Annals of DAAAM for 2010 & Proceedings of the 21st International DAAAM Symposium, Volume 21, No. 1, ISSN 1726-9679
ISBN 978-3-901509-73-5, Editor B. Katalinic, Published by DAAAM International, Vienna, Austria, EU, 2010
Make Harmony Between Technology and Nature, and Your Mind will Fly Free as a Bird
3rd DAAAM-ICAT

DEGRADATION BEHAVIOR AND MATERIAL PROPERTIES OF PA12-PLASTIC POWDERS PROCESSED BY POWDER BASED ADDITIVE MANUFACTURING TECHNOLOGIES

KUEHNLEIN, F[lorian]; DRUMMER, D[ietmar]; RIETZEL, D[ominik] & SEEFRIED, A[ndreas]

Abstract: *Selective mask and laser sintering are powder based, additive manufacturing technologies, which allow the production of complex parts layer-by-layer. Due to the high building chamber temperature during processing, a physical and chemical degradation of the used plastic powder occurs. To reuse the unmolten material and to realize reproducible part properties it is necessary to refresh the partcake powder and establish constant powder properties.*
In this publication PA12-powders are conditioned in a model experiment at building chamber temperatures for different periods. Process relevant material properties like phase transition temperatures or melt viscosity are analyzed. Also the influence of material pretreatment on resulting material and mechanical part properties by the use of degradated powder are investigated.
Key words: *degradation, aging, polyamide 12, mask sintering, laser sintering*

1. INTRODUCTION AND MOTIVATION

Due to thermal loads (building chamber temperature and radiation energy) in selective mask (SMS) or laser sintering (SLS) of thermoplastics, in contrast to metal based layer-wise building techniques, aging and material degradation occur within the used PA12 powder (Ehrenstein et al, 2004). These affect process relevant properties of the powder and thus the building process as well as properties of generated parts (e.g. orange peel). Therefore these building processes only have limited reproducibility and varying part properties are their essential weakness. Today a refreshing fraction of about 50 % is used to enhance process reproducibility. For SMS and SLS material costs have a great impact on total costs, thus it is of special interest to reuse aged polymer powders. The trend from rapid prototyping to direct manufacturing requires efficient and stabile fabrication processes. Hence the effects of aging on the processes have to be understood first and controlled afterwards (Drummer et al, 2010; Wendel et al, 2008; Kruth et al, 2007; Dotchev & Yusoff, 2009; Pham et al, 2008).

High building chamber temperatures, dissolved oxygen and water in the polymer as well as long heat exposure times may affect aging during the building process. The occurring degradation can be differentiated in physical and chemical (thermal, thermo-oxidative and hydrolytic) degradation. Major effects known from injection molding polyamides are chain scissions and changes of chemical structure due to autoxidation as well as branching or cross linking as a result of macro radical recombination (Ehrenstein et al, 2004; Schnabel, 1981).

2. USED MATERIAL AND EXPERIMENTS

As a basic material for the investigations, an unmodified PA12 laser sintering powder (PA 2200, Fa. EOS in Krailing, Germany) was selected and stored in an oven with defined conditions. Exposure time to a temperature of 170 °C was varied, in order to simulate the thermal loads of the laser sintering process, slightly below crystalline melting temperature. Furthermore the effect of a material pretreatment (120 °C, vacuum, 19 h), in order to remove water from the used powder, was studied.

To characterize the PA12-powder before and after oven storage, the process relevant material properties, such as melting and flow behavior were determined.

Degradation and cross linking may cause a shift of melting and crystallization range and thus change processing temperature window as well as melt viscosity. In order to study these effects differential scanning calorimetry (DSC) was utilized. By controlled heating (10 K/min) and cooling (10 K/min) of a small sample (3 mg), the amount of heat absorbed and dissipated was measured, which enables to determine the material`s melt and crystallization behavior under defined conditions.

The materials flowability in the molten state is of essential relevance for the preasureless sintering processes to produce dense parts with high surface quality and good mechanical properties.

A change in average molecular weight, which is directly linked to the materials flowability, is investigated by solution viscosity measurements (viscosity number) as well as melt volume rate (MVR). Usually m-Cresol is used as a solvent to investigate viscosity number of PA12. Due to health and security issues a measurement method with a less harmful solvent (sulfuric acid) at a measuring temperature of 25 °C was developed at the institute of polymer technology. MVR was measured according to DIN EN ISO 1133 at a temperature of 250 °C with a load of 2.16 kg.

To characterize the influence of degradated powders on the mechanical properties of parts, material was used for five building processes (ca. 5 h/cycle), without refreshing the partcake. Tensile bars according to EN ISO 3167 type A were fabricated in x-y-direction by SLS (Sinterstation 2000, DTM). To analyze the mechanical properties of these specimens, tensile tests according to DIN EN ISO 527 were conducted, and Young`s modulus, tensile stress and elongation at break were determined.

3. RESULTS AND DISCUSSION

Fig. 1 shows DSC curves of predried and non pretreated PA12 powder after oven storage compared to fresh powder (0 h storage). Crystalline melting peak temperature rises with storage time and melting peak broadens. This indicates further crystallization of the material during oven storage (Schnabel, 1981). During cooling crystallization shifts to lower temperatures for a storage time of 4 h, which may be caused by cross linking (Ehrenstein et al 2004). After a storage time of 64 h, crystallization peak moves to higher temperatures. Chain scission of macromolecules may superpose the effect of cross linking on crystallization due to a strong nucleating effect (Ehrenstein et al, 2004) of short chain molecules. Considering a material`s processing range for SLS or SMS between melting an crystallization temperature, where a two phase zone exists, shows a broadening of the processing window with increasing aging. Thus greater temperature fluctuations in the building chamber can be tolerated. This effect has to be considered combined with the material`s melt viscosity, which is important for building dense parts with good surface quality.

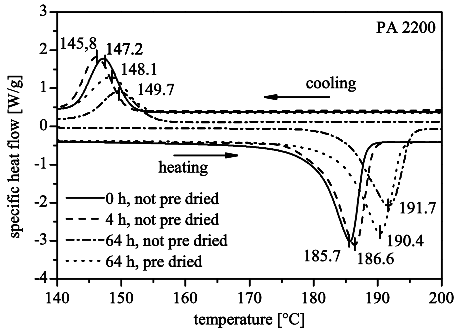

Fig. 1. DSC measurements of PA12 powder

Predrying the material under vacuum at 120 °C for 19 h reduces water content measured by Karl Fischer titration of the PA12 powder from 0.45 % to 0.11 %. Comparing predried and non predried powders with a storage time of 64 h shows reduced further crystallization as well as chain scission if water is excluded from the powder, Fig. 1.

To characterize material`s flow behavior MVR and viscosity number measurements were conducted. Both methods show a reduced flowability of the material with increasing oven storage time which may be cause by a cross linking of the macromolecules, Fig. 2.

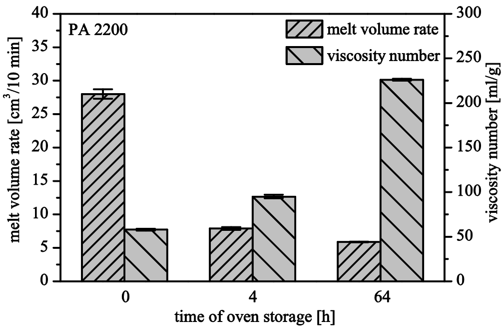

Fig. 2. MVR and viscosity number measurements of PA12 powder

This was already detected in DSC measurements together with superposed polymer chain degradation. After 4 h MVR falls from 28 cm^3/10 min to 7.5 cm^3/10 min, oven storage for 64 h only slightly reduces MVR further. Viscosity number is more sensitive to aging effects, thus a significant difference between storage time of 4 and 64 h can be detected.

In order to determine the effect of material properties after aging on the resulting part properties, processing experiments were carried out and the fabricated specimens where mechanically tested. Results show that with each process cycle and therefore with increasing aging, Young`s modulus and tensile stress at break are reduced, Fig. 3.

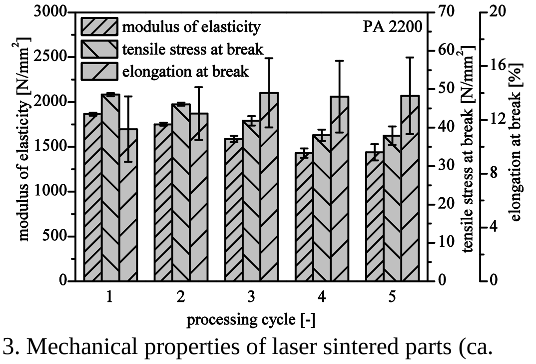

Fig. 3. Mechanical properties of laser sintered parts (ca. 5h /cicle)

This can be an effect of the reduction of strength and stiffness of the polymeric material as well as an effect of its changed processing behavior. As a result of high building chamber temperatures material aging occurs, which also influences process relevant powder properties. For example the described shift of crystalline melting to higher temperatures may lead to insufficient melting of the powder since building chamber temperature and laser induced energy are the same for all five building cycles. Thus mechanical properties decrease with each building cycle. Contrary to this, no significant changes in elongation at break can be detected. Generally, laser sintered parts show a great dependence of elongation at break from part surface quality. In the SLS process powder particles adhere to the surface of the molten part geometry; hence the part surfaces are rough. When applying a mechanical load to laser sintered parts theses adhered particles act as notches. This effect may overlie the reduction of ductility by aging.

4. CONCLUSION

The presented investigations show an influence of SLS or SMS process relevant building chamber temperatures on PA12 material properties. Melting and crystallization temperatures from DSC reveal cross linking as well as chain degradation during oven storage. An increase of average molecular weight with heat exposure time leads to higher viscosity numbers. Thus chain degradation, cross linking and crystallization are simultaneous aging effects of the used PA12 powder under high thermal load. Predrying the material under vacuum at 120 °C significantly reduced water content. This leads to reduced chain degradation.

These investigations form the basis for further research in the area of material degradation in powder based layerwise building techniques. Especially polyamide 12 with its absorption of water and tendency of cross linking shows opposing effects in analytic results. Only comprehensive knowledge about these aging processes allows to systematically reduce them and thus to realize reproducible production processes as well as improved part properties.

5. ACKNOWLEDGEMENTS

The authors would like to thank the Bavarian Research Foundation for funding the work. We also extend our gratitude to our industrial partner FIT GmbH, Parsberg, Germany.

6. REFERENCES

Dotchev, K.; Yusoff, W.: Recycling of polyamide 12 based powders in the laser sintering process, Rapid Prototyping Journal, 2009. 15(3): p. 192-203

Drummer, D.; Kühnlein, F.; Rietzel, D.: Selektives Lasersintern von teilkristallinen Thermoplasten. RTejournal - Forum für Rapid Technologie, 2009

Ehrenstein, G.W.; Riedel, G.; Trawiel, P.: Thermal Analysis of Plastics, Carl Hanser Verlag, Munich, 2004

Kruth, J.P., et al., Consolidation phenomena in laser and powder-bed based layered manufacturing. CIRP Annals - Manufacturing Technology, 2007. 56(2): p. 730-759

Pham, D.T.; Dotchev, K.D.; Yusoff W.A.Y.: Deterioration of polyamide powder properties in the laser sintering process. Proceedings of the Institution of Mechanical Engineers -- Part C -- Journal of Mechanical Engineering Science, 2008. 222(11): p. 2163-2176

Schnabel, W.: Polymer Degradation – Principles and Partical Applications; Hanser Verlag, Wien, 1981

Wendel, B.; Rietzel, D.; Kühnlein, F.; Feulner, R.; Hülder, G; Schmachtenberg, E.: Additive Processing of Polymers in: Macromolecular Matierials and Engeneering, 293 (2008), S. 799-809