

Investigation of the Mechanical Properties of Acrylonitrile Butadiene Styrene (ABS)-Nanosilica Reinforced Nanocomposites for Fused Filament Fabrication 3D Printing

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Abstract. To expand the capabilities of 3D printed structures generated from commercial thermoplastic printers, this paper presents the fabrication of polymer filaments that contain inorganic nanoparticles. Nanosilica was dispersed ultrasonically into acrylonitrile butadiene styrene (ABS) and extruded into filaments for fused filament fabrication (FFF) 3D printing. The produced filaments had nanosilica compositions of 5% and 10% wt. A dynamic ultra-micro hardness tester was used in order to characterize the mechanical behavior of the filaments. Also, 3D printed tensile specimens were used to obtain the strain-strain curves and monitor the tensile strength of such structures. The morphology of the nanosilica/ABS composite was studied with a scanning electron microscope (SEM). The results from the dynamic ultra-micro hardness tester reveal that the incorporation of nanosilica particles increases the stiffness and hardness of the ABS material especially in the case of 10%wt concentration. However, for such concentration 3D printing was not possible due to the severe embrittlement of the material. 3D printed structures produced in the form of tensile specimens from the 5%wt nanocomposites display a higher breaking point stress and stiffness than those printed from the pure ABS polymer.

1. Introduction

3D printing processes have had a tremendous impact on the field of design, in the form of rapid prototyping and toolmaking and, more recently, part production. It has been widely used in various manufacturing fields such as aerospace, automobile, biomedical, building and many others [1-4]. Novel materials are now fabricated incorporating additives with unique characteristics. Fused filament fabrication takes advantage of such novel materials produced by combining the base polymers with additives in specific concentrations and structures. The vast majority of the materials used in FFF machines are ABS, PLA and Nylon, with bulk strengths between 30–100 MPa and elastic moduli in the 1.3–3.6 GPa range with those numbers greatly reduced in printed components [5]. However, recently composite materials have been used in 3D printing processes and novel materials are now fabricated incorporating additives with unique characteristics [6-9]. Such studies aim towards the understanding of how well these filaments perform when used in 3D printing and what enhancements are realized when additives are added to the unfilled polymer. It is critical though that such 3D printed materials might result in a range of unidentified mechanical properties of the final part



due to the additive nature of 3D printing. Also, the effects of an array of processing parameters, such as raster angle, printing speed, layer thickness on the mechanical properties of FFF 3D printed parts have been well researched as documented in the literature [10-15].

An alternative technique for the determination of the mechanical properties of polymers is the instrumented indentation technique. This is a simple but powerful testing technique, which can provide useful information about the mechanical properties of materials [16]. Various studies have compared the results obtained from indentation instrumented test with the results obtained from the traditional tensile tests especially for the elastic modulus calculation [17-18].

The current paper aims to characterize the material behavior of 3D printing materials using the instrumented indentation technique. Filaments were produced with ABS reinforced with 5% and 10% nanosilica. The morphology of the nanocomposite systems was characterised by scanning electron microscope. 3D printed constructs were also realised in the form of tensile specimen in order to assess the effect of the nanoadditive in the 3D printed state.

2. Materials and fabrication of 3D printed specimens

The main material that has been used in the current paper is Acrylonitrile Butadiene Styrene (ABS) which is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. Such material was provided in pellets form ColorFabb (Netherlands). Nanosilica particles of 14nm in diameter with concentrations of 5 and 10%wt were dispersed in diluted in acetone ABS over 30 minutes at room temperature in a probe sonicator (UP200S by Hielscher Ultrasonics GmbH). The 5%wt nanosilica reinforced ABS filaments provided good 3D prints, however the concentration of 10%wt was not possible to be printed due to the overall embrittlement of the filament and fracture during handling and processing. Figure 1 shows the ABS and 5%wt nanosilica/ABS filaments as taken from an optical microscope.

Tensile specimens were 3D printed using a BCN3D Sigma printer with a 3 mm extrusion nozzle insert. Each specimen was printed individually at the centre of the printing bed in order to produce all specimens as similarly as possible. Only system integrated (default) variations of 3D printing parameters were employed in the comparative analysis. The printing parameters employed were: nozzle extrusion temperature of 210°C, heat bed temperature of 55°C, deposition line (layer) height 0.2 mm, deposition line width 0.4 mm and printing speed of 50 mm/sec. Deposition speed was therefore not considered a variable in this study and a constant extrusion velocity was selected for all specimens, based on device parameters (e.g. effective printing range). Also, printing was carried out in a standard laboratory conditions without temperature or humidity control. The specimens employed were rectangular with no rounded edges. The specimens were printed in vertical orientation a monolithic shell.

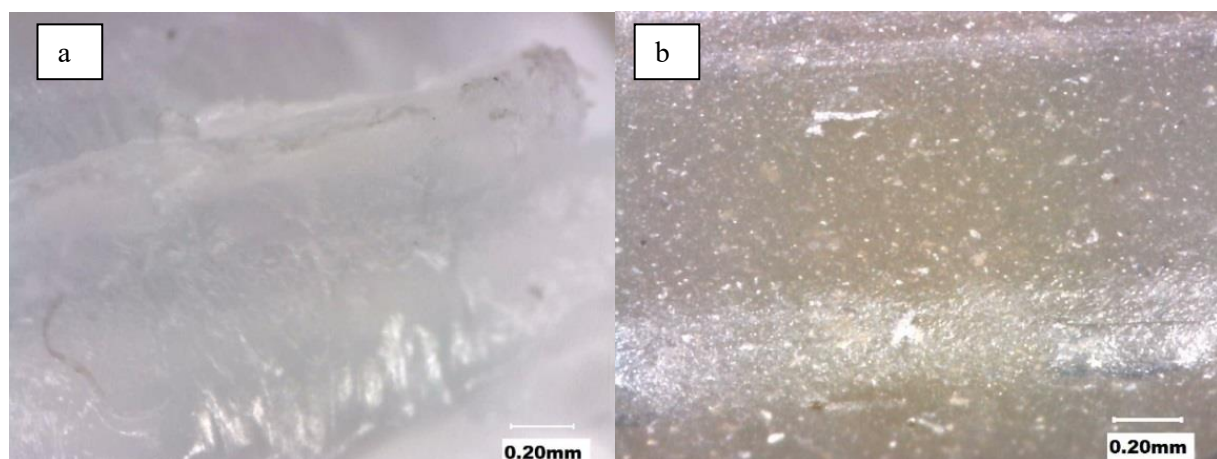


Figure 1. The filaments used for the 3D printing process: a) ABS and b) 5%wt nanosilica/ABS

3. Experimental tests

3.1. Dynamic ultra-micro hardness test

Investigation of the mechanical behavior of the filaments was performed using a dynamic ultra-micro-hardness tester (DUH-211; Shimadzu Co., Kyoto, Japan) fitted with a triangular pyramid indenter tip (Berkovich indenter). The specimens were fixed onto an attached holder. Dynamic micro-indentation mainly involves applying a controlled load (P) through a diamond tip that is in contact with a surface. The penetration depth (h) of indentation is continuously recorded as a function of load. Figure 2 shows a schematic illustration of the typical micro-indentation load–penetration depth curve obtained from dynamic micro-indentation tests. During indenter loading and unloading, the specimen is subjected to both plastic deformation (h_p) and elastic deformation (h_e). The total deformation (h_t) is the sum of h_p and h_e in the micro-indentation load–penetration depth curve. Moreover, the indentation hardness and elastic modulus can be obtained from the indentation load and penetration depth data. The indentation hardness (H_{it}) of the samples is a measure of the resistance to permanent deformation damage and it was calculated from the following equation

$$H_{it} = \frac{P_{max}}{A_p} \quad (1)$$

where P_{max} is the maximum force and A_p is the projected area of contact between the indenter and the sample. A_p is calculated from the following equation:

$$A_p = 23,96 h_c^2 \quad (2)$$

where h_c is the depth of contact of the indenter with the sample calculated as follows:

$$h_c = h_t - \frac{3}{4}(h_t - h_r) \quad (3)$$

where h_r is derived from the load-displacement curve and is the intercept of the tangent to the unloading cycle at P_{max} with the displacement axis.

The elastic modulus (E) of the sample was calculated from the following equation:

$$\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i} \quad (4)$$

where $E_{i,s}$, and $\nu_{i,s}$ are the elastic modulus and Poisson's ratio, respectively, for the indenter and the specimen. For a diamond indenter, E_i is 1140 GPa and ν_i is 0.07.

In this study, the dynamic micro-indentation test was carried out with peak loads (P_{max}) of 500 mN. The load rate was kept constant at 13.324 mN/s, and the hold time at the maximum load was set to 3 s. The dynamic micro-indentation results, such as indentation hardness and elastic modulus, were obtained as the average values of five measurements.

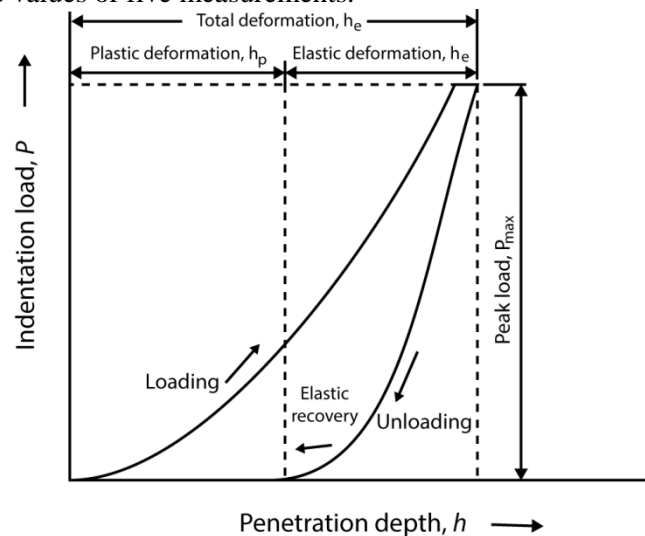


Figure 2. Schematic illustration of the micro-indentation load versus penetration depth curve obtained from the testing.

3.2. Tensile Test

Tensile tests were performed at room temperature (23°C) on a Testometric (UK) universal testing machine equipped with a 50KN load cell at a constant crosshead speed of 2 mm/ min. The dimensions of the 3D printed specimens shown in Figure 3. The modulus was calculated within the linear part of the stress–strain curves. All presented data corresponds to the average of at least five measurements.

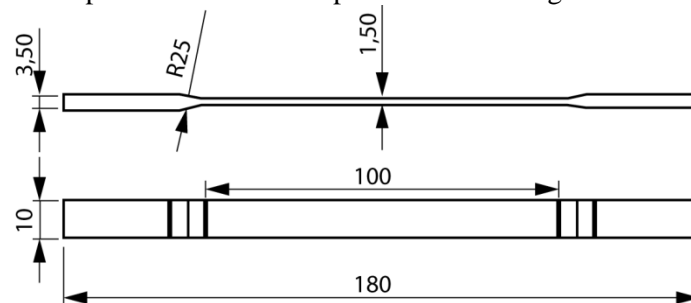


Figure 3. Tensile test specimen dimensions.

4. Results and discussion

The morphology of the ABS reinforced with nanosilica particles was studied using Scanning Electron Microscope (SEM) Phenom ProX and the results are shown in Figure 4. Clearly, the insertion of nanosilica had a profound effect on the overall microscopic appearance and surface texture of the filament which has almost perfect cylindrical form following the extrusion procedure as seen from Figure 4(a). The surface texture is rough with characteristic local fracture areas as illustrated in Figure 4(b,c). At much higher magnification as shown in Figure 4(d), although the image is a bit out of focus due to the limit of the SEM capabilities, it becomes obvious that the dispersion of the nanosilica is not very good judging from the agglomerations that are formed as large circular patterns. These nanosilica agglomerated regions could behave as stress concentrators during testing, which would probably contribute to lowering the durability of 3D printed parts. Typical indentation force–penetration depth curves of the materials under study in a filament form are shown in Figure 5(a). The indentation force–penetration depth curves were obtained during indenter loading and unloading. For all samples the indentation force–penetration depth curves for various indentation peak loads correspond very well with one another. This indicates the high accuracy and reproducibility of the indentation method for the studied materials under mechanical load. The indentation force–penetration depth curves for all materials under test indicated creep phenomenon of the specimen at the peak force of 500 mN. There were no large differences in creep behavior among the samples while no discontinuities or steps were found on the loading curves, indicating that no cracks were formed during indentation. The indentation depths at the peak load range approximately between 14 to 17 μm while the ABS/nanosilica 10wt% curve showed characteristically higher elastic recovery (high elastic deformation).

The indentation modulus for the ABS samples was 1310 MPa and the hardness 117,1MPa. The addition of 5%wt silica nanoparticles increased the modulus to 2015 MPa, which is approximately 54% increase, while the addition of 10%wt nanosilica increased the modulus to 2242MPa which is approximately 71% increase as compared to neat ABS. As expected the hardness also increased at around 10% and 20,2% by the addition of 5%wt and 10%wt silica nanoparticles with values of 128.9 MPa and 140.89 MPa respectively. There is a marked difference of stress–strain curves under tension between the unfilled and nanosilica filled ABS polymer of as shown in Figure 5(b). The maximum stress is 45,6 MPa for the pure polymer and 51,8MPa for the nanocomposite with lower strain to failure values. The modulus of pure ABS was calculated as 2288 MPa and it was improved by the addition of the nanosilica up to 2751MPa. Overall, this trend can be profoundly attributed to the softness of the polymer chain structure of neat ABS and the stiffness of the nanosilica particles. These values are not directly comparable with the results obtained from the dynamic ultra-micro hardness test since such test measures the performance of the bulk material, while the tensile tests account for the layering structure of the 3D printing operation.

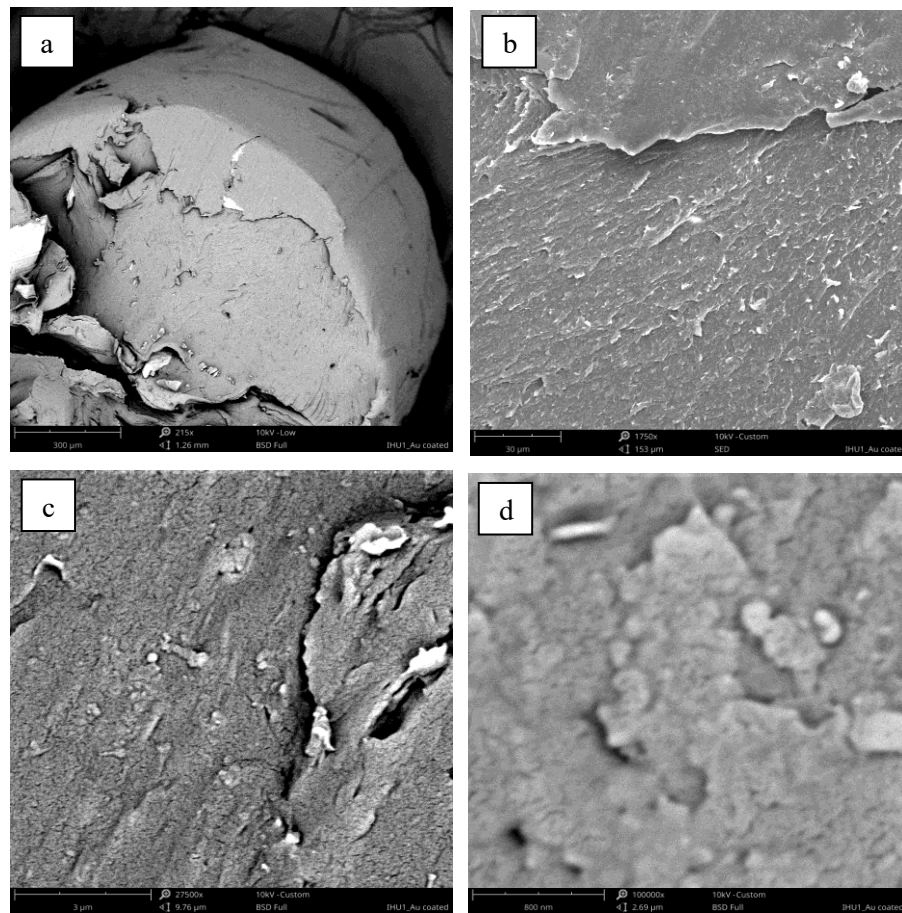


Figure 4. Scanning electron microscope (SEM) micrographs of ABS/ nanosilica 5%wt nanocomposite showing a) low magnification of the filament with the characteristic cylindrical shape, b, c) higher magnification of the nanocomposite showing a relatively rough surface probably from the nanosilica addition, and d) very high magnification and low focused image, depicting rounded- shaped agglomerations.

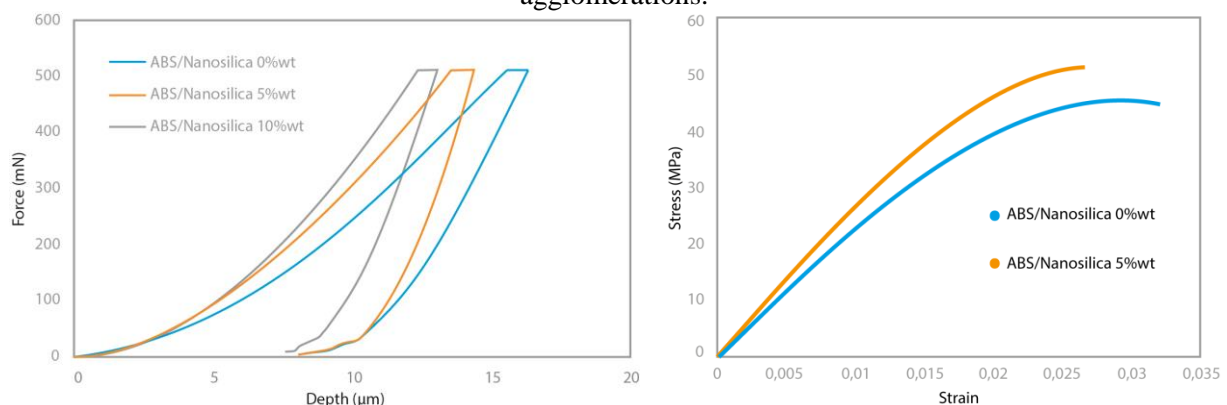


Figure 5. a) Force–depth indentation profiles of ABS and its nanocomposites as a function of nanosilica loading, b) Stress-strain curves of ABS and nanosilica/ABS 3D printed specimens

5. Conclusion

The current paper presents results for mechanical testing of generated filaments for 3D printing by the addition on nanosilica particles in ABS matrix. Nanocomposites of 5% and 10%wt were formed and

tested using a dynamic ultra-micro hardness test. The results reveal that the stiffness and hardness of the ABS material especially in the case of 10%wt concentration is increased. However, for such concentration 3D printing was not possible due to the severe embrittlement of the material. Morphological examination of the filament have shown characteristic roughness due to nanosilica and agglomerated nanomaterial areas from relatively pure dispersion. Tensile specimens were 3D printed using the same comparative printing parameters for both pure ABS and 5%wt nanocomposite. Deposition speed was not considered a variable and all specimens were 3D printed vertically only with a shell. As expected, the 3D printed structures produced in the form of tensile specimens from the 5%wt nanocomposites have shown a higher breaking point stress than those printed from the pure polymer.

6. References

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