tension of the solid with the sessile drop method.

The article shows that the surface tension influences both the contour accuracy as well as the sinking depth. A higher surface tension of the powder leads to a higher spreading coefficient and results finally in a larger contour accuracy. However, the increase of the surface tension causes in theory capillary effects which conduct larger sinking of the melt into the powder bed. The sinking depth increases in the shown investigations slightly. That is why further investigations in this field are necessary.

The functionalization therefore makes sense if the contour accuracy plays a major role. But, if the improvement of the surface quality is of main importance an increase in the surface tension of the powder is not conducive.

ACKNOWLEDGEMENTS

The authors would like to extend their thanks to the German Research Association (DFG) for funding the Collaborative Research Centre 814, project A3. This support has enabled the investigations in the area of additive manufacturing which have led to the results presented in this article.

REFERENCES

1. T. Wohlers, *Wohlers Report 2009 - Rapid Prototyping - State of the Industry*, 2009.
2. B. Wendel, E. Schmachtenberg, and C. Dallner, *Additive processing - New developments in Selective lasersintering of polymers*, *SPE Proceedings ANTEC*, Milwaukee, USA, 2008.
3. A. Gebhardt, *Grundlagen des Rapid Prototyping*, *RTEjournal*, p. S. 1 - 16, 2004.
4. J.-P. Kruth, *Consolidation phenomena in laser and powder-bed based layered manufacturing*, *CIRP Annals - Manufacturing Technology*, p. 730-759, 2007.
5. T. Seul, *Ansätze zur Werkstoffoptimierung beim Lasersintern durch Charakterisierung und Modifizierung grenzflächenenergetischer Phänomene*, Institut für Kunststoffverarbeitung, RWTH Aachen, 2004.
6. G. Alscher, *Das Verhalten teilkristalliner Thermoplaste beim Lasersintern*, Universität Essen, 2000.
7. G.W. Ehrenstein and G. Ahlers-Hestermann, *Handbuch Kunststoff-Verbindungstechnik*, Hanser, München, 2004.
8. E. Schmachtenberg and T. Seul, *Model of isothermal laser-sintering*, 60th Annual Technical Conference of the Society of Plastic Engineers (ANTEC), San Francisco, California, 2002.
9. A. Kopczynska, *Oberflächenspannungs-phänomene bei Kunststoffen - Bestimmung und Anwendung*, Friedrich-Alexander-Universität Erlangen-Nürnberg, Lehrstuhl für Kunststoff-technik, 2008.
10. A. Kopczynska and G.W. Ehrenstein, *Polymeric surfaces and their true surface tension in solids and melts*, *Journal of Materials Education*, p. 325 - 340, 2007.
11. D.W. Van Krevelen, *Properties of Polymers - Their estimation and correlation with chemical structure*, Amsterdam, Oxford, New York Elsevier Scientific Publishing Company, 1976.