Upcycling Macadamia Nut Shells: The effect of Particle Size and Moisture Content on 3D printed Nutshell-Plastic Composites

Jordan Girdis[1], Gwénaëlle Proust[1], Sandra Löschke[2], Andy Dong[1]

[1] School of Civil Engineering, The University of Sydney, NSW 2006 Australia

[2] Faculty of Architecture, Design and Planning, The University of Sydney, NSW 2006 Australia

Abstract - **This paper investigates the effects of particle size and moisture content on the structure and material properties of extruded composite filaments composed of macadamia nutshell (MN) flour and acrylonitrile butadiene styrene (ABS), using Scanning Electron Microscopy (SEM). The moisture content of the MN flour was reduced to 7.05% by a three-hour drying process. The size of the particles of MN flour in the composites was varied by using different sieves; despite the size variation, a morphology study of the particles shows that the shape of the particles remains similar for each size range. The SEM micrographs show that large voids were introduced into the sample during the extrusion process to create the filaments, with larger but less frequent voids occurring in the dried samples. The micrographs also show the samples were homogenously mixed by using the single screw extruder. The paper also examines how the optimization of printing variables were used leading to a superior sample**

I. INTRODUCTION

Whilst Wood Plastic Composites (WPCs) have been well studied and have been used as a sustainable alternative to natural wood products in the construction industry for the past two decades [1], less literature exists on the use of WPC's for the growing industry of 3D printing applications. 3D printing forms a disruptive technology to traditional manufacturing processes enabling rapid prototyping using varied materials with great accuracy and relatively low cost [2]. Few commercially available WPC composites exist, with the exception of Laywoo-D3 [3] and Woodfill [4] that provide two options for WPC printing.

The use of other by-products from the forestry and agricultural industries has been largely overlooked in WPC production to date. Macadamia nutshells (MN) present similarities with wood and could be upcycled through their use in the production of composite materials. Girdis et al. found that a MN polymer composite of 19%MN, 78% acrylonitrile butadiene styrene (ABS) and 3% maleic anhydride (MA) binding agent provided a greater specific strength than the commercial Woodfill filament as shown in Figure 1[5]. In Australia, MN are a crop residue and represent a woody waste, largely used as compost or fuel [6] and as binding agent in glue [7]. Finding valuable uses for this waste material could therefore be of great interest for economic reasons.

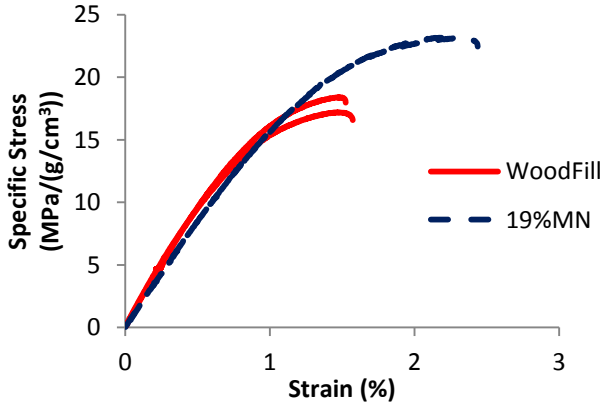

Figure 1 – Specific stress – strain behavior displayed by tensile coupons produced with Woodfill and 19%MN filaments [5]

In this study, MN – polymer composite filaments for 3D printing were produced with varying water

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content and MN particle sizes to optimize the performance of the final 3D printed product.

II. EXPERIMENTAL TECHNIQUES

The investigation involved full preparation of raw materials for an extruded filament. To achieve this, MN flour was first sieved into varied grades of particle size. These grades were then analyzed using Malvern Morphologi G3 equipment to confirm the particle size and determine the particle shapes. Subsequently, the flour samples were dried at 105 ^{o}C to remove as much moisture as possible by measuring the weight of the samples at regular intervals during the drying process until the weight stabilized. This process took 3 hours. The moisture content was then determined on the dried flour sample. The dried MN flour, ABS pellets and maleic anhydride (MA) were then mixed in specific ratios as shown in Table 1 and extruded at 167^{o}C using a Noztek Pro filament extruder with a 3mm extrusion head. This process was undertaken within a short time period using the same extruder to control humidity and temperature settings and to avoid the introduction of any other parameters that could affect the results.

Table 1 – Composition of the samples produced for this study.

Sample	Sieve Component (µm)	%wt MN	%wt MA	%wt ABS
90MN-Dried	90-150	19	3	78
150MN-Dried	150-212	19	3	78
150MN-Undried	150-212	19	3	78
212MN-Dried	212+	19	3	78

These filaments were then verified as a printable filament by use in a Fused Deposition Modeling 3D printer. The printer used was a commercially available Lutzbotz Taz 5. The temperature used for printing was 250 ^{o}C at the print head and 100 ^{o}C bed temperature to allow adequate adhesion. 100% infill and a 0.8mm print head were used to print tensile test specimens with a test cross section of 3mm x 10mm.

III. RESULTS AND DISCUSSION

Figure 2 shows the reduction in weight through the drying process revealing that the MN particles contained 7.05% of water. This moisture loss occurred over three hours, with the weight of the sample stabilizing after this time. This value of 7.05% is compared with the nut in shell (NIS) moisture of MN which can be as high as 22-25% [7]. [7] also points out that the relative humidity has a large impact on the NIS moisture content. The relative humidity at Sydney Observatory Hill just prior to the sample being placed in the extruder was 47% [8].

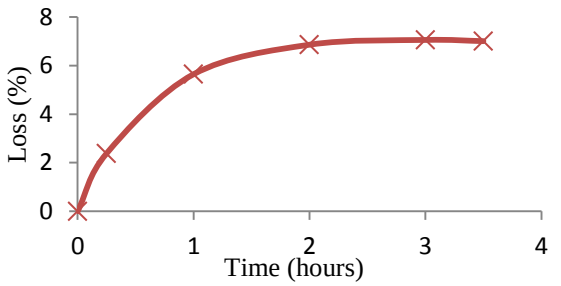


Figure 2 – Weight loss due to moisture content being removed from the MN flour at a constant temperature of 105^{o}C.

Figure 3 shows that the process of sieveing had varying levels of success in grouping particles by particle size. These graphs show a tight distribution for the 90MN sample, with an increasing spread for the larger particle size samples. This could be due to a lack of smaller particles passing through the smaller sieve sizes. As shown in Table 2, whilst the samples were sieved into different compents, all of the samples were on average smaller than these sieve component values. This is due to the difficulty to sieve the MN material: Because of its low density and particular nature and the humid nature of the environment, often the smaller particles would remain stuck inside the higher value sieves. Whilst this effect was noted for these particle sizes, the process of sieving was still effective in producing samples of flour presenting different particle size distributions similar, if not exactly equal, to those intended. It was therefore still possible to see the particle size effect on the fabircated filaments. For this investigation, a sieve smaller than 90µm was used, however, a very small amount of material passed through this sieve size and was not usable for this study.

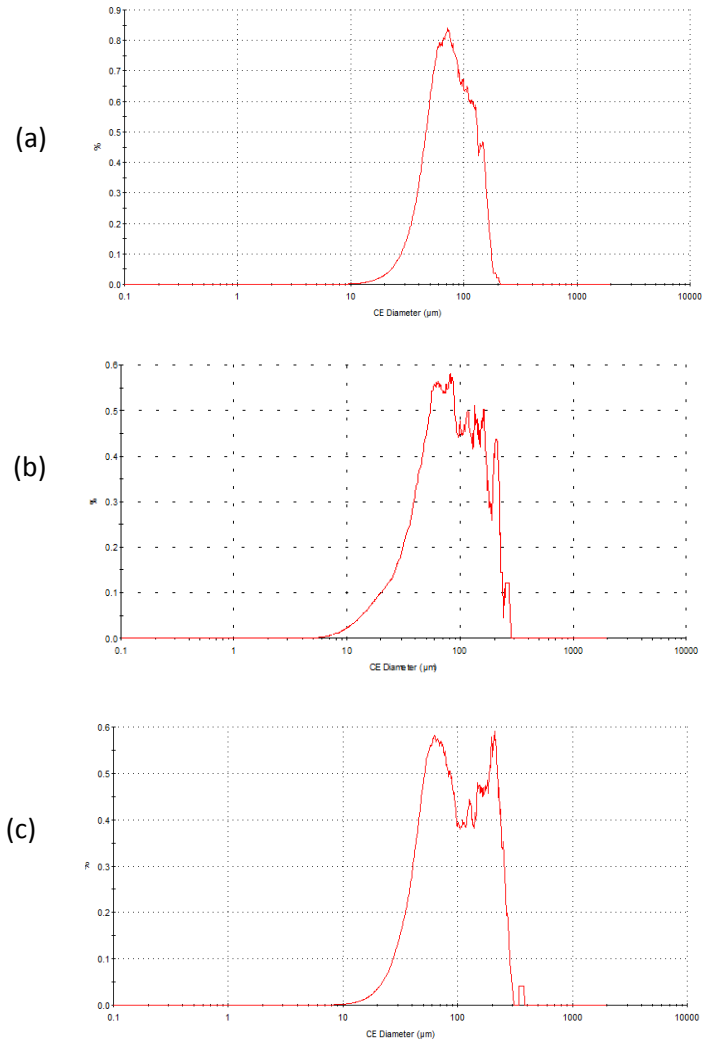


Figure 3 – Circular equivalent (CE) diameter comparison of MN particle size by volume distribution (smoothed over 11 points), (a) 90MN, (b)150MN, (c)212MN.

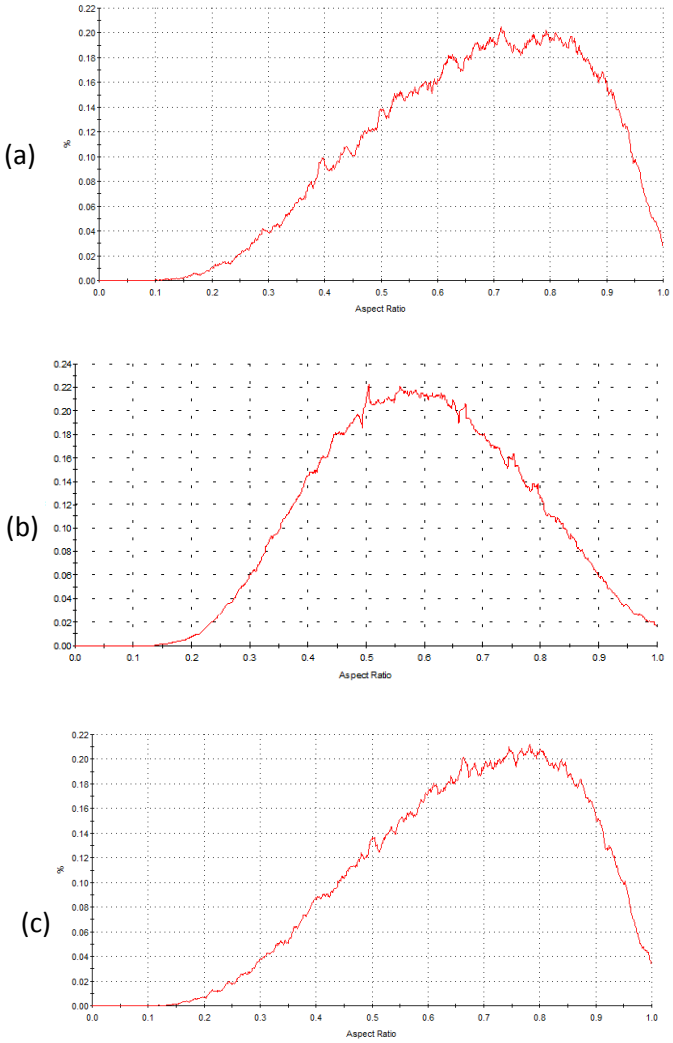


Figure 4 – Comparison of the aspect ratio of the MN particles (a) 90MN, (b) 150MN, (c) 212MN.

Figure 4 presents the distribution of the aspect ratios of the particles obtained by using the Malvern Morphologi G3 particle anyalser. These graphs show a consistant apect ratio between the 90MN and 212+ samples, however a slight reduction in the aspect ratio is observed for the 150-212 particles. The results obtained from the data anlysis are presented in Table 2. The reason for this discrepancy will form the subject of future work.

Table 2 – Measured particle size (CE) and aspect ratio of sieved MN flour

Sieve Size (µm)	Average Circular Equivalent Particle Size (µm)	Aspect Ratio
90-150	81.14	0.669
150-212	93.73	0.597
212+	112.5	0.675

Table 3 shows the densities of the filaments produced from the MN flour, presenting various particle size distributions. From the table it can be seen that all dried samples display a constant density. This result is important as it shows there is no significant difference in density caused by particles of different sizes with the same ABS matrix. Similarly, the undried sample presents a density far higher than that of the dried samples. This is to be expected as the undried sample has already proven to contain 7.05% moisture content, adding 7.05% to the total weight of the sample. However, the difference in density is higher than just the 7.05% moisture content. The reason for this might be the moisture content within the sample leading to amalgamation of the particles and tight clumping within the ABS matrix. This could again reduce the presence of voids and hence increase the density of the sample.

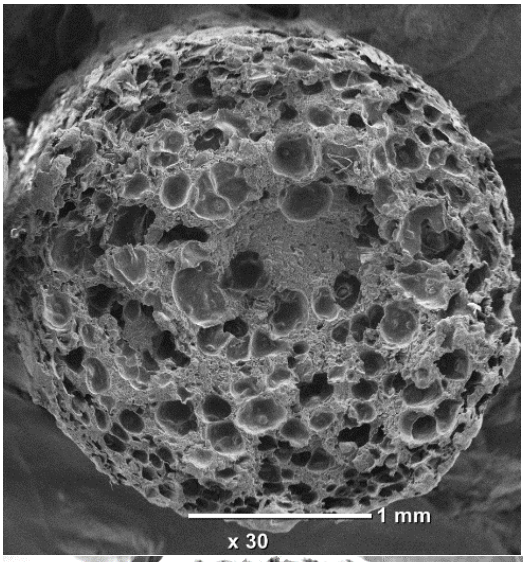
Table 3 – Densities of produced filaments

Specimen	**Average Density (g/cm^3)**
212MN-Dried	0.69
150MN-Dried	0.67
150MN-Undried	0.83
90MN-Dried	0.70

The evidence for this amalgamation is however not supported by the analysis of the SEM data presented in Figure 5 as no aggregate of MN particles is evident on the micrographs. Figure 5(a) of the undried sample shows a greater number of voids within the filament than Figure 5(b) of the dried sample whilst the dried sample shows much larger voids than that of the undried sample. These voids within the sample are not cavities created by the removal of MN particles during the prepartion of the cross-section specimen as these are too large in comparison with the particle size used. The void size for the dried sample reaches a diameter of up to 500µm, which is far higher than that of the average size of the MN particles.

A possible explanation for the smaller voids in the undried sample is that as the MN particles were heated up throughout the extrusion process to 167°C, so that water vapour emerged and formed small, homogenous voids within the sample. However this does not explain the large voids encountered in the dried sample. A possible explanation for the emergence of large voids in both samples is the extrusion process. The Noztek extruder is a single screw extruder open to the environment at the hopper end. It is possible that air becomes entrapped within the polymer of wood flour particles and may pass through the extruder to form part of the extruded sample.

(a)



(b)

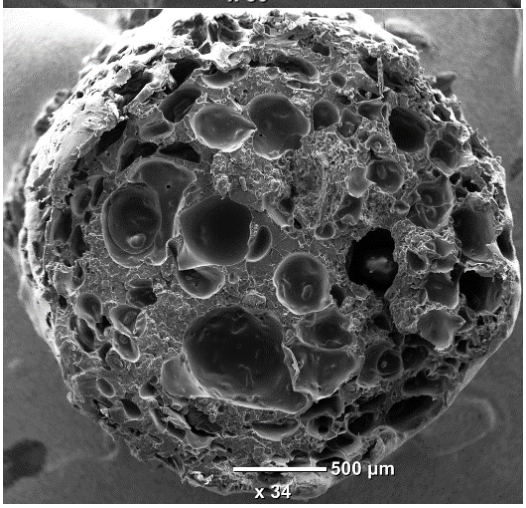


Figure 5 – Secondary electron images of NM-polymer composite filaments, (a) using undried flour, (b) using dried flour.

Due to the voids observed in the SEM imagery, it was noted that the printing parameters would need to be optimised to avoid voids forming in printed samples. This was confirmed through the printing of test samples, with the voids formed clearly visible in Figure 6.

Figure 6 –Standard printed sample (left) and optimised printed sample (right)

In order to reduce the voids present in the printed sample, the printing parameters were altered to compensate for the voids present in the extruded filaments. The aim of this optimisation was to match the volumetric rate of material deposited of the extruded samples to that of a homogenous cross section. To achieve this, the theoretical no air voids densities of each filament was computed using mass volume calculations with known densities of component materials. This computed density was compared with measured density obtained through mass/volume calculations. It was found that the extruded specimens exhibited a density 67% of the theoretical no air voids density.

This reduction in density correlates to a reduction of material deposited on the printing bed compared with a no voids sample if printed at the same rate. In order to compensate for this 67% reduction of filament the printing parameter of print extrusion was altered to 150%, matching the volumetric deposition rate of the print bed between the sample with and without voids. This process was highly effective with the printed sample as shown in Figure 6 produced with this optimisation technique providing a far more homgoenous sample.

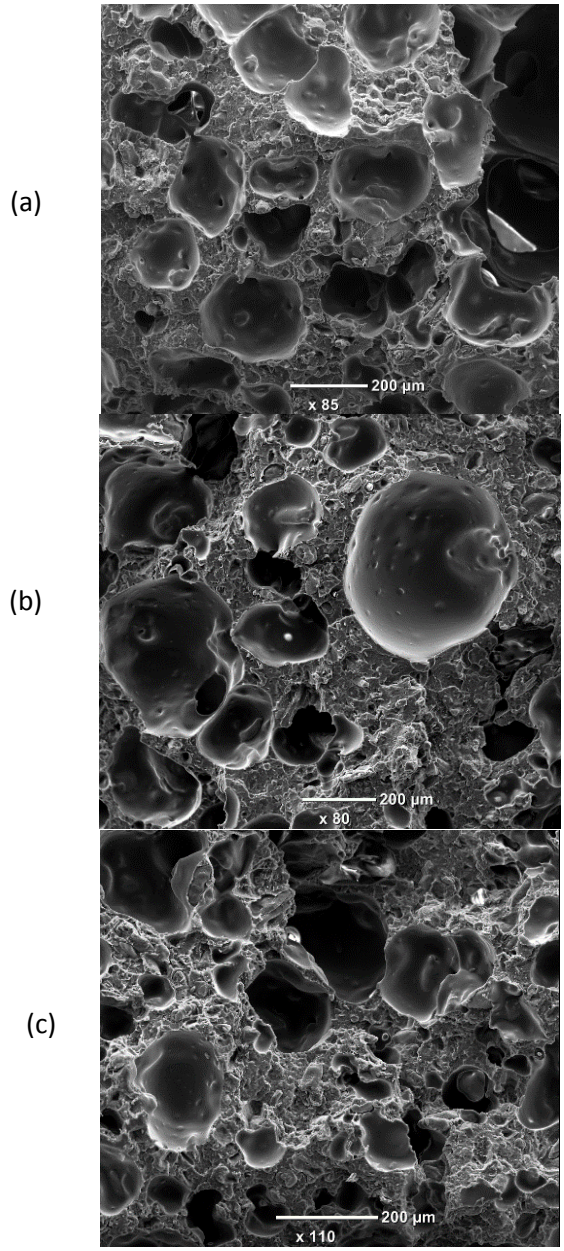


Figure 7 – Secondary electron images of filaments containing different particle size, (a) 90MN - dried, (b) 150MN - dried, (c) 212MN - dried

Figure 7 shows samples produced using different particle size MN flour and demonstrates the variance between them. It can be observed that the extrusion process led to a homogenous matrix between the voids, altough no major difference in structure is observed in the samples. At this scale, it should be possible to see the MN flour particles as the average particle size for all samples in 100µm, however the absence of such observation points towards a homogeounous mixture of the ABS polymer and MN flour.

IV. CONCLUSION

MN flours of varied particle size were combined with ABS polymer to produce a WPC filament. There was no observable trend between the aspect ratio of the particles and the size grades. The MN powder contained 7.05% of water which was removed using an oven at 105^{o}C after three hours before the production of the filaments by extrusion. The density of the filament was significantly lower when the MN flour was dried prior to extrusion, with no significant variation in density of filaments containing particles of varied sizes. SEM analysis revealed that there was a large presence of voids within all samples due to the extrusion process, with a high degree of homogenoity within the WPC. The voids present in the filaments were able to be negated in printed samples through printing parameter optimisation. Further reasearch will be conducted to examine the behaviour of the specimens under mechanical testing, along with further analysis of the physical characteristics of the WPC matrix.

This investigation highlights the significant potential of exploring the upcycling of waste and by-products from the forestry and agricultural industries into innovative goods. The initial results point to the need for future research into the composition and material properties of new composites.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

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