SHELF LIFE OF POLYAMIDE 12 (PA2200) LASER SINTERING POWDER

I. Kletetzka*, H. Klippstein*, I. Sural*, H.-J. Schmid*

* Direct Manufacturing Research Center (DMRC) and Particle Technology Group,
Paderborn University, Germany

Abstract

It is a very well-known fact that polyamide powders age during processing in laser sintering. Therefore, the recycling rate of used powder is typically limited to around 50 % and it has to be mixed with new, virgin powder, before the next build job can be started. The aging of the polymer powder between its production and processing, in contrast, has hardly been investigated so far and has received little attention. In order to investigate the effects of storage time, optical, thermal and rheological tests were carried out on two batches of PA2200 powder, which had been stored for 5.5 and 6.5 years respectively. Compared to freshly produced powders, aging effects were clearly visible.

Introduction

In the past, numerous investigations on the aging behavior of polyamide (PA) powder in the laser sintering process have already been carried out [1–6]. However, the focus of these investigations so far has been on the aging behavior of polyamide powder under the process conditions of laser sintering and the effects of temperature history on powder aging and component properties. In addition to setting a suitable powder refresh rate, these investigations often served to build up a general process understanding for laser sintering. To the authors' knowledge, no studies on the aging of polyamide 12 powder upon long-time storage in the period between powder production and processing have been carried out so far. The aim of this work is therefore to determine the permissible storage life of PA2200 laser sintering powder by analyzing aging phenomena of powder which has been stored for up to 6.5 years before processing.

Aging of a polymeric material is generally defined as the totality of all irreversible chemical and physical processes occurring in the material over time [7]. There are different methodologies for classifying aging mechanisms. A distinction is often made between internal and external aging effects or between physical and chemical aging processes. Thermodynamically unstable states are examples for an internal cause of polymer aging, while mechanical stresses, temperature changes, radiation and the influence of chemicals are examples of external causes [8]. A selection of chemical and physical aging mechanisms is shown in figure 1. These different aging processes often occur in parallel and overlap in their effects. Therefore, aging of polymer materials is a complex topic that is still not fully disclosed [9]. In the following, a short overview of PA12 specific aging mechanisms, which could be relevant for the storage of the powder, will be given.

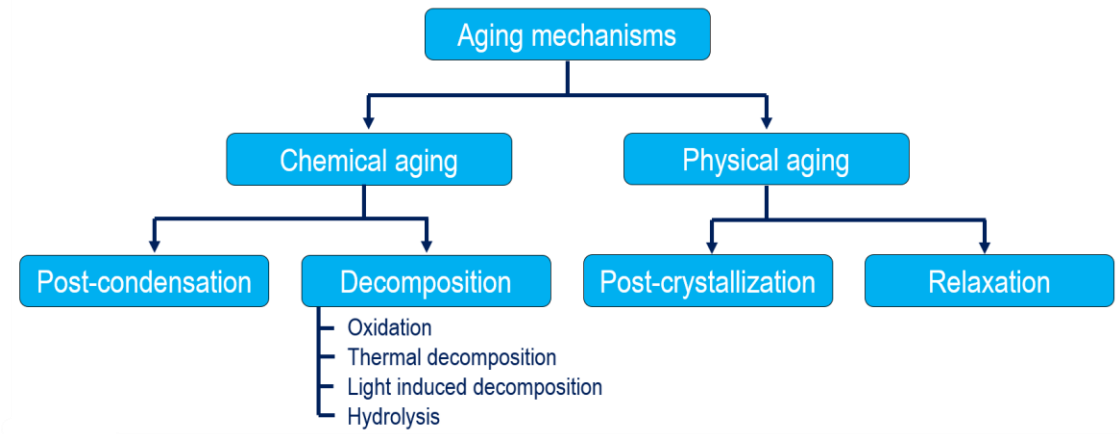

Figure 1: Aging mechanisms of polymers

(Thermo-)oxidative aging: as soon as polyamides are exposed to oxygen, oxidative aging mechanisms take effect. An increase in temperature further accelerates this process [10, 11]. Oxygen attacks the hydrocarbons within the polymer chain and form peroxides. The single bonded oxygen atoms within the peroxide are not stable and form primary radicals. These primary radicals react with undamaged parts of the polymer chain and form water molecules by splitting hydrogen atoms from the polymer chain. The newly formed radicals on the polymer chain can recombine with oxygen and form new peroxide radicals. These react again with a hydrogen atom of an undamaged polymer chain, again creating new radicals. This process is accelerated over time and is called autooxidation [10]. Stabilizers are added to the polymer to retard the thermo-oxidative aging of LS polyamide. The stabilizers typically react with radicals to prevent accelerated chain degradation and are consumed in the process. The stabilizers typically used in polyamides turn yellow in the process and therefore cause yellowing of the part [12]. The investigated PA2200 powder was stored in plastic bags, but these were not fully sealed. Furthermore, oxygen can diffuse into the plastic bags. Therefore, the storage conditions allow oxidative aging to occur.

Radiation- or light-induced aging: is another variant of the chemical aging processes. In general, aging also takes place here via the reaction of the polymer chains with radicals. The only major difference is that the primary radicals are generated by the energy of electromagnetic radiation and not by oxygen. After the formation of primary radicals, the same reactions as for oxidative aging occur [10]. In addition to stabilizers against oxidation, UV absorbers are used against light-induced aging [13]. However, since the investigated laser sintering powder was stored in a windowless room and in cardboard boxes, the influence of light-induced aging is considered to be irrelevant in this case.

Post-Condensation: the polymer chain ends of polyamide 12 (PA2200) are still reactive after the synthesis. Amino groups can still react with carboxyl groups of neighboring polymer chains whereby water molecules are split off (polycondensation). This reaction therefore causes an increase in the molecular weight of the polymer. The reaction can occur in solid and liquid phase but it requires some mobility of the polymer chains and therefore mainly occurs above the glass transition temperature [9].

Hydrolysis: since the polycondensation is an equilibrium reaction a reverse reaction may occur in the presence of water. This decomposition reaction is called hydrolysis. The polymer chain

splits at an amide group while reacting with water [14]. This causes a reduction of the molecular weight of the polymer. Since the PA2200 powder investigated was stored at approximately norm climatic conditions (23°C and 50% relative humidity) and water can diffuse through the plastic storing bags, hydrolytic decomposition of polymer chains is considered possible during storage due to the absorption of atmospheric moisture.

Post-crystallization: crystalline areas can continue to grow even after the end of processing. This secondary crystallization can be influenced by various factors such as humidity, but generally only occurs above the glass transition temperature. This process can cause residual stress due to shrinkage of amorphous areas and a change in thermal properties due to the growth of spherolites [9]. Since the storage temperature of the investigated material (approx. 23°C) is below the glass transition temperature of PA12 (approx. 49°C [14]), no significant post-crystallization might be expected.

Materials and Methods

The investigations were carried out with three different batches of PA2200 powder. The powders were purchased from EOS at different times and then stored in unopened original packaging at approx. standard climate conditions. Standard EOS packaging for powders consists of cardboard boxes containing plastic bags with powder. The bags are not sealed, but closed with zip ties. EOS recommends the use of the powder within two years of its production. The batch numbers and corresponding storage duration before the investigations are:

- Batch 918216 (produced March 2015) → stored for ca. 6.5 years
- Batch 918422 (produced July 2016) → stored for ca. 5.5 years
- Batch 919336 (produced August 2021) → stored for less than 0.5 years

For studying the particle morphology, a Phenom World **scanning electron microscope** (SEM) was used, which allows magnification up to 24,000 times. Beforehand, the samples were sputtered to create the electrical conductivity required for SEM imaging.

The thermal behavior and the processing window of the different batches was investigated by **differential scanning calorimetry (DSC)** according to DIN EN ISO 11357-3. A DSC 214 Polyma from Netzsch was used as the measuring instrument. In DSC analysis, small sample quantities (5 ± 0.3 mg) are heated up to a defined temperature and cooled down again, whereby the heat flow between the sample and an empty reference pan is continuously measured and recorded. During the investigations, the samples were heated up to 250 °C at a heating and cooling rate of 10 K/min, respectively. [15]

In addition to the process window, the **oxidation induction time** was determined using further DSC measurements [16]. At the beginning of the measurement, the sample is heated up to 200°C under a nitrogen atmosphere at a heating rate of 10 K/min and kept isothermal for 5 min. Subsequently, the sample is exposed to an oxygen-nitrogen mixture in a 50%/50% ratio. The oxidation induction time is defined as the time from the first oxygen contact to the start of oxidation. The start of oxidation can be detected by a bend in the DSC curve (heat of reaction).

For the determination of the **melt volume-flow rate (MVR)**, a capillary rheometer of the manufacturer Zwick Roell is used. The test procedure is described in DIN EN ISO 1133-1. Thus, the material to be tested is filled into a cylinder which is heated and melted with a duration of 5 minutes. A piston loaded with a weight generates a pressure which forces the melt through an extrusion nozzle. Before testing, the powder samples were dried in a laboratory oven for 30 min at 105°C to avoid bubble formation and hydrolysis. The test temperature was set to 235 °C and a weight of 5 kg was used. For each batch, a minimum of three tests was carried out and the average MVR value was calculated. [17]

The **yellowing** of plastics is a well-known phenomenon of aging. To determine the yellow value (b*) of the different powders, a colorimeter type CR410 from Konica Minolta is used. The CIELab color space, which is standardized in DIN EN ISO 11664-4, is used for the measurement. It allows the exact representation of the color in the color space by the coordinates L* for the brightness, a* for the red-green axis and b* for the blue-yellow axis [18]. Each measurement is repeated five times.

Results

First, SEM images were taken of the different batches of powder. Figure 2 shows the image of the powder that has been stored for 6.5 years and the fresh reference powder.

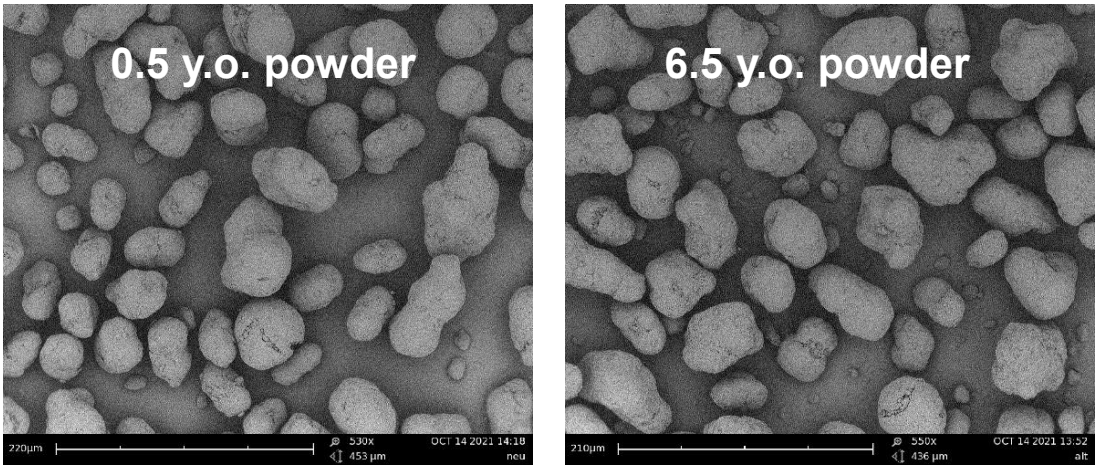

Figure 2: SEM images of powder stored for 6.5 years and freshly produced powder

The SEM images of both powder batches appear to be very similar. The PA2200 powder has a relatively spherical, potato-like particle shape for both batches. As expected, storage did not cause deformation or fragmentation of the particles. Increased formation of agglomerates is also not visible.

Even with the naked eye, however, a visual difference could be seen between the prolonged stored powder and the freshly produced powder. The longer the storage period of the powder was, the more yellowing of the powder was noticeable. Therefore, in order to quantify the yellowing, yellowness measurements were carried out as described in the method section for virgin powder

and for recycled powder that already went through one build cycle. The measurement results are shown in figure 3. It can be seen, that the b* value increases with storage time before processing the powder. Recycled powder generally has a higher b* value compared to virgin powder. For recycled powder the same trend is visible as for virgin powder. A higher yellowing was measured if it was stored for prolonged duration before processing.

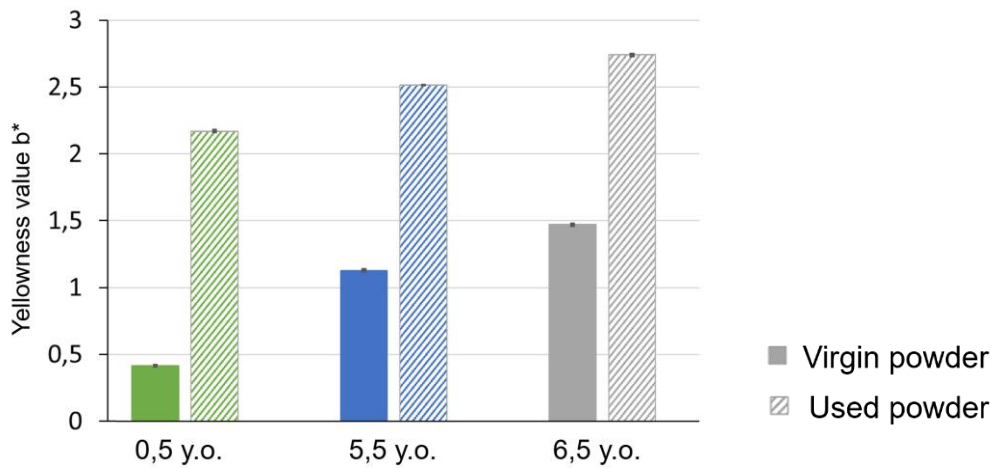

Figure 3: Yellowing of polyamide powder during storage and after processing

A higher yellowing indicates that aging processes have already taken place in the plastic. The stabilizers typically used to prevent oxidation of the polymer itself will get used up instead and turn yellow in the process [12, 19]. Since the powder was stored in cardboard boxes, light induced aging is not relevant, therefore the contact with oxygen (residual oxygen in bags and oxygen from the environment via the open bags or via diffusion) is most likely the cause of the visible aging.

The thermal properties of the different powder batches were investigates using DSC measurements. In order to determine the processing window test samples were heated to 250 °C with a heating rate of 10 K/min and then cooled back down. The process window determined in this way for virgin powder of the individual powder batches is plotted in Figure 4.

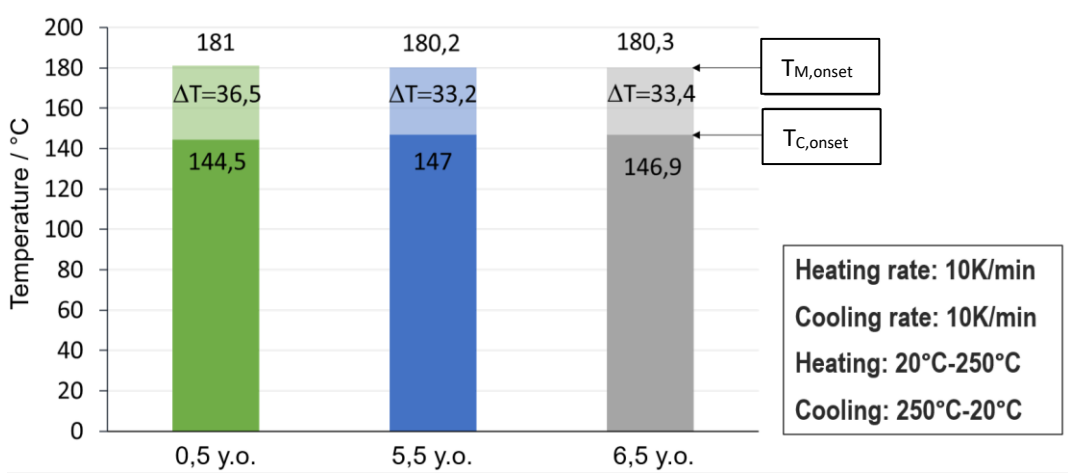

Figure 4: Thermal processing window of stored and freshly produced polyamide powder

The freshly produced virgin powder exhibited the largest process window with a difference of 36.5 °C between melting and recrystallization onset respectively. For the stored powder, the processing window was slightly narrower. Both the melting temperature and the recrystallisation temperature shifted slightly.

As well as the yellowing of the powder, the change in thermal properties can also be an indication of aging of the powder. However, since the differences are relatively small, the normal variation between different powder batches should also be considered here. It has been reported, that low molecular weight oligomers can act as an nucleating agent within polyamides [12]. Accordingly, a possible explanation for the increased recrystallization temperature could be the increase in low molecular weight fractions due to chain scission. The shifted melting point could be caused by a different crystallinity; however, the melting enthalpy remained the same. Therefore, a change in the mean molecular weight is suspected.

In addition to the characterization of the thermal processing window, the oxidation induction time was measured with the DSC for virgin powder from the three different powder batches. The results are plotted in figure 5.

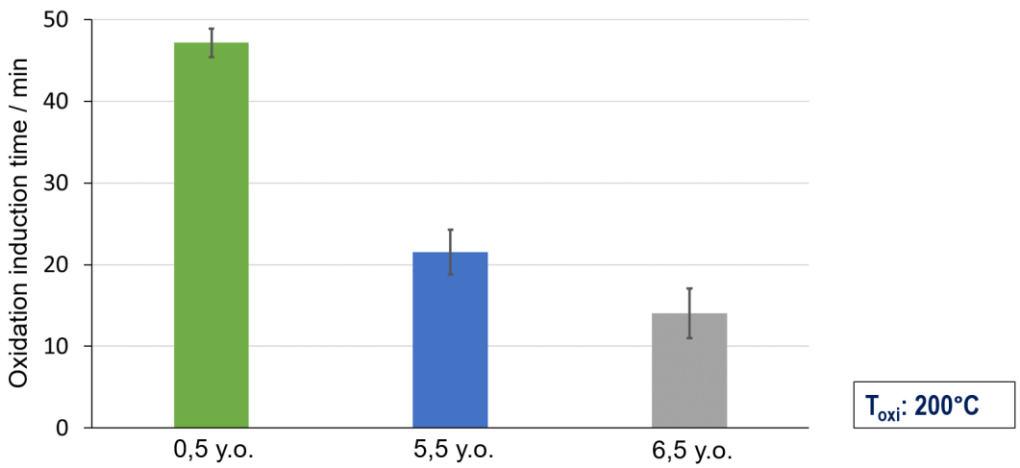

Figure 5: Oxidation induction time of stored and freshly produced polyamide powder

The oxidation induction time was significantly shortened by storing the powder for a prolonged duration before testing. This clearly indicates, that the oxidation inhibitors are already partly used up and therefore the oxidation process of the polymer chains starts faster compared to freshly produced powder. This can lead to polymer degradation during processing or can cause a shortened service live of the final component since the stabilizers can not prevent oxidation during usage if they are already consumed.

Another investigation that was carried out are melt volume flow rate measurements. MVR measurements characterize melt viscosity for a shear rate that results from the influencing variables of the measurement. A lower MVR value generally indicates a higher melt viscosity. Melt viscosity can provide information about the average molecular weight of a plastic. A higher viscosity indicates a higher average molecular weight if the measurement conditions and the plastic type are

otherwise the same [9]. It has already been disclosed, that polyamide powder ages under processing conditions. The high temperature in combination with a nitrogen atmosphere (remaining oxygen fraction generally lower than 1.5 %) cause post condensation and therefore an increase in mean molecular weight. This is indicated by the much lower MVR value for used powder compared to virgin powder (figure 6). In addition to the differences between virgin and used powders differences in between stored and freshly produced powders are also visible. Powder stored for prolonged durations has a higher MVR value both in virgin and used state. This indicates, that the mean molecular weight of these powders is lower. A lowered mean molecular weight is also a sign of aging since chain scission caused by hydrolysis or oxidation can be the cause.

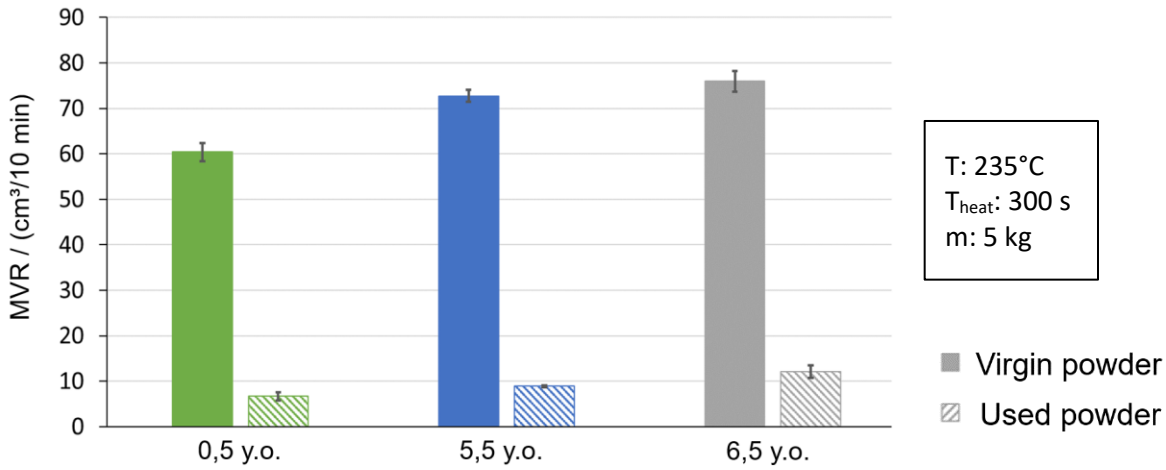

Figure 6: Melt volume flow rate of stored and freshly produced polyamide powder

Summary and Outlook

In summary, it can be stated that PA2200 polyamide powder shows significant signs of aging after a storage period of 5.5 or 6.5 years. While the particle morphology has not changed, the powder shows noticeable yellowing, indicating oxidative aging. Furthermore, it appears that the processing window slightly narrowed due to a higher crystallization temperature and a slightly lower melting temperature of stored powder. Processing the stored powder might therefore require better control of the temperature or adapted build job layouts with bigger part-free areas towards the edges of the build platform. Measurements of the oxidation induction time show a significant reduction for the stored powder batches. This means, that these powders have a reduced stability against oxidative aging. The oxidation inhibitors have most likely already been partly consumed during the storage. This is also substantiated by the yellowing of stored powder. Therefore, parts built with the stored powder might have a shortened service life, since the polymer might degrade faster in usage depending on the operating conditions. MVR measurements revealed a slightly lower viscosity of stored powder, both in virgin and recycled sate. This indicates chain scission by hydrolysis or oxidative aging during storage, effectively lowering the mean molecular weight Consequently, if polyamide powder is to be stored for a longer period of time, it would be advisable to use sealed bags or even a nitrogen atmosphere inside the bags to slow down hydrolysis and oxidative aging.

In addition to the effects of the storage duration on the powder properties, studies are currently being carried out on the effects on component properties and processability. The results on mechanical properties and part resolution will be published in a follow up paper.

References

[1] S. Josupeit, "On the Influence of Thermal Histories within Part Cakes on the Polymer Laser Sintering Process," Dissertation, Shaker; Shaker Verlag, Paderborn, 2019.

[2] S. Josupeit, L. Ordia, and H.-J. Schmid, "Modelling of temperatures and heat flow within laser sintered part cakes," *Additive Manufacturing*, vol. 12, pp. 189–196, 2016, doi: 10.1016/j.addma.2016.06.002.

[3] S. Josupeit, H.-J. Schmid, S. Tutzschky, and M. Gessler, "Powder ageing and material properties of laser sintered polyamide 12 using low refresh rates," in *Neue Entwicklungen in der Additiven Fertigung*, G. Witt, A. Wegner, and J. Sehrt, Eds., Berlin, Heidelberg: Springer Berlin Heidelberg, 2015, pp. 63–78.

[4] D. Drummer, K. Wudy, and M. Drexler, "Modelling of the aging behavior of polyamide 12 powder during laser melting process," in *PROCEEDINGS OF PPS-30*, Cleveland, Ohio, USA, 2015, p. 160007.

[5] M. Blattmeier, *Strukturanalyse von lasergesinterten Schichtverbunden mit werkstoffmechanischen Methoden*. Wiesbaden: Vieweg+Teubner Verlag, 2012.

[6] K. Wudy, D. Drummer, F. Kühnlein, and M. Drexler, "Influence of degradation behavior of polyamide 12 powders in laser sintering process on produced parts," in *PROCEEDINGS OF PPS-29*, Nuremberg, Germany, 2014, pp. 691–695.

[7] *Begriffe auf dem Gebiet der Alterung von Materialien - Polymere Werkstoffe*, 50035, DIN, Berlin, 2012.

[8] G. W. Ehrenstein and S. Pongratz, *Resistance and stability of polymers*. München: Hanser, 2013.

[9] E. Baur, S. Brinkmann, T. A. Osswald, N. Rudolph, E. Schmachtenberg, and H. Saechtling, *Saechtling Kunststoff Taschenbuch,* 31st ed. München: Hanser, 2013.

[10] R. Dahlmann, E. Haberstroh, and G. Menges, *Menges Werkstoffkunde Kunststoffe,* 7th ed. München: Hanser, 2022.

[11] W. Kaiser, *Kunststoffchemie für Ingenieure: Von der Synthese bis zur Anwendung,* 5th ed. München: Hanser, 2021. [Online]. Available: https://www.hanser-elibrary.com/doi/book/10.3139/9783446466029

[12] R.-D. Maier and M. Schiller, Eds., *Handbuch Kunststoff-Additive,* 4th ed. München: Hanser, 2016.

[13] G. W. Ehrenstein, *Polymer-Werkstoffe: Struktur - Eigenschaften - Anwendung,* 3rd ed. München: Hanser, 2011.

[14] H. Domininghaus, P. Elsner, P. Eyerer, and T. Hirth, *Kunststoffe*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2012.

[15] *Kunststoffe – Dynamische Differenz-Thermoanalyse (DSC) – Teil 3: Bestimmung der Schmelz- und Kristallisationstemperatur und der Schmelz- und Kristallisationsenthalpie*, 11357-3, DIN EN ISO, Berlin, 2018.

[16] *Kunststoffe – Dynamische Differenz-Thermoanalyse (DSC) – Teil 6: Bestimmung der Oxidations-Induktionszeit (isothermische OIT) und Oxidations-Induktionstemperatur (dynamische OIT)*, 11357-6, DIN EN ISO, Berlin, 2018.

[17] *Kunststoffe – Bestimmung der Schmelze-Volumenfließrate (MVR) und Schmelze-Massefließrate (MFR) von Thermoplasten*, 1133, DIN EN ISO, Berlin, 2009.
[18] *Farbmetrik – Teil 4: CIE 1976 L*a*b* Farbraum*, 11664-4, DIN EN ISO, Berlin, 2020.
[19] G. W. Ehrenstein and S. Pongratz, *Beständigkeit von Kunststoffen*. München: Hanser, 2007. [Online]. Available: http://deposit.dnb.de/cgi-bin/dokserv?id=2799749&prov=M&dok_var=1&dok_ext=htm