

Effect of water conditioning on the fracture behavior of PA12 composites processed by selective laser sintering

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ABSTRACT

This study aims to elucidate the combined effects of reinforcing particles and water on PA12 processed by selective laser sintering (SLS). PA12 is one of the toughest polyamides. However, PA12 processed by SLS is rather brittle due to the presence of voids and the relative low molecular weight of the polymers used in SLS. It is demonstrated that humidity impoverishes the mechanical properties of neat PA12, including ductility and toughness. A ductile/brittle transition was detected, which was attributed to the competition between the plasticizing effect and the hydrolyzation of PA12 molecules plus the increase in crystallinity which counteracted this mechanism. It has been found that addition of hard particles, such as glass spheres and ceramic fibers, prevents the ductile/brittle transition by water conditioning at high temperature to happen.

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1. Introduction

When intricate pieces in small series are needed to be produced, additive manufacturing technologies are the ideal option. Particularly, selective laser sintering (SLS) allows for polymers, metals and ceramics to be processed from powder-like material into solid pieces. SLS is an additive manufacturing technique that uses a high power laser to fuse small particles into a mass representing a desired 3-D object. The laser selectively fuses powdered material by scanning cross-sections generated from a 3-D digital part on the surface of a powder bed. After each cross-section is scanned, a new layer of material is applied on top. Both, the sintered and the unsintered areas serve as support for the next layer. The process is repeated until the part is completed.

Among polymers, PA12 is widely used for SLS processing since it exhibits a large difference between melting and crystallization points ($\sim 40^\circ\text{C}$) and a large enthalpy of fusion [1]. These characteristics allow for the temperature in the sintering chamber to be held at a high level, resulting in low shrinkage on solidification and good dimensional stability of the sintered pieces. Furthermore, PA12 has a very high toughness [2] and fatigue resistance [3] compared to

other thermoplastics and even relative to other polyamides, good tribological performance [4] and high chemical resistance [5].

One of the main disadvantages of the PA12 processed by SLS is its high porosity and low molecular weight, which deteriorate its mechanical properties, especially ductility and toughness [6]. There have been attempts to compensate for this drawback by adding particles (rectorite [7], potassium titanium whisker [8], silica nanoparticles [9]) or blending with other resins [10]. While there were no significant enhancements in regards to toughness and ductility, addition of hard particles or blending clearly improved the strength and modulus of PA12.

Polyamides are hygroscopic, and eventually, they take up moisture when exposed to humid air. In PA12 processed by melting techniques (e.g. injection, extrusion) this is advantageous in terms of toughness and ductility which are increased due to the plasticizing effect of the water [11]. For this reason, water saturation is often accelerated by submerging the polyamidic parts in hot water.

To our knowledge, the consequences of accelerated water conditioning in PA12 processed by SLS have not been investigated yet. Hence, the objective of this research is to cover this gap and quantify for the first time the effect of humidity in the fracture behavior of SLS processed PA12. Furthermore, different reinforcement particles will be used as fillers in order to determine whether a combination of the particles and water moisture yields a tough and strong material. Furthermore, an in-depth analysis of the change in fracture micromechanisms of these SLS materials due to water conditioning will be carried out.

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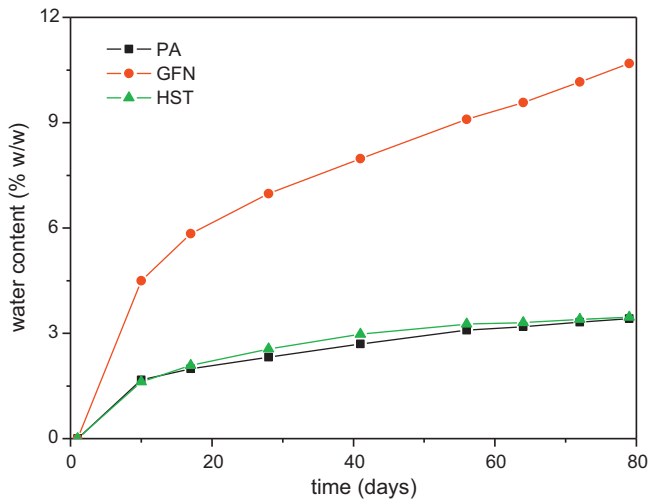


Fig. 1. Sorption curves of the SLS materials.

2. Experiments

2.1. Materials

The three materials under study were PA12 based materials with different fillers, suitable for SLS fabrication. The materials belong to the SLS materials family of Duraform® and were manufactured by 3D Systems. Their commercial names are PA, GFN and HST. PA

Table 1
Density and porosity of the SLS materials.

| Material | Density (g/cm ³) | | Porosity (%) |
|----------|------------------------------|-----------------|--------------|
| | Bulk | Sintered powder | |
| PA | 1.00 | 0.97 | 2.9 |
| GFN | 1.49 | 1.27 | 14.6 |
| HST | 1.20 | 1.19 | 0.9 |

is an unreinforced PA12, GFN contains 43% weight of glass beads and HST has 25% weight of ceramic short fibers, as determined by thermogravimetric analysis.

2.2. Conditioning

Two sets of specimens for each of the three materials were prepared, namely, dry and wet samples. Half of the samples were dried in oven at 90 °C during 24 h. The residual moisture of the samples was ~0.15% weight as measured with thermo-gravimetric analysis. The other half of the samples were saturated under accelerated conditions by submerging the specimens in water at 90 °C for 80 days. The specimens were periodically weighed in a precision balance to evaluate its moisture content. As the glass beads and short fibers do not absorb water, the water weight fraction in the matrix, φ_w , was calculated as:

$$\varphi_w(t) = \frac{1}{\varphi_m} \left(\frac{w(t) - w_0}{w_0} \right) \quad (1)$$

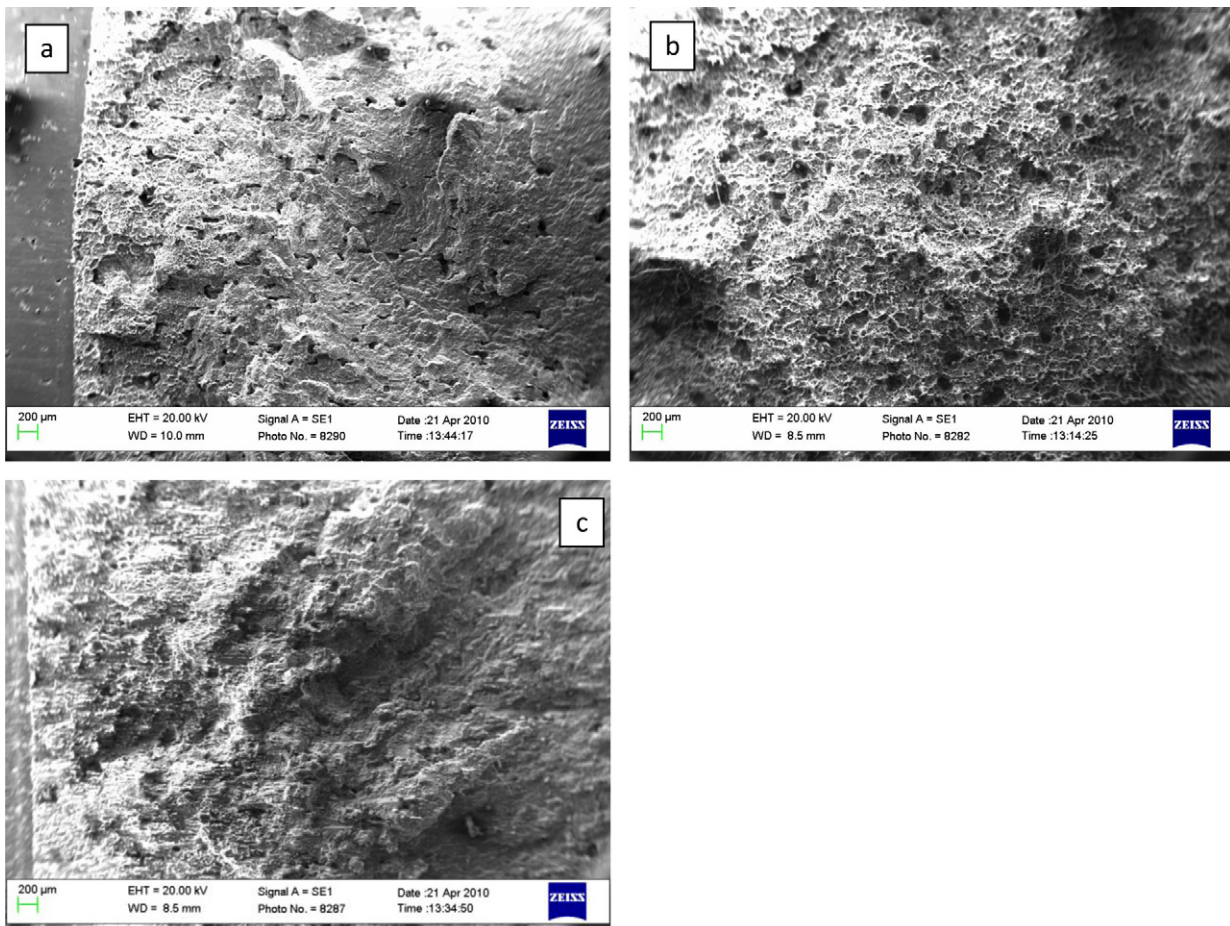


Fig. 2. SEM images of the SLS materials showing their porosity. (a) PA, (b) GFN and (c) HST.

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