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Book of Abstracts

Printing and characterization of 3D high-loaded nanocomposites structures

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ABSTRACT

Additive Manufacturing (AM) technologies are spreading rapidly both in academic research and industrial environments [1]. Nanomaterials have proven to provide new size-dependent properties compared to traditional bulk materials [2]. The integration of nanotechnology into AM opens new and interesting challenges in manufacturing advanced nanocomposite materials with custom-made properties and geometries [3]. Synergy between nanomaterials, such as metal and oxide nanoparticles, and AM can in fact result in improved functional and structural performance of manufactured devices, filling the gap between design and production of a specific tool. For instance, silica nanoparticles (SiO_2 NPs) are increasingly used as nanofillers, thanks to their excellent mechanical properties, to fabricate nanocomposites used in a wide range of applications [4]. Stereolithography (SLA) represents one of the most widespread AM technologies used to fabricate 3D engineered structures. The general procedure for building objects with SLA involves photo-polymerization of liquid monomer into solid resin by means of an ultraviolet (UV) laser, which creates targeted cross-linked regions where the light irradiates the matrix [5]. SLA AM of nanocomposites usually involves mixing of *ex situ* synthesized nanoparticles with commercially available acrylic monomers, followed by an optimized printing process. Stable dispersion of colloidal SiO_2 NPs in acrylate monomers or oligomers are commercially available, such as Nanocryl product family commercialized by Evonik. These products are traditionally used in adhesive and electronic applications, such as highly scratch-resistant coatings for fiber optic cables, conformal coatings, UV curing adhesives for printed circuit boards and can be successfully employed in AM of high-loaded nanocomposites. The produced 3D-printed specimens were employed to characterize the nanocomposites microstructure and thermo-mechanical properties respectively by means of scanning electron microscopy (SEM) and dynamic-mechanical analyses (DMA).

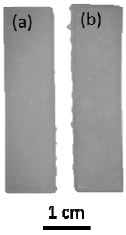

Figure 1. Photographs of printed samples: (a) filled and (b) unfilled resin.

Printable acrylate-based nanocomposites containing 45% of SiO_2 NPs were obtained by photo-curable hybrid formulation, based on a mixture of Evonik Nanocryl A215 (TPGDA - Tri Propylene Glycol Di Acrylate and SiO_2 NPs) 90 %, MAT3D 3DGlass (photocurable acrylic resin) 10 % and BASF Irgacure 819 (photo-initiator for SLA process) 2 phr.
Printed nanocomposites were compared with unfilled samples, consisting only of acrylate matrix (Allnex TPGDA – 90 %, MAT3D 3DGlass – 10 %, BASF Irgacure 819 – 2 phr) (Fig.1).

Printed samples microstructure was investigated by SEM analysis (Fig. 2). Compared to the reference unfilled sample, the presence of nanoparticles can be observed within the printed polymer matrix. Nanoparticles have approximately spherical shape and are well dispersed in the matrix with no significant aggregation after printing. The observed nanoparticles have diameters ranging between 10 and 50 nm and can be ascribed to the presence of silicon dioxide in the considered system, as confirmed by EDS spectra (Fig. 2(a)).

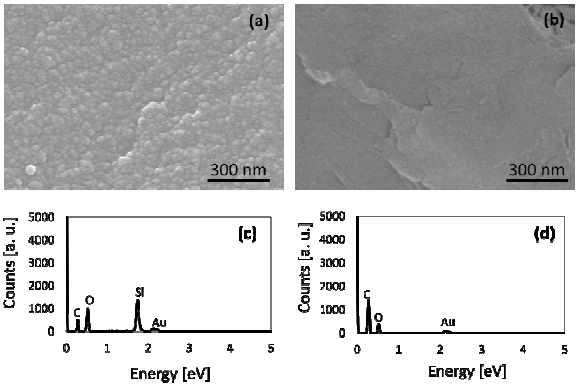

Figure 2. SEM micrographs and EDS spectra respectively of filled (a, c) and unfilled (b, d) resin.

DMA analysis was carried out on all printed specimens, giving information on the thermal and viscoelastic properties of the materials in a large temperature range. Storage modulus (E′) and damping factor (tan δ) curves, as a function of temperature, are shown in Fig. 3. From the DMA curves, a shift of about 15°C toward higher temperature of tan δ peak, associated to the glass transition temperature (T_g), was observed (Fig. 3b): T_g is detected respectively at 62 and 87°C for pristine and filled samples. The higher storage modulus of nanocomposite filled sample was evident in the whole analysed thermal domain and in particular beyond the T_g, expanding effectively the applicability range of nanocomposite (Fig. 3(a)). This behaviour can be attributed to the impediment, induced by the SiO_2 NPs in the polymer network, to the segmental motion of the polymeric chains . The increase in segmental motions constrains in the polymeric chains is mainly due to the uniform distribution of the silica nanoparticles which was also evidenced by SEM analysis.

This study shows the possibility to obtain SLA printed nanocomposite objects using the laser radiation of a commercial stereolithography printer to cure a hybrid formulation based on acrylic monomer and SiO_2 NPs. After the printing process, SiO_2 NPs are well dispersed and homogeneously distributed in the crosslinked matrix as evidenced by SEM analysis. The presence of the filler causes an increase in the physical and mechanical properties of the samples that become significantly stiffer and stronger than the pristine matrix. Thermo-mechanical tests provided promising results for the use of the developed formulation in the building of 3D polymeric structures with improved multistructural properties, providing further rapid prototyping option to research and development of new products.

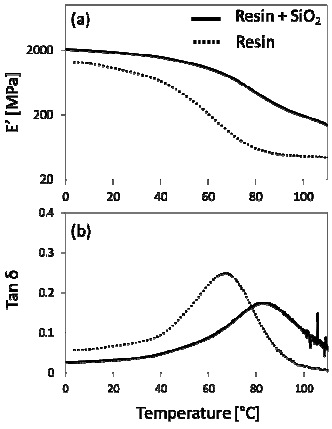

Figure 3. Storage modulus (a) and damping factor (b) curves of both filled and unfilled resin.

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