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SHORT COMMUNICATION

Improved mechanical properties of 3D-printed parts by fused deposition modeling processed under the exclusion of oxygen

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Abstract 3D printing via fused deposition modeling (FDM) has developed to the probably most common rapid prototyping technology due to its easy of use and broad range of available materials. Nowadays, FDM printed parts are on the way to be used in various applications ranging from all-day use to more technical purposes. As a matter of fact, the mechanical strength is one of the main parameters to be optimized by the choice of the material and the 3D-printing settings, such as layer height, nozzle temperature and printing speed. Here, we report on the improvement of the mechanical properties of printed parts by use of an inert gas atmosphere during the print. A typical FDM printer has been inserted into the nitrogen atmosphere of a glove box and used without modifications to print parts made of acrylonitrile butadiene styrene and polyamide as printing materials with a high mechanical load tolerance. Probably partly due to the prevention of oxidation processes, a significant increase in elongation at break and tensile strength was observed. This may be explained by a reduced degradation of the polymer surface at the comparatively high printing temperature. 3D printing under the exclusion of oxygen may be realized comparatively easy by flooding the printing chamber with nitrogen in future applications for the production of FDM-printed parts with improved mechanical properties.

Keywords Fused deposition modeling · Tensile tests · Inert gas · Acrylonitrile butadiene styrene · Polyamide

1 Introduction

3D printing is affecting daily life in various ways. 3D-printed parts have found their way into the production of customized toys as well as complex technical applications and can substitute injection molded parts by uniquely optimized geometries. The "Fused Deposition Modeling" (FDM) technique has shown up to be the easiest printing technology and FDM printers are widely available in market stores nowadays. In some cases, 3D-printed parts are exposed to high mechanical stress, as an example the use of printed elements in unmanned aircrafts [1]. Consequently, the use of polymers with a high mechanical load tolerance such as acrylonitrile butadiene styrene (ABS) is favored and special polymers are available for the production of mechanically resistant parts, such as specialized nylon filaments [2]. During the FDM process, the polymer filament is molten at a comparatively high temperature (200–280 °C) and layer by layer printed on a printing bed. The layer height usually is in the range of a few hundred micrometers, which results in a large surface area of the warm polymer exposed to air during the printing process. This is in contrast to other manufacturing processes such as injection molding. Consequently, during the FDM process, the polymer surface of each layer is suspect to degrade which may influence the mechanical properties. The degradation of various polymers at higher temperatures has

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been investigated in detail. In the case of ABS, oxidation processes lead to a degradation of the material at higher temperatures in the presence of oxygen. Mainly the polybutadiene phase (which is in possession of reactive double bonds) is affected by oxidation reactions, which lead to a significant reduction in mechanical properties [3]. For “Selective Laser Sintering” (SLS), where a laser beam is used to fuse particles of the raw starting material to form the desired object, the complex decomposition processes of the printing material such as nylon have been investigated in detail [4]. In the presence of oxygen, degradation processes can lead to a decrease of the molecular weight. SLS usually is processed under an inert atmosphere. Here, we present a short comparison of FDM-printed parts at normal operation conditions compared to the printing process performed under the strict exclusion of oxygen. We report on a significant improvement of the mechanical properties such as yield strength if the print is performed inside a glove box flooded with nitrogen (Fig. 1). Such glove boxes usually are used for chemical syntheses with highly reactive substances. The enhanced properties of parts printed under inert gas conditions were discovered as the print of reaction vessels for highly oxygen and water sensitive substances was performed directly under the nitrogen atmosphere. The method presented here may lead to a rather simple enhancement of FDM printers.

2 Materials and methods

An UP Plus 2 3D-printer from TierTime Technology Co. Ltd. (PP3DP) was used for all prints without modifications. The printer fits into the standard vacuum chamber of a common glove box (M. Braun, Labmaster 130) and was evacuated together with all necessary equipment for one night before insertion into the glove box. The glove box was operated under nitrogen with a pressure of +5 mbar (vs. atmospheric pressure) and a flow rate of 12 m^3 h^{-1}. The gas flow was directed in a significant distance from the printer. To enable the USB communication with the printer, the USB signal was transmitted via ethernet [USB over Ethernet Server (UE204, B&B Electronics)]. The ethernet connection into the glove box was realized by PowerLAN. UP! Software 2.13 was used for all prints. A nozzle with a diameter of 0.4 mm was used. The platform was leveled before each print and preheated to 100 °C (ABS) or 50 °C (Taulman 910) for 15 min. Printing was performed with a layer height of 0.15 mm and “fine” printing settings (scan speed of 30, scan width of 0.47, hatch layer: 3). In deviation from the standard parameters, a hatch width of 0.32, hatch speed of 30, jump speed of 50 and hatch scale of 1.0 was set to obtain completely filled objects [5]. Nozzle temperature was set to 263 °C (273 °C for the first and 268 °C for the second layer to obtain better adhesion of the raft on the printing platform) for ABS and Taulman 910. All objects printed at air and under the nitrogen atmosphere were positioned at exactly the same place and with the same orientation on the printing platform to achieve an identical way of printing. 3D-models were constructed with SketchUP Make 15.3.330 and checked with Netfabb basic 5.2.1.

The 3D-printing materials ABS (natural, Orbi-Tech GmbH, Leichlingen, Germany) and nylon copolymer (Taulman 910, taulman3D, Saint Peters, USA) were bought as 1.75 mm filaments, dried over night at 85 °C and left for one night in the vacuum chamber before insertion into the glove box.

Tensile tests have been performed with a Zwick/Roell BZ1-MM14450.ZW05 universal testing machine equipped with a 10 kN load cell and with a speed of 1 mm min^{-1} at 23 °C/50 % rel. humidity. Tensile strength and elastic modulus were calculated from the results of the tensile tests

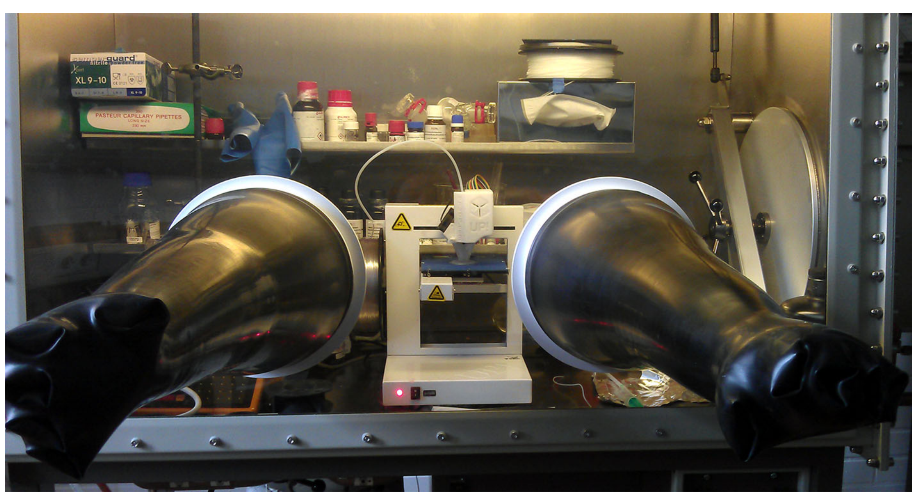

Fig. 1 3D-Printer within the *glove box* under a nitrogen atmosphere

and the cross-sectional area of the printed samples. Three test specimens have been measured per sample set. Differential scanning calorimetry was performed with a Mettler-Toledo DSC-1 apparatus with a heating speed of 10 K min^{-1} under nitrogen. A heat of fusion of 230 J g^{-1} was assumed for pure crystalline Polyamide 6 [6]. X-ray powder diffractograms were measured with a Stoe & Cie diffractometer STADI P (Cu Kα radiation, $\lambda_{Cu} = 1.54056$ Å) with small printed parts (13 × 13 × 10 mm).

3 Results and discussion

The mechanical properties of various polymers are well known. The mechanical properties of FDM-printed test specimen have been investigated by tensile tests and differ from injection molded parts [7]. Since the main interest of this work was to investigate the layer adhesion of the printing process in absence and in presence of oxygen, test specimen was printed with the longest side orthogonal to the printing platform (and shortest side parallel to the moving direction of the platform) to maximize the number of layers. The influence of the printing direction on the mechanical properties has been analyzed in detail [8–10]. The print of the test specimen according to EN ISO 527-2 (type 1B) as long and thin objects orthogonal to the printing platform revealed certain difficulties [11]. Smaller test specimen (type 1BB, 30 × 2 × 2 mm) would result in a very small printed layer area (4 mm^2). Consequently, test specimens were printed as small plates (30 × 10 × 3 mm). This leads to a layer area of 30 mm^2 and allows a more reliable comparative investigation of the layer adhesion. As a consequence, absolute values reported here may not be compared directly to values derived from tensile tests of test specimen of a different geometry.

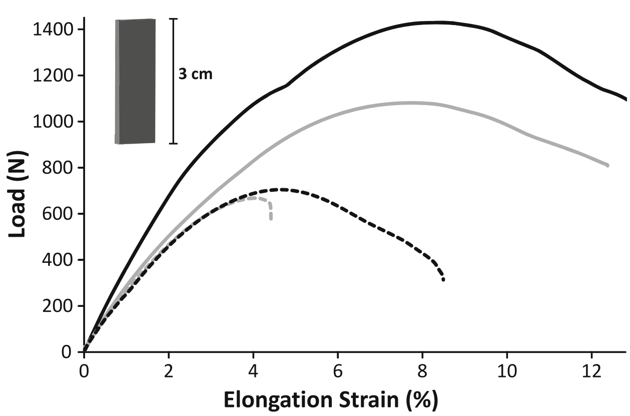

Fig. 2 Averaged load–strain curves of plates made of ABS (*dashed line*) and nylon copolymer (*solid line*) printed at air (*gray*) and under a nitrogen atmosphere (*black*). *Insert* orientation of the test plate during print

Figure 2 shows averaged load–strain curves obtained from the tensile tests of the printed plates made of ABS and nylon copolymer (Taulman 910) at air and inside the oxygen-free inert gas atmosphere of the glove box. At first sight, the increased elongation at break is obvious for ABS, while the nylon copolymer shows a significantly increased tensile strength and an increased elastic modulus.

The averaged results obtained from all tensile tests are summarized in Table 1. For plates made of natural ABS a significantly improved elongation at break from $\varepsilon_B = 4.4 \pm 1.5$ % to 10.7 ± 2.6 % is obtained. This may be explained by a better layer adhesion of the FDM printed layers. The values for the elastic modulus and the tensile strength are generally quite identical and within the expected range for ABS before and after 3D printing [7, 12]. A slight improvement (+10 %) of the tensile strength is noted for the plates printed under a nitrogen atmosphere. As a comparison, printed test specimen of type 1BB results in an elastic modulus of $E = 1.56 \pm 0.07$ kN mm^{-2} and a tensile strength of $\sigma_M = 25.5 \pm 0.9$ N mm^{-2}, which is in good accordance with results reported in literature [7].

For the nylon copolymer Taulman 910, which is generally more extendible (tearing was not observed during the test conditions) a significant increase in tensile strength from $\sigma_M = 36.0 \pm 2.2$ N mm^{-2} to 49.9 ± 13.8 N mm^{-2} is achieved under exclusion of water and oxygen. The tensile strength generally is in the range expected for the material [2]. Additionally, an increasing elastic modulus was observed (Table 1). Lowering the printing temperature for the dried nylon copolymer to 240 °C (as suggested by the manufacturer) led to a decrease of the tensile strength to $\sigma_M = 33.6 \pm 3.8$ N mm^{-2} and to $E = 1.01$

Table 1 Summary of averaged results obtained from tensile tests of 3D-printed plates made of ABS and nylon copolymer (Taulman 910) at air and under an inert gas atmosphere

Sample	E (elastic modulus) (kN mm^{-2})	σ_M (tensile strength) (N mm^{-2})	ε_M (elongation at σ_M) (%)	ε_B (elongation at break) (%)
ABS (air)	0.87 ± 0.04	19.4 ± 0.8	3.9 ± 1.1	4.4 ± 1.5
ABS (inert gas)	0.85 ± 0.04	21.6 ± 0.2	4.7 ± 0.2	10.7 ± 2.6
Nylon (air)	1.03 ± 0.02	36.0 ± 2.2	8.5 ± 1.9	
Nylon (inert gas)	1.34 ± 0.10	49.9 ± 13.8	8.9 ± 3.2	

± 0.04 kN mm^{-2} (plates, inert gas). If the nylon copolymer was not dried before printing at air, the tensile strength is reduced to $\sigma_M = 19.9 \pm 2.2$ N mm^{-2} and the elastic modulus to $E = 0.60 \pm 0.11$ kN mm^{-2} (plates, air). This clearly shows the general influence of the water on the mechanical properties of nylon, which is a well-known fact. For all other prints at air and under the nitrogen atmosphere, a rigorous drying procedure of the nylon filament was applied.

For SLS, it is well known that the crystallinity of polyamides changes with the degree of particle melting, which strongly affects the mechanical properties [13, 14]. For polylactide (PLA), the influence of the extruder temperature on the crystallinity and mechanical properties has been investigated [15]. We compared the crystallinity of the nylon copolymer printed at air with samples printed under the inert gas atmosphere. At first look, the X-ray powder diffraction (XRD) measurements show slight differences at the typical signal of semicrystalline polyamide around $2\Theta = 21°$ (see Fig. S4 of the supplementary material) [16]. With the help of differential scanning calorimetry (DSC) measurements, a higher crystallinity for the nylon plates printed at air was determined. According to the DSC measurements, the samples printed at air are 15 % more crystalline (roughly 20 % crystallinity) than the samples printed under a nitrogen atmosphere as shown in Fig. 3, which may explain the improved mechanical properties for prints performed under an inert gas atmosphere.

ABS is a purely amorphous polymer. As a consequence, crystallinity cannot be affected by the printing conditions. Accordingly, the XRD measurements of both samples are identical and in agreement with an amorphous polymer and the DSC heating curves do not show a melting peak (see Fig. S1 of the supplementary material). The second glass transition (T_g) of ABS is found around 110 °C, which is in accordance with the material properties. According to literature, the oxidation of the polybutadiene phase of ABS can be monitored by a large shift of the first glass transition, which is located around −65 °C, to significantly higher temperatures. Unfortunately, the first glass transition is rather broad and gets even broader upon oxidation and it was not possible to determine the first glass transition from the DSC measurements at low temperatures (see Fig. S2 of the supplementary material) [3]. In all cases, the printed plates made of ABS and nylon copolymer printed under inert gas conditions were pure white without the slightest discoloration, while all plates printed at air showed a slight yellow/brownish coloring in direct comparison. This is in accordance with the expected beginning of degradation of the polymers printed at air. Overall, at the current point it may be concluded that the suppression of oxidation processes leads to a better layer adhesion in case of ABS (leading to a higher elongation at break) while the extremely dry atmosphere may affect crystallization of the polyamide and is responsible for the improved tensile strength.

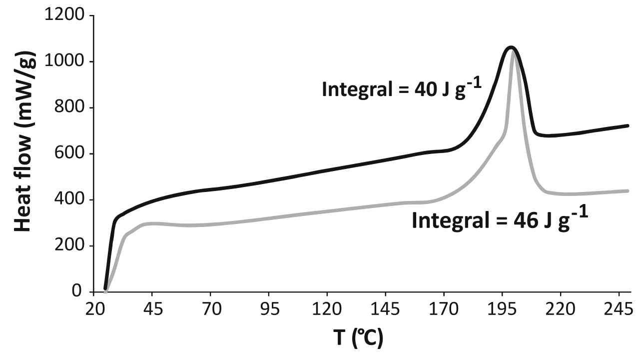

Fig. 3 First heating curves of the DSC measurements for samples made of the nylon copolymer printed at air (*gray*) and under a nitrogen atmosphere (*black*)

4 Conclusions

The data obtained from the tensile tests of plates printed at air compared to those printed under a nitrogen atmosphere allow to conclude that improved mechanical properties are achieved for prints performed under the inert gas atmosphere. This results in a higher elongation at break for the harder material ABS and a higher tensile strength for the more extendible nylon. The increase in tensile strength is in the range of 30 % which may justify the bigger effort of printing under a nitrogen atmosphere in some cases, where improved mechanical properties are needed. Further work (and analyses of prints performed in a dry, but oxygen-containing atmosphere) is needed to specify the influence of water and oxygen on the printing process. Printing under an inert gas atmosphere is a comparatively easy enhancement of FDM printers, which may be realized for example by a simple setup based on flooding the printing chamber of a FDM printer with nitrogen to build a cheap and routinely usable system.

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