Geometry-Independent Surface Finishing

Influence of Chemical Post-Treatment on Glass-Filled Polyamide 12 Samples

In many technical applications, laser-sintered components still have inadequate surface topology. New methods of cost-effective and geometry-independent surface finishing of the laser-sintered specimens are therefore needed. Chemical post-treatment of laser-sintered PA12 components imparts enhanced mechanical characteristics as well as a reduction in roughness to ~85 %.

The growth in additive manufacturing (AM), and particularly laser sintering (LS) processes, has resulted in the development of new material systems. Polyamide 12 (PA12), which is widely used in LS, has the advantages of good suitability as well as relatively high mechanical strength and stiffness. However, in the specific areas of application in which the part is required to have high stability and endurance, its mechanical properties are not always competitive with those produced by conventional manufacturing processes. The addition of various fillers to the PA12 contributes to enhancing its material properties and opens up additional areas of application. In this study, PA12 filled with borosilicate glass beads was processed via laser sintering. One part of the manufactured samples was chemically post-treated, while the other was left untreated.

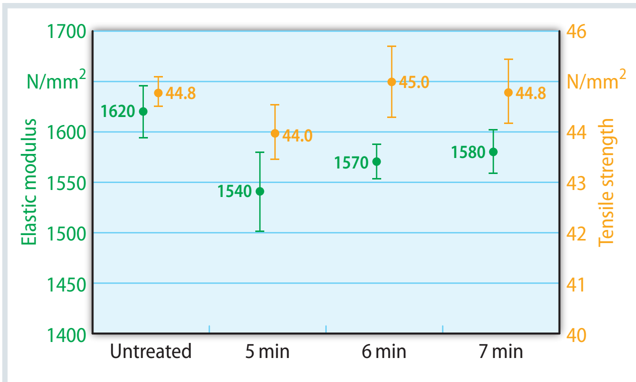

Fig. 1. Elastic modulus and tensile strength of PA12 Source: University of Duisburg-Essen; graphic: © Hanser

Growing Demand for Post-Treated Additive Manufacturing Components

Prominent applications of laser sintering can be found above all in the aviation and automotive industries [1]. LS is an additive manufacturing process, which enables the production of parts with modest mechanical characteristics [2]. These characteristics can be improved by reinforcing LS polymer materials with various fillers, which differ in their properties, shape, and size [3–7].

However, due to the layered structure, the process-related resolution, and powder adhesion, the LS components do not have a smooth surface. The development of methods for reducing surface roughness is, therefore, a necessary step toward widespread adoption of LS technology. In this study, chemical post-treatment was examined concerning its effect on sintered parts made of glass-filled PA12. As a filler, borosilicate glass (E-glass) was chosen for reinforcing the PA12. Compared to common lime glass (A-glass) it offers better elastic modulus along with better thermal resistance [8–11]. Regarding the filled LS materials, no chemical post-treatment has been performed so far. The aim of this study was therefore to investigate the influence of treatment with trifluoroacetic acid (TFA) on the mechanical and topological characteristics of the additively manufactured glass-filled PA12 specimens.

Experiment no.	Material	Surface energy density E_S [J/mm²]	Laser power P [W]	Processing Temperature T [°C]
V1	PA12 + 30 vol.% glass beads	0.018	36.6	175
V2		0.021	42.7	
V3		0.024	48.8	
V4	PA12	0.02	40.6	180

Table 1. Process parameters for tensile specimens made of glass-filled and unfilled PA12
Source: University Duisburg-Essen

Post-Treatment Methods

LS materials with various fillers have already been studied regarding their suitability for LS and effect on the characteristics of the manufactured parts. Some of the fillers that were investigated for their possible use in LS included carbon fibers, aluminum, various nanomaterials, and glass beads. All of them modified the tensile and flexural properties of the laser-sintered specimens. [10, 12, 13]

According to the state of the art, vibratory finishing offers an already investigated method for smoothing the surfaces of PA12 components and reduces the roughness to one third of its initial value using ceramic or plastic abrasives [14,15]. However, depending on the parts' geometry, the grinding bodies may not be able to reach all of the surface, particularly in slits or small openings.

Promising approaches to high-quality finishing of AM plastic components are post-treatment methods using a liquid or vapor active medium [15–17]. Compared to other post-treatment options, a liquid or vapor medium offers the advantage of near-contour surface modification. It is essential to select the active medium using the solubility parameter [15,18]. Depending on the solubility of the chemicals used – this can be influenced by changing the concentration by heating – smoothing of the surface takes place [19]. Since the solubility parameters are not always given in the literature and are generally difficult to determine, the post-treatment times are usually selected independently of the acid [18]. Since these data are only available for a few acids, the immersion time was investigated as a parameter.

In earlier research, Wiedau et al. [20] treated laser-sintered PA12 samples with trifluoroacetic acid (TFA) and reduced the surface roughness R_z to ~10 µm. This active medium was considered a sound alternative for the finishing of components of any geometry, so that even fine structures were successfully post-treated without any damage. Furthermore, the dimensional accuracy of the post-treated laser-sintered PA12 specimens was retained.

Experimental Setup

In this study, two materials were investigated, unfilled and filled PA12. The unfilled PA12 (PA2201, EOS) was used as reference material. The filled PA12 was a mixture of PA2201 and 30 vol. % of borosilicate beads (Spheriglass 3000E CP03, manufacturer: Potters Industries). Glass-filled PA12 was processed on an upgraded LS machine Sinterstation 2500 ATG (manufacturer: DTM) with an advanced heating and laser scanner system. Unfilled PA12 was sintered on a Vanguard HiQ HS (manufacturer: 3D Systems). For the mechanical tests, tensile specimens of type 1A (DIN EN ISO 3167 [21]) were sintered in the x-direction, with the parameters listed in **Table 1**. Hatch distance and layer thickness were kept constant at 0.2 and 0.1 mm, respectively. A laser scanning speed was set at 10.16 m/s for both materials.

Chemical Post-Treatment

In the chemical post-treatment, the component can either be directly immersed in the liquid acid or exposed to a vapor medium. During post-treatment with acid, dissolution of PA12 molecules together with equalization of the amorphous surface area of the semi-crystalline structure occurs [20,22,23].

In previous studies, PA12 samples were already chemically post-treated with various acids [20]. Immersion in a TFA bath for 120 s caused a reduction of the surface roughness R_z of laser-sintered PA12 samples of 87 % [24]. TFA dissolves PA12, so that the surface softens. To prevent softening of the PA12 surface, the acid on the sample's surface should be neutralized immediately after the post-treatment.

Post-treatment with the vapor has the advantage that small quantities of the corrosive acid can be used [25]. That is why, in this study, the samples were post-treated by the acid vapor. TFA was chosen as a chemical medium due to its high volatility. The examined PA12 samples were post-treated in a special post-treatment station, the bottom of which was completely covered with TFA. The propeller integrated into the chamber contributed to the air circulation inside the station for effective vaporization of the acid. In a preliminary experiment, samples were exposed to the acid vapor for 5, 6, and 7 min. After the roughness measurement, the post-treatment time for the tensile samples was set at 6 min. »

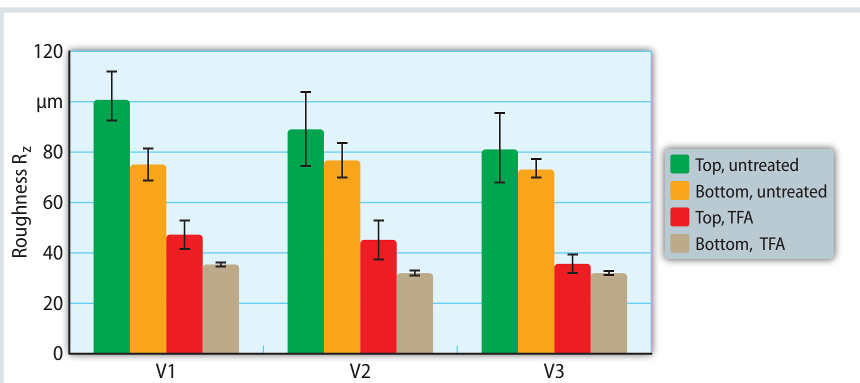

Fig. 2. Influence of post-treatment on glass-filled PA12 Source: University of Duisburg-Essen; graphic: © Hanser

The Authors

Livia Carmen Wiedau is a research assistant at the Institute of Manufacturing Technology at the University Duisburg-Essen, Germany; livia.wiedau@uni-due.de
Anna Tarasova worked as a research assistant at the Institute of Manufacturing Technology, University Duisburg-Essen.
Prof. Dr.-Ing. Habil. Gerd Witt is Head of the Institute of Manufacturing Technology, University Duisburg-Essen.

Note

This paper is the result of two projects: The iGF project (19623 N) with the title "Resource-saving Small Series Production by Polymer Laser Sintering – Influence of the Anisotropy and Surface Structure on the Long-term Dynamic and Mechanical Properties of Laser- sintered Parts" of the research association Institute of Energy and Environmental Technology e.V. (iUTA).
The iGF project (19646 N) with the title "Influence of the Material Composition and Surface Structure of Laser-Sintered Model Propellers on Predicting the Accuracy of Propulsion Experiments" of the research association Development Centre for Ship Technology and Transport Systems e. V. (DST).
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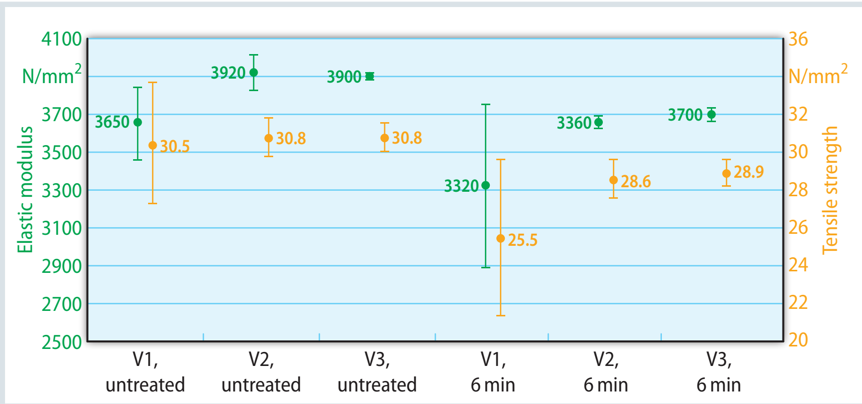

Fig. 3. Elastic modulus and tensile strength of glass-filled PA12 Source: University of Duisburg-Essen; graphic: © Hanser

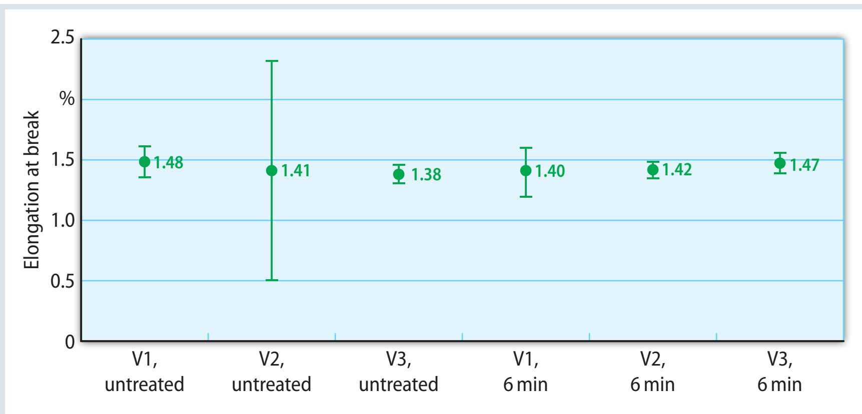

Fig. 4. Elongation at break of glass-filed PA12 Source: University of Duisburg-Essen; graphic: © Hanser

The roughness measurements were carried out with a SJ-400 roughness measuring instrument (manufacturer: Mitutoyo) in accordance with DIN EN 4288 with an accuracy of 0.001 mm. Subsequently, tensile tests were conducted under DIN EN ISO 527–1 [26] with a testing speed of 5 mm/min on a Z020 M tensile testing machine (manufacturer: Zwick).

Surface Roughness Reduced

Initially, the samples of unfilled PA12 were examined. For the untreated samples, the roughness R_z was ~83 µm. With increasing post-treatment time, the roughness of the samples decreased gradually, resulting in a roughness of ~18 µm after chemical post-treatment.

A graphic demonstrates the elastic modulus and tensile strength of PA12 specimens and their dependence on the post-treatment time (**Fig. 1**). The results were compared with those of the untreated PA12. Post-treatment times of 6 and 7 min led to a slight increase in elastic modulus in comparison to the post-treatment time of 5 min. However, all the post-treated values were still lower than the elastic modulus of the untreated PA12. Nevertheless, this reduction of the elastic modulus was insignificant. At the same time, the tensile strength remained almost constant. This showed that the post-treatment did not have any apparent negative influence on the tensile strength of the laser-sintered PA2201 specimens either. Post-treated samples performed a slight increase in values of elongation at break: From 20.1 % (untreated) to 19.7 % (5 min), 24.4 % (6 min), and 22.1 % (7 min).

In the next step the glass-filled PA12 was laser-sintered and examined before and after the post-treatment. **Figure 2** shows the surface roughness of the top and bottom sides of untreated and post-treated samples at the different manufacturing settings (**see Table 1**). After exposure of the samples in TFA vapor for 6 min, the surface roughness of the samples was reduced almost twofold.

The process parameters showed a significant influence on the modulus of elasticity of the untreated glass-filled specimens. After the post-treatment with the TFA vapor, the glass-filled PA12 demonstrated the same tendency as in the case of the unfilled PA12: elastic modulus was reduced slightly due to the post-treatment, e.g., elastic modulus of the V1 samples was reduced from 3650 to 3320 N/mm². In contrast to the unfilled PA12, the glass-filled PA12 demonstrated the decline of the tensile strength after the post-treatment, e.g., the tensile strength of V1 samples reduced from 30.5 to 25.5 N/mm². The results are shown in a graphic (**Fig. 3**).

Examination of the elongation at break showed a slight decrease in the values with increasing energy density. After the post-treatment, all acquired values of the elongation at break were almost constant at ~1.43 % (**Fig. 4**).

Influence of Process Parameters and Chemical Post-Treatment

This study demonstrated the influence of TFA vapor on the mechanical and surface properties of the virgin and glass-filled PA12 specimens manufactured via LS. After the chemical post-treatment, the roughness R_z of the bottom surface was reduced to 17 % of the initial value for the unfilled PA12 and almost twice for the glass-filled one. The same trend was observed for the top surface.

Glass-filled PA12 demonstrated an enhancement of elastic modulus of 140 %. However, its elongation at break reduced significantly, which is known behavior among reinforced materials.

The exposure to the TFA vapor resulted in a slight reduction of elastic modulus of both unfilled and glass-filled PA12 samples by 5 and 8 %, respectively. No influence of the TFA post-treatment on the tensile strength of the unfilled PA12 was observed. However, the tensile strength of the glass-filled PA12 decreased from 30.8 to 28.6 MPa after the post-treatment. The influence of the TFA vapor on the elongation at break of both materials could not be accurately assessed due to the scattered results. Further investigation of the effect of post-treatment with TFA vapor on the properties of the LS parts is therefore required. ■