Selective laser sintering of polymer nanocomposites

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Abstract

This paper describes the fabrication and characterization of polymer nanocomposite (PNC) materials for use in the selective laser sintering (SLS) process. PNC materials are of great interest generally because of their excellent physical properties, and offer excellent potential in rapid manufacturing of structural polymeric parts. Three different nano additive materials have been used: cerium oxide IV, yttrium stabilized zirconia, and layered Hectorite clay. These materials have been used to reinforce PA6 polymer using solution blending and spray drying to create powder with particle sizes in the range of 5-40 μm. The mechanical properties and microstructure of the PNC materials have been evaluated and the results compared to those of unfilled polymer.

1. Introduction

Selective laser sintering (SLS) is a layer manufacturing (LM) technique and has been used to produce prototypes as well as functional components [1]. The advantage of the SLS process is that it can be use to manufacture parts from polymer, metal and ceramic materials [2]. The aerospace industry has recognised the advantages of SLS as a production process for the fabrication of aircraft and aerospace components [3-4].

However, the availability of high performance material is still one of the key issues in SLS. The materials and the properties of the SLS component often fail to match their moulded or machined counterparts [5]. Many efforts are under way to develop high-performance SLS material that have promise for engineering applications, including enhanced mechanical properties [6-9] and flammability [9]. Polymer nanocomposites (PNC's) are based on controlling microstructure by incorporating nanometer-size additives as second-phase dispersions into polymer matrice. Improvements in strength and modulus of 30-50% have been reported [10] to have arisen as a result of addition 2-5wt% of nano clay.

The aim of this study was to examine the suitability of PNC's prepared from solution blending for the SLS process. Although there are a number of studies on properties evolved from PNC's, none are devoted to PNC that has been produced from a solution method, which is an established route for the preparation of the PNC. The method can produce a randomly exfoliated structure and reduce agglomeration in the matrix [11].

2. Experimental procedure

2.1 Materials

Three different types of nano additive materials have been used to reinforce Polyamide 6 (PA6). PA6 powder with an average size of 15-20μm was purchased from Goodfellow (UK)

[12]. The nano additive materials are:

- Cerium oxide (CeO_2)
  The CeO_2 is a nano-dispersion (nitrate-stabilised) material with particle size of 5-7nm by TEM received from AMR Ltd company. The component of the material are (in wt%); Cerium IV oxide 40%, Nitric Acid 1.5-3% and water > 57% [13].
- Yttrium stabilized zirconia (YSZ)
  YSZ is a ceramic base material and was received from AMR Technologies. It contains zirconium oxide >94% and yttrium oxide at 5.4%. The key properties of the YSZ are high fracture toughness, high hardness and thermal resistance [14].
- Hectorite clays
  Modified organoclay BENTON166 was received from Elementies Specialist (UK). The BENTON166 is an alkylaryl ammonium hectorite clay material and it has been developed as an additive for most polymer systems. The key properties are high mechanical strength and improved flame retardance [15].

2.2 Preparation of polymer nanocomposites

The preparation procedure is shown schematically in Figure 1 and aimed to prepare materials with a good dispersion of the additive in the polymer matrix.

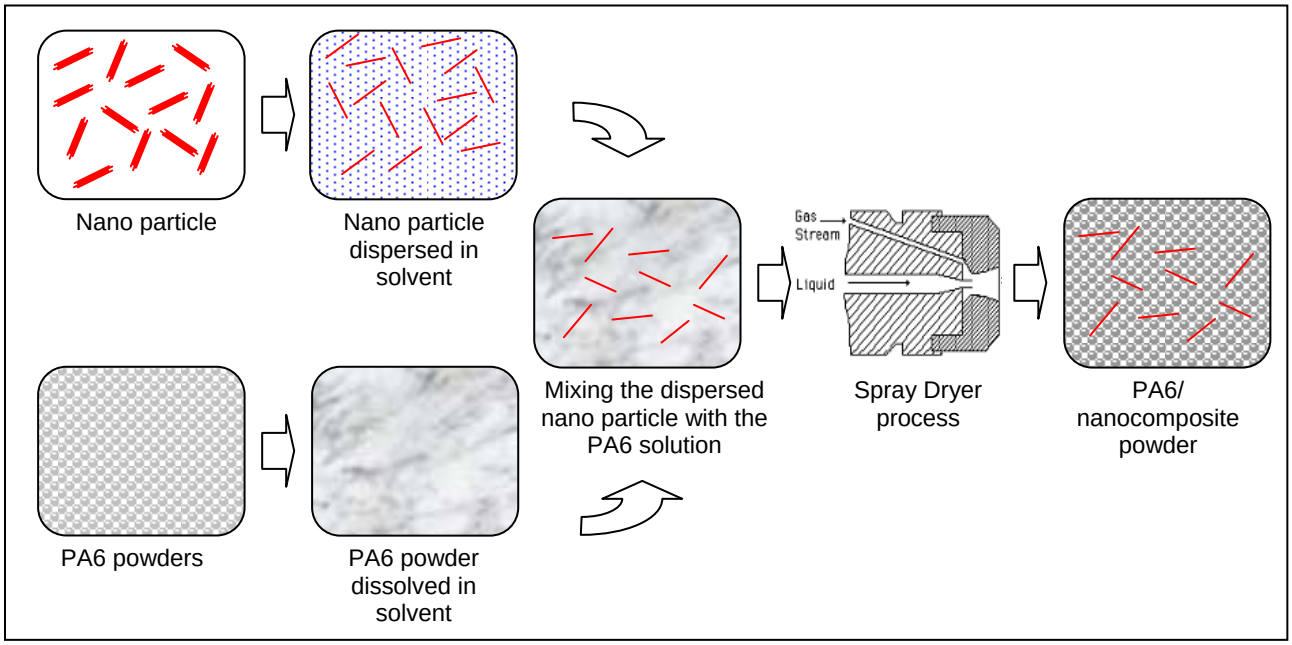
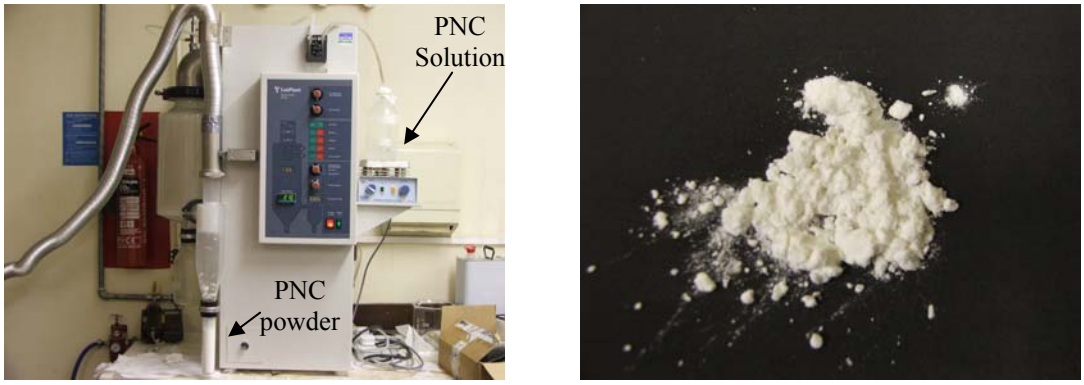


Figure 1. Schematic representation of preparation procedure for PNC, consisting of nano additive particle and PA6 by using a solution method

The PA6 powder as well as the nano particles were dissolved in formic acid (HCO_2H) in separate containers and stirred at room temperature for 3hrs. Then the dispersed nano particles were added into the PA6 solution at 5wt% and stirred for another 4hrs. A Labplant model SD05 spray dryer has been used in the production of powder. Spray drying involves the atomization of a liquid feedstock into a spray of droplets and drying of the droplets with hot air in a drying chamber as shown in Figure 2(a). The powders obtained from the process, Figure 2(b) were then further dried in an oven at 70^{o}C for another 4hrs. The powder was then ball milled for two hrs to break up any agglomerated particles. The preparation finished with a sieving process starts using mesh sizes from 200 μm to 70 μm.

2.3 Characterisation

Differential scanning calorimetry (DSC) was performed on a Perking-Elmer DSC 7 under nitrogen purge at a heating and cooling rate of 10°C/min. 10mg of samples were heated from room temperature 30°C to 250°C. Measurement of tensile strength was carried out using DARTEC tensile machine with 5kN load cell and the cross head movement of 1 mm/min. Specimens were fabricated using SLS experimental machine based on ASTM D638 type V standard [16]. TEM (Philips CM200) and SEM (Philips XL30) were used to observe the dispersion of nano additive and analyzed the fracture surface morphology of the processed material. The fracture surfaces of the tensile specimens were investigated to study the fracture behaviour of different composites and the mechanisms of the enhanced mechanical properties.



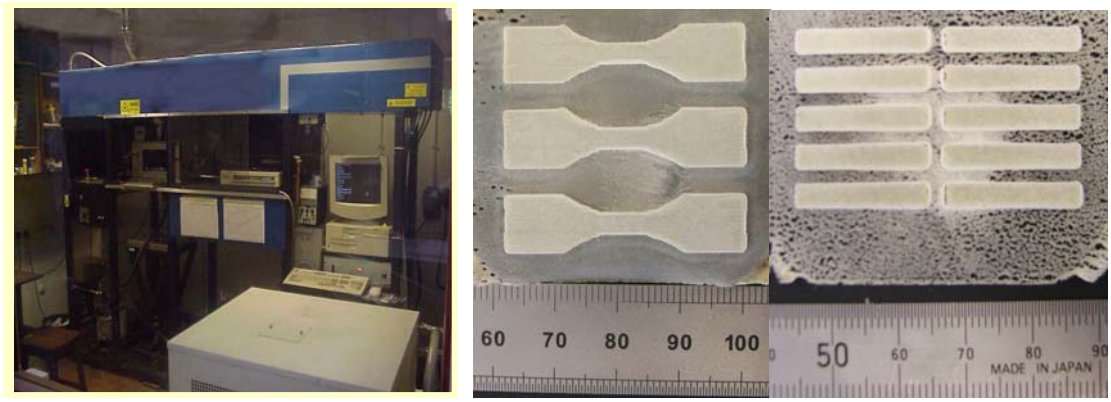
(a) (b)

Figure 2. (a) SD-05 spray dryer machine used in production of powder,
(b) Photograph image of the spray dried powder

2.4 SLS processing

A CO_2 SLS experimental machine with the build volume 75mm x 75mm x 100mm has been used to fabricate the test specimen as shown in Figure 3(a). The machine was constructed at the University of Leeds [17].

The test specimens have been fabricated using process parameters of 10 Watt laser power, 500 mm/s scanning speed, 0.6 mm spot size on the bed, 0.1 mm scan spacing and 0.1 mm layer thickness. During processing the powder chamber is heated to 195°C through heating elements in the piston. Figure 3(b) shows tensile and density test specimens produced.



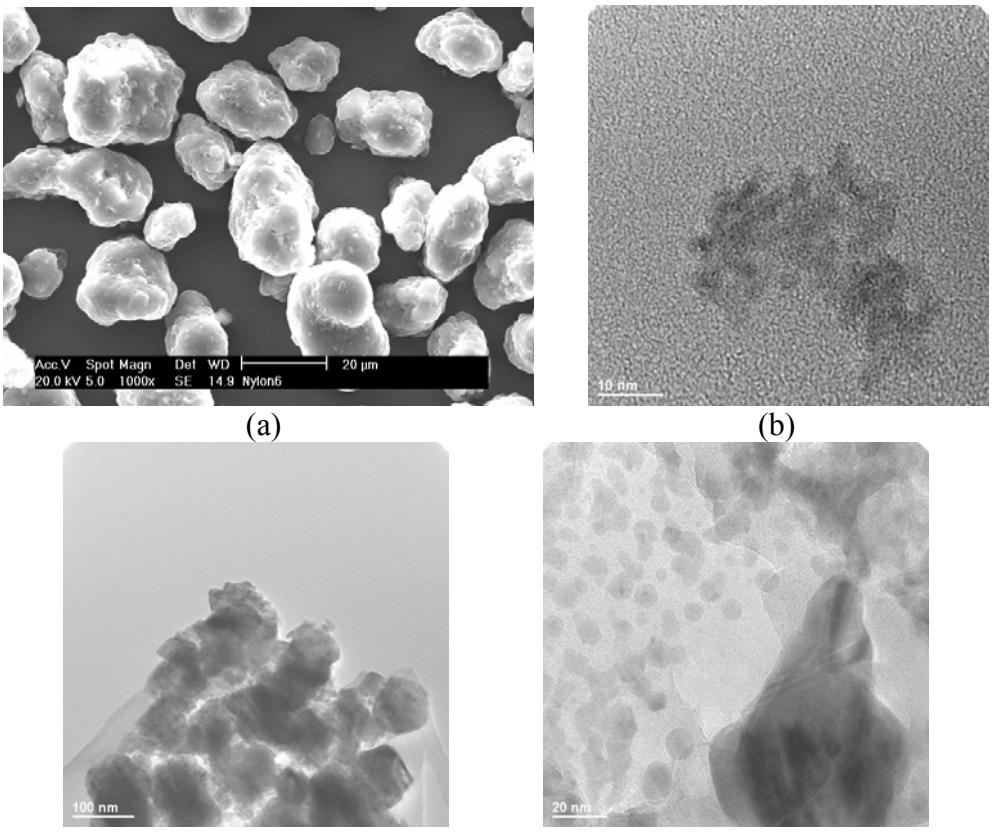
(a) (b)

Figure 3. (a) CO2 SLS experimental machine used to fabricate test specimen (b) Tensile and density test specimen.

3. Results and discussion

3.1 Morphology

Figure 4 Shows a general view of the as received PA6 powder as well as the additives. The PA6 powder Fig. 4(a) has an irregular shape with a rough surfaces observed on SEM. The additives all been observed using TEM after dispersion in the solvent material. The CeO_2, Fig. 4(b) and the YSZ, Fig. 4(c) are the particulate materials whereas the clay, Fig. 4 (d) is in layered particle form.



(a) (b)

(c) (d)

Figure 4. Morphology images of the raw material:
(a) PA6 powder (b) CeO2 (c) YSZ (d) Clay

3.1 Dispersion of additive in PA6 matrix

Figure 5 shows SEM images of different PNC powder produced from the spray drier process. Spherical powders with an average size of 5-40 µm were observed.

Patches of white contrast material were found on PA6/CeO_2 powder and were confirmed by EDX analysis to be CeO_2. This was thought to arise from separation between the CeO_2 and PA6 during the mixing and spray drying, suggesting that the material was not well dispersed in the matrix. This material was not continued for further processing as a result. A different phenomenon was found for PA6/YSZ material where there was also white contrast material observed but of a small size and uniformly distributed on the powders. This is believed to be coarse particles present in the YSZ. The PA6/clay was found to have good dispersion.

The PA6/YSZ and PA6/clay were continued for SLS processing with further dispersion analysis carried on the processed material. This was done by taking a section around 200nm thick using a Microtom and making a TEM observation.

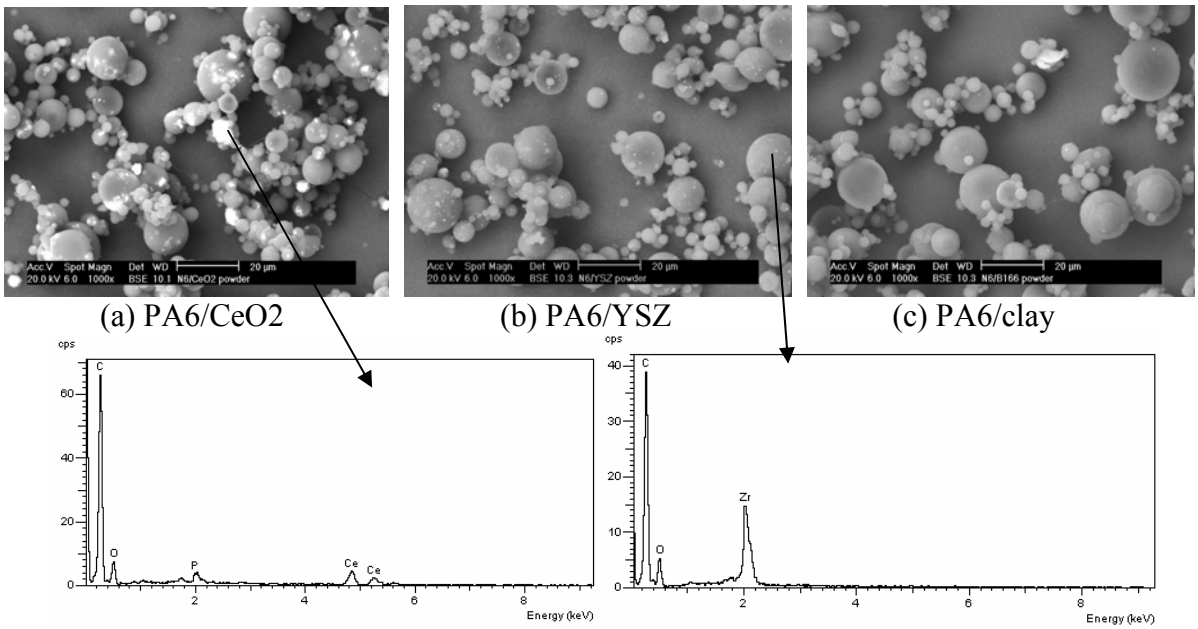


Figure 5 SEM images of PNC powders produced from spray dryer process and EDX analysis.

Figures 6 and 7 shows the TEM images sectioned of the PA6/YSZ and PA6/clay material after having been processed by SLS. As been suggested from Figure 5, some coarse YSZ particles can be seen in the matrix as well as the finer one with higher magnification. The dispersion of YSZ and the clay was random across the PA6 matrix suggesting good dispersion was achieved using the preparation method described in section 2.2.

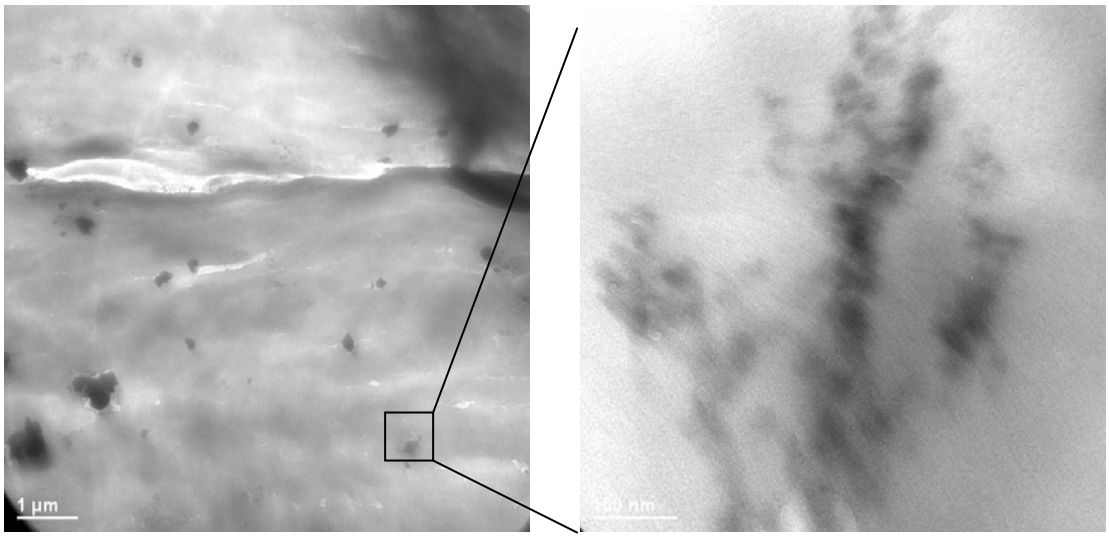


Figure 6 TEM images of the SLS processed PA6/YSZ nanocompsoites

3.2 Thermal properties

Figure 8 shows DSC results for PNC's and the unfilled PA6, highlighted at the peaks area during heating and cooling process. During the heating process, the PA6 and the composites show endotherms with two melting peaks, while only one recrystallisation peak is observed during the cooling process. The melting temperature and recrystallisation temperature for spray dried PA6 and the composite were slightly higher that the original PA6 material.

3.4 Part density

The apparent density of the sintered specimens was measured by weighing SLS'd specimens

of approximately 20 x 5 x 2 mm. The average density was obtained from 10 measurements and the results are shown in Table 1. The density of spray dried material was slightly lower than the as received PA6 material.

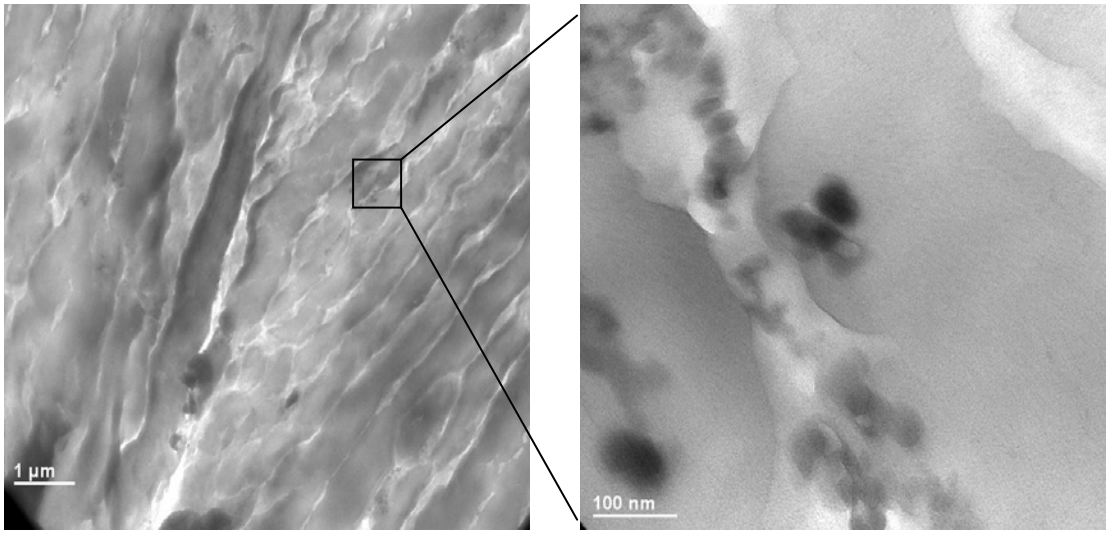
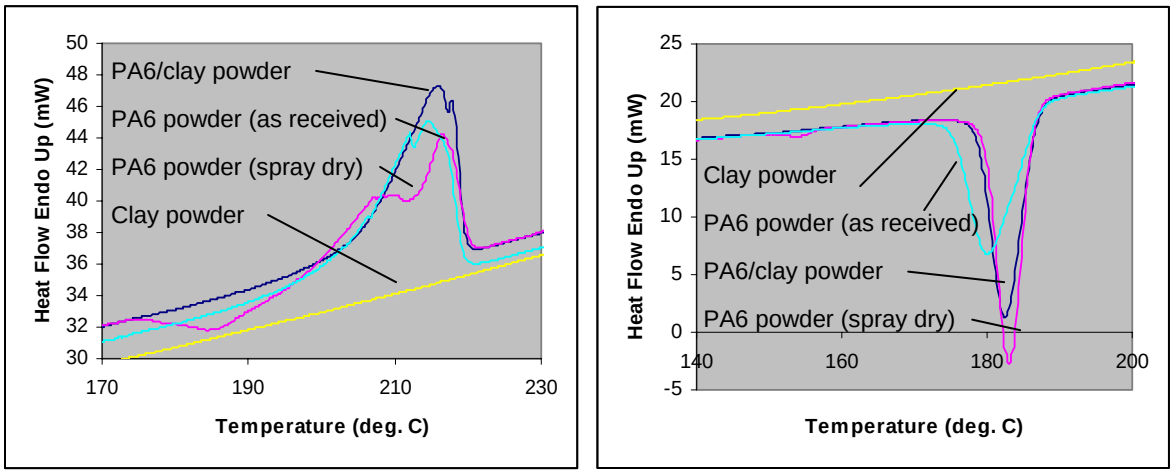


Figure 7 TEM micrographs of the spray dried PA6/clay



(a) Heating (b) Cooling

Figure 8. Melting and cooling peaks of PNCs material

Table 1 SLS part density

Materials	**Density, ρ (kg/m^3)**
As received PA6 (0wt%)	840
Spray dried PA6 (0wt%)	811
Spray dried PA6/YSZ (5wt%)	806
Spray dried PA6/clay (5wt%)	779

Note: Density for moulded part PA6 material = 1120 kg/m^3 [9]

3.5 Tensile properties

Figure 9 shows stress-stroke curves of the PNCs together with the unfilled PA6. The as received PA6 shows very consistent result with the higher stroke value as compared to the spray dried material.

Figure 10 shows the result of the average tensile properties of the PNCs and the unfilled PA6. The result has shown a reduction of tensile strength for spray dried PA6 material as compared to the as received PA6. Similar result also was found for the PA6/YSZ and PA6/clay nanocomposite materials where the tensile strength are lower that the as received unfilled PA6 material, but it's slightly higher than the spray dried PA6.

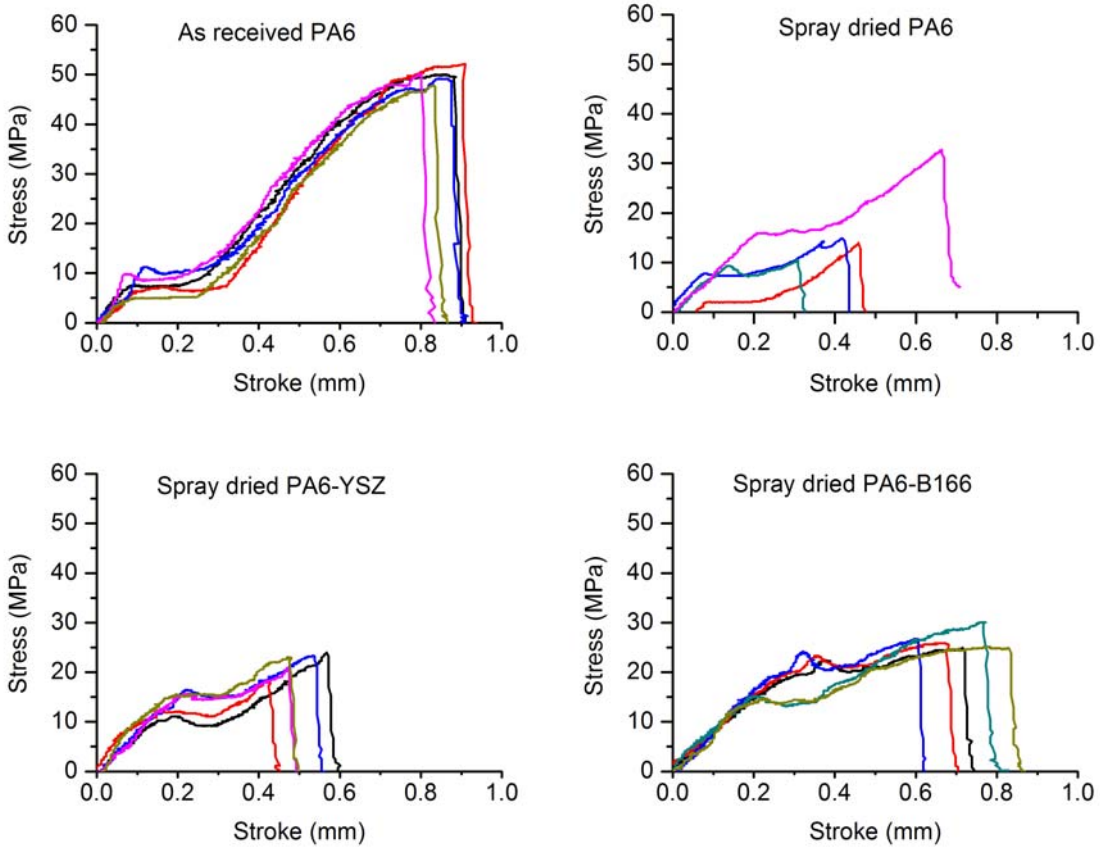


Figure 9 Stress-stroke curves of the (a) As received PA6 (b) Spray dried PA6 (c) Spray dried PA6-YSZ and (d) Spray dried PA6-B166

3.6 Microscopy of tensile fracture surface

Figure 11 shows the morphology of the tensile fracture surface for PNC and the unfilled PA6. The sintered specimens for the spray dried material contains voids which would act to reduce density and strength. Most of the voids for the spray dried material are spherical in shape and bigger than those in the as received PA6. This suggests that the cause was trapped gases generated from residual solvent from the spray drying being driven off during laser sintering.

4. Conclusions

The following conclusions were drawn from this study:

1. PA6/YSZ and PA6/clay nanocomposite material have been successfully prepared by solution blending, followed by spray drying.
2. The TEM observation on SLS processed PNC materials have shown that good dispersion of the YSZ and clays in PA6 matrix were achieved.
3. SLS fabrication of near-full dense samples for the PNC material was possible.
4. The spray drying process was found to reduce the tensile strength of the PA6 material.
5. Spray dried PA6/YSZ and PA6/clay nanocomposite materials with 5wt% additives

were found to have strengths 50-60% higher on average than that of spray dried PA6 without reinforcement.

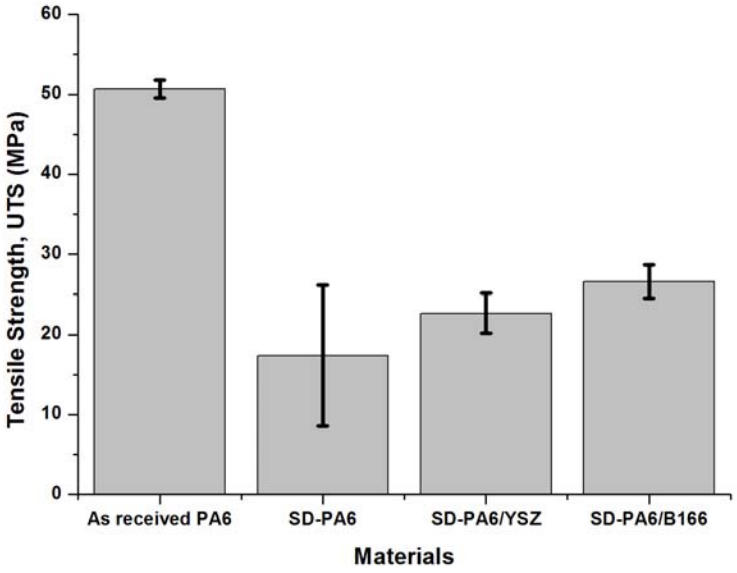


Figure 10 Tensile strength result for the PNCs and the unfilled PA6.

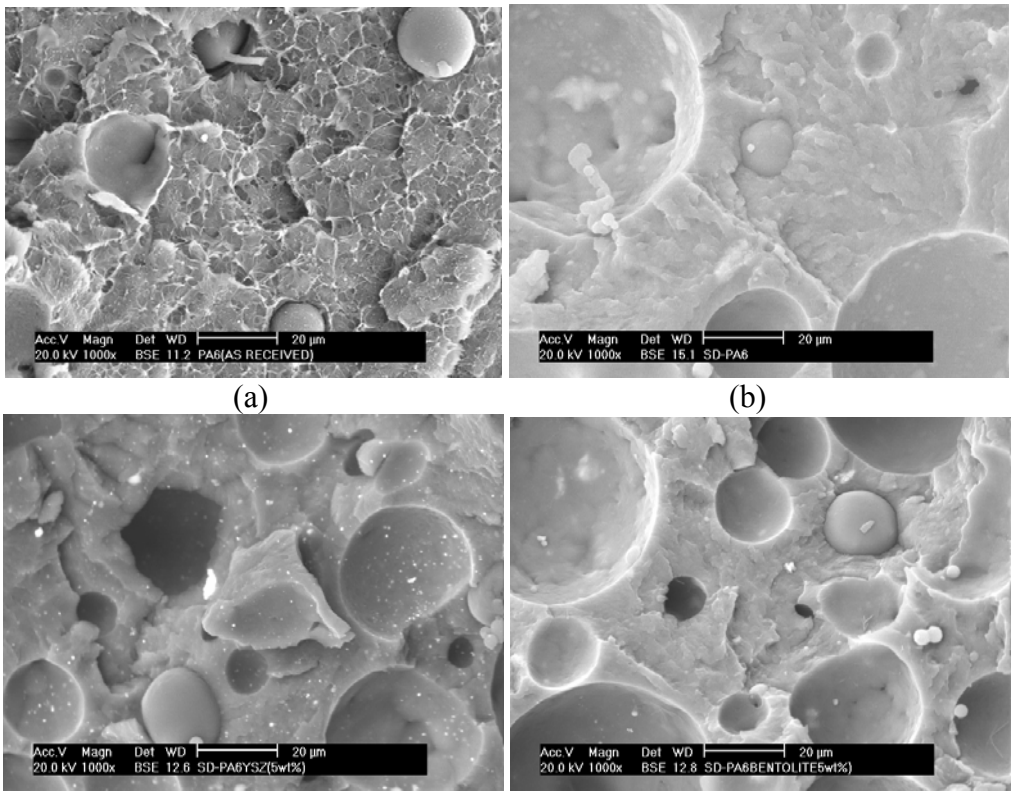


Figure 11. SEM images of tensile fracture surface of (a) as received PA6 (b) spray dried PA6 (c) spray dried PA6/YSZ (5wt%) (d) spray dried PA6/B166 (5wt%)

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