3D printing of carbon nanofiber-PLA composite

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Abstract

The aim of this research study was to study the mechanical properties of carbon nanofiber (CNF) and Polylactide (PLA) composite. The composite material was developed by mixing Polylactide with carbon nano fiber using a three dimensional printer. The research study presents the following; the mixing ratios which were used, time intervals, mixing equipment and mixing method. After the composite material was developed, the mechanical properties of the material were studied. These mechanical properties include the ultimate tensile strength and yield strength between the two materials that is PLA and PCM composites. The effect of processing methods and conditions on the properties of CNF/PLA composites were also taken to consideration due to the impact they might have in the results obtained. An excel Anova software was also used to compare the UTS of the two materials and conclude if there is a significant difference between the parent material and the developed composite material. The Ultimate tensile strength improved by 4.16% from the initial ultimate tensile strength obtained from PLA samples, while the yield strength increased by 38.05% from the PLA. These results obtained conclude that the mechanical properties of the PCM have improved. At the end of the paper, recommendations of possible future challenges for CNF/PLA composites will be presented.

Keywords: Carbon nanofiber; Poly(lactic acid) or Polylactide (PLA); Chloroform; 3D printer

List of abbreviations

PLA – Poly(lactic acid) or Polylactide

CNF – Carbon nanofiber

CVD – Chemical vapor deposition

PMC's – Polymer matrix composites

MMC's – Metal matrix composites

CMC's – Ceramic matrix composites

CCM's – Carbon carbon composites

3D printing – Three dimensional printing

UTS – Ultimate tensile strength

PCM – Polymer composite material

1. Introduction

Polymer composite materials (PCM) are materials made by merging two or more materials. According to Jan and Ali Munawar [1], composites are materials that contain a strong load carrying material (strengthening) implanted in a weaker material (matrix) [1]. As reported by Royal Society of Chemistry (RSC) [2], the key advantage of using composite materials is that they are very light and strong. The reinforcement provides strength and inflexibility while the matrix maintains the position and alignment of the reinforcement [2]. The use and applications of PCM has increased over the years and this is due to its many features. These features include its low weight density, competitive cost, and flexibility for processing and superior corrosion resisting abilities [Mohamed]. The applications of PCM include three-dimensional printing (3D) which has evolved overtime and has been given much attention of late especially in the engineering field. This technology (3D printing) is preferred where costs of producing the initial samples during the product development stages are to completed, however it is still very difficult for complex geometries. The very first 3D printing concepts and techniques were developed in the 1980s. Charles W Hull of 3D systems Corp developed the first commercial 3D printer known as SLA-250 [3]. 3D printing is a process of straight digital manufacturing has provides the skills of manufacturing a wide range of geometrical parts using a variety of materials [4]. 3D printing is gaining momentum very fast in industries like locomotive and aerospace for prototyping of car and aircraft components. The material used in a 3D printer can vary from ceramics, ceramic powder to metal and polymer composites. Ceramic composites have high strength, high hardness, high facility temperature and low density. Metal composites are composites commonly used and are suitable for design; these composites include Aluminium, Magnesium and Titanium. Polymer composites are low cost, high strength with simple manufacturing principles, have great strength and corrosion resistibility. The most common PCMs are acrylonitile butadiene styrene (ABS) and Polylactide (PLA). ABS is very popular in the industry but with a limited range compared to PLA, which has a wider range with almost similar popularity. Literature suggests that soon ABS will be replaced by PLA. However, there is always a gap that will need to be filled regarding the PLA aspect ratio [5], [6], [7].

PLA is a recyclable thermoplastic material made from sustainable resources. The properties of this material include physical treatment and copolymerizing; however, it is not strong enough. Polylactic acid is also used in many clinical situations for bone repair and modernization. Solid free system fabricated methods, such as 3D printing can produce multifaceted-shaped objects straight from a CAD model [8]. 3D printing process develops mechanisms by ink-jet printing a binder into successive powder layer [8]. In this research, the interest is more on the mechanical properties of PLA. PLA occurs as a polymetric spiral, with an orthorhombic unit cell [9]. PLA fits to a family of aliphatic polyesters normally made from α-hydroxy acids, which contain polyglycolic acid and are reflected decomposable and compostable [9]. This are classified as thermoplastic with high strength and high modulus that can be prepared from rapid sustainable resources to a variety of complex articles that can be used in industrial packaging field. PLA experiences thermal deprivation at temperatures above 200 ℃ by hydrolysis, lactic reformation and inter- or intramolecular transesterification reactions [9]. PLA has a glass-change temperature of about 55℃ and a melting temperature of about 175℃. The mechanical properties and representation behaviour of PLA is very reliant on the molecular load and stereochemical nature of the backbone [9].

Due to the complexity of certain structures that can be printer in 3D printers, certain mechanical properties of PLA need to be enhanced. This has been the desired objective in order for the PLA to take the lead. Traditional inorganic fibers (glass and carbon fibers) and organic fibers (aramid) have been in use for ages and have proven to increase the mechanical properties of polymers. Carbon nanofiber is a lined, discontinuous filament that is different from continuous and numerous micrometer diameter fiber [10]. This fiber can produced from the catalytic chemical vapor deposition (CVD) [10]. Carbon nanofiber is also one of the traditional filler used to reinforce and boost the mechanical properties of polymers [11]. These fibers have reinforcing capabilities, which results in the increase of the Ultimate tensile strength (UTS). Carbon nanofibers exhibits high specific area, elasticity and super strength because of their nano-sized diameter [11].

2. Experimentation

2.1. Materials and equipment

The materials used for this research study compose of the following; the matrix was Polylactide (PLA) which was reinforced with Carbon nanofiber (CNF). The Polylactide (PLA) which was used is made from recycled properties such as corn starch and is one of the most comprehensively researched polyester [12]. Carbon nanofiber was selected as a reinforcement due the outstanding mechanical properties which include electrical and thermal conductivity [13]. Another material which was used was Chloroform to functionalize the solution.

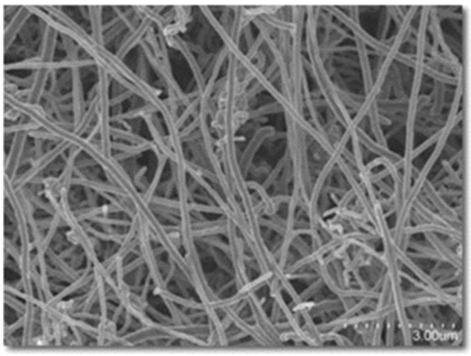


Fig. 1. Carbon nanofibers microstructure [14]

The equipment which was used includes the following; A Wanhoa Duplicator 5s 3D printer, this is one of the newest printer in the market with remarkable build capacity, tensile tester machine (MTS) for tensile tests, experiment beakers, normal paint brush for mixing, scanning electron microscope (SEM) for microstructure and a Rockwell hardness machine for hardness test.

2.2 Method

Pure PLA samples were printed from the 3D printer following the recommendation on ASTM D638 – 02a Standard. Carbon nanofiber-chloroform solution (1.2 wt %) was prepared by mixing carbon nanofiber with chloroform to form a functionalized solution. This was conducted following similar approach to Jonoobi [15] who mixed chloroform and carbon for the extrusion of their materials. A batch size of 6 samples was considered for printing per cycle so to fully utilize the space and 3D sprinter capacity. The 3D printer was be started and printing allowed for the first 20 minutes and after every 20 minutes the solution would be applied evenly while printing continues. For every 20 minutes, 2 grams of the solution would be applied using the paint brush. The average time taken for each batch of samples was 432 minutes. Fig. 2 presents the printing process where PLA samples were printed. The tensile specimen on figure 2 were printed in batches of 8 per cycle and these samples were compared with those printed with the addition of carbon nanofibers.

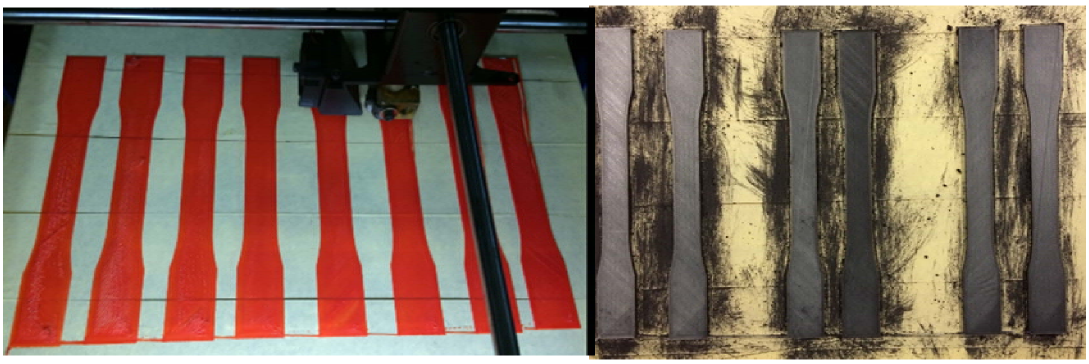


Fig. 2. PLA (parent material, left) and PCM sample (right) printing

Fig. 3 presents the 3D polymers printed tensile specimens used as samples. Samples were divided categorically, some printed using PLA and others PCM. After printing, tensile specimens were allowed to cool to room temperature and tensile tests were performed after an average of 3 days.

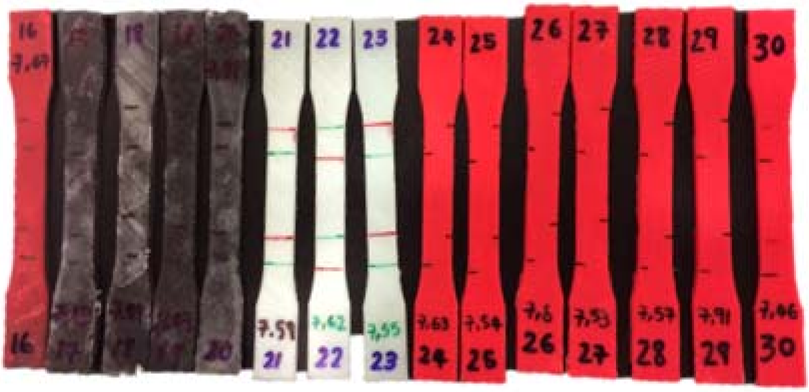


Fig. 3. 3D printed PLA and PCM tensile specimens

Fig. 4 represents the round printed samples from both PLA and PCM printed according to ASTM D785-03 specifications. On the left hand side of the figure it shows the process which happens before the SEM microstructure, the samples required coating prior to use the SEM machine and on the right hand side, the figure shows some of the round samples during the Rockwell hardness test.

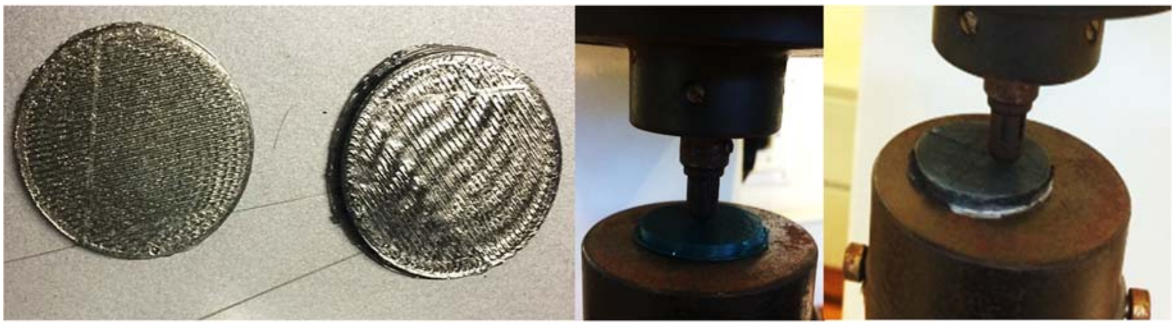


Fig.4. Round samples for SEM microstructure and Rockwell hardness test

3. Results and Discussions

Table 1 shows the average UTS and yield strength values obtained from the MTS tensile tester machine. The results indicate that the addition of carbon nanofibers in the parent material improved the mechanical properties. The average yield strength improved significantly whilst the UTS shows some improvements as well.

Table 1. PLA and PCM mechanical properties comparison

Materials	Average maximum force (kN)	Average elongation after break (%)	Average yield strength (Offset = 0.2%) MPa	Average ultimate tensile strength (MPa)
Parent material (PLA)	2.158	2.040	28.635	47.087
PCM composite	2.323	1.122	42.025	49.896

The actual mechanical properties obtained from the tensile tester for both materials were analyzed using Anova. Anova is a statically analysis function available on Microsoft excel. The P-value obtained is 0.013 and shows that there is a statically significant difference between the 2 materials compared.

Table 2. Anova analysis and results

ANOVA: Single factor							
Summary	*Groups*	*Count*	*Sum*	*Average*	*Variance*		
	A (PLA)	13	612.131	47.087	2.899		
	B (PLA/CNF)	13	648.644	49.896	11.515		
ANOVA	*Source of variation*	*SS*	*df*	*MS*	*F*	*P-Value*	*F – Critical*
	Between Groups	51.277	1	51.277	7.115	0.013	4.260
	Within Groups	172.970	24	7.207			
	Total	224.247	25				

Fig. 5 below illustrates the comparison between the ultimate tensile strength of PLA and PCM composite. The results on the graph revealed that the CNF used as a reinforcement material made a significant improvements to the mechanical properties of the PCM.

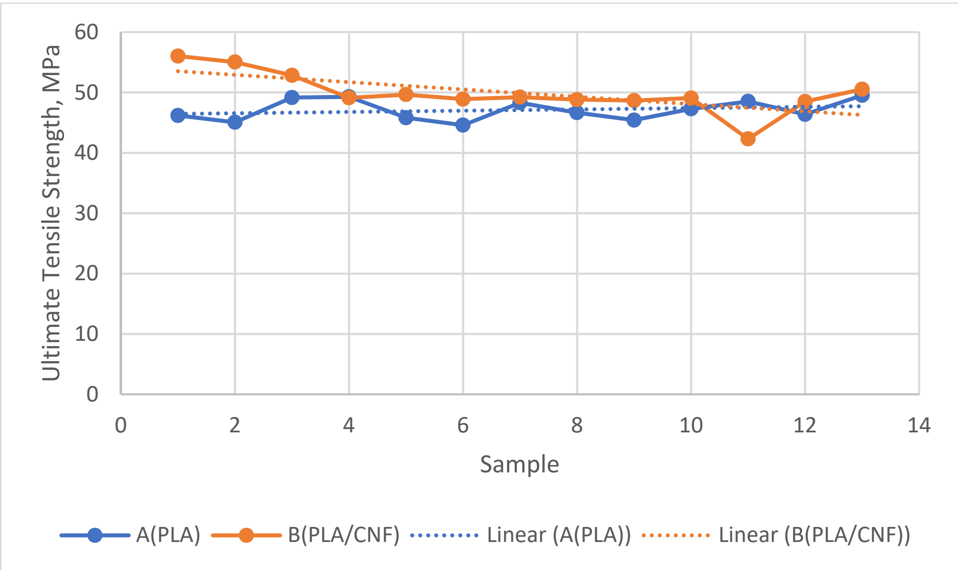


Fig. 5. The ultimate tensile strength of PLA and PCM composites

Fig. 6 illustrate the comparison of the yield strength for both the materials, PLA and PCM. It can be concluded that the addition of CNF to the parent material contributed to the improvement of the UTS.

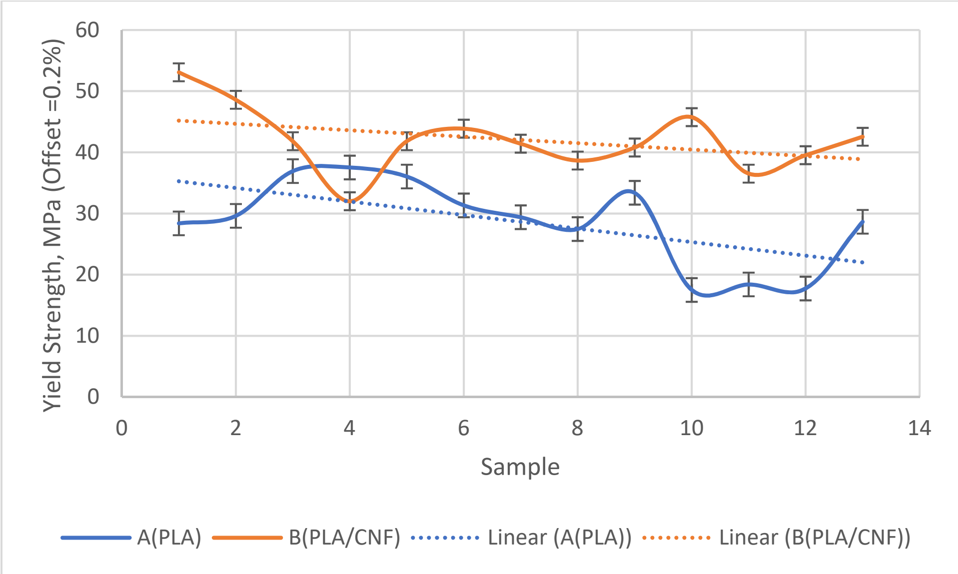
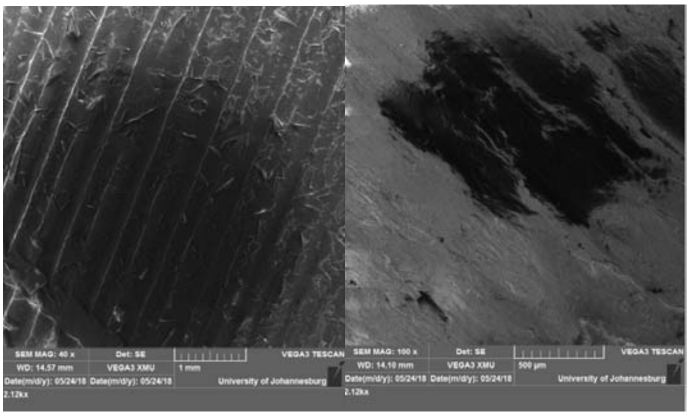


Fig. 6. The comparison of yield strength for PLA and PCM composites

Fig. 7 shows the microstructure samples of the parent material (PLA) which is labelled A and the PCM composite labelled B. A high-magnification, high resolution SEM microscope was used to obtain the images.



A B

Fig.7. SEM microstructure for both PLA and PCM

The purpose of a microstructural analysis is to examine the surface fracture of a material, when examining the images, it appears as if the PCM composite has a smoother surface area than the parent material (PLA), though in reality the PCM composite is had a rougher surface arear than PLA. With the above obtained images, these no significant difference discovered on the surface area due to the less conductivity plastic has than metals.

Table 3 below shows the Rockwell hardness test results obtained on six samples, three are PLA samples and the other three are PCM composites.

Table 3. Rockwell hardness results

Rockwell hardness results for 60kg			Rockwell hardness results for 100kg		
PLA	**PCM**		**PLA**	**PCM**	
7	20	1	13	22	1
19	23	2	10	24	2
18	17	3	12	19	3
13	21	4	10	18	4
20	25	5	13	25	5
15.4	**21.2**	**Average**	**11.6**	**21.6**	**Average**

Fig. 8 shows the line graph which depicts the hardness results obtained from PLA and PCM composites for a load of 60kg.

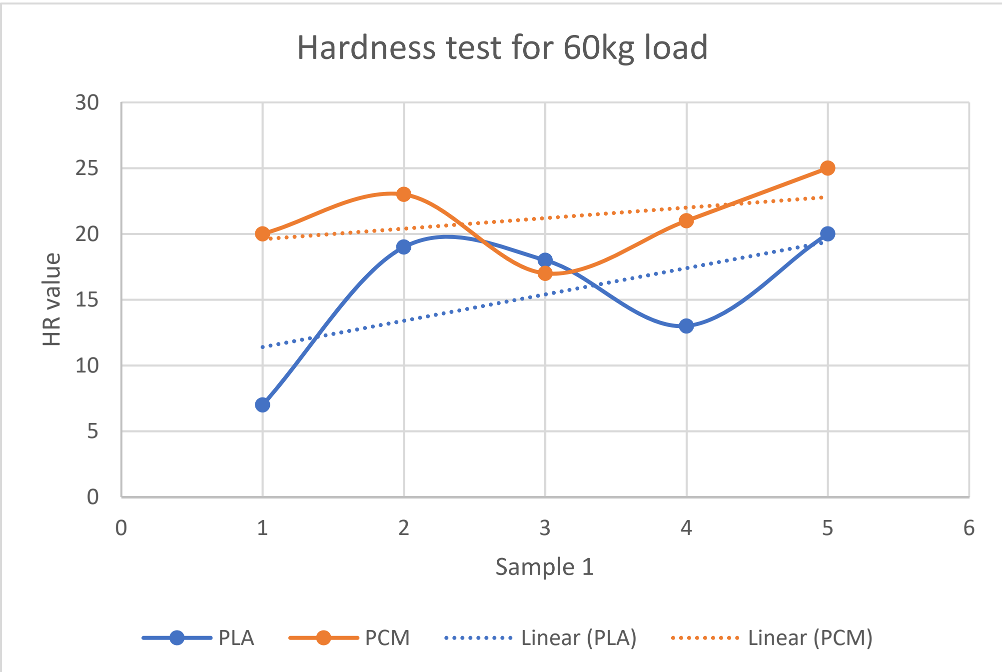


Fig. 8. Hardness test comparison between PLA and PCM composites for a 60kg load

Fig. 9 below shows the hardness results obtained from PLA and PCM composites compared for a load of 100kg.

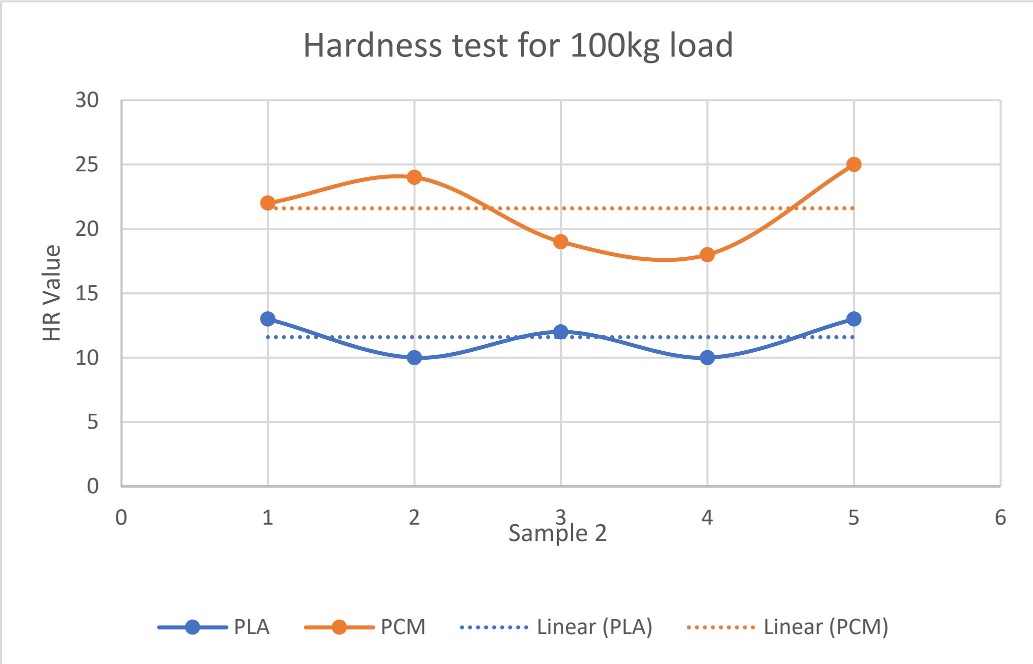


Fig.9. Hardness test comparison between PLA and PCM composites for a 100kg load

The results shown in the graphs above clearly indicate an improved reinforced material. The PCM composite, when comparing to the initial hardness of the parent material, was found to be 37.66% tougher under the 60kg load. And when faced with a 100kg load, PCM composites incurred an increase of 86% compared to the PLA.

4. Conclusion

Carbon nanofiber (CNF) with chloroform was successfully added to PLA using the Wanhoa Duplicator 5s printer. Tensile specimen samples were printed for both materials PLA and PCM and the tensile test was conducted. The results obtained from the tensile test shows improved mechanical properties of the reinforced material. The ultimate tensile strength and yield strength of the PCM increased from the PLA with a standard deviation of 1.7 to 3.4. Based on the Anova analysis, the P-value obtained was 0.013, which is less than 0.05. This concludes that theirs a statically important positive relationship between the parent material (PLA) and the PCM composite. The aim of this study was to improve the mechanical properties of PLA, as well as assuring that the ultimate tensile strength was better than the initial strength. The parent material (PLA) and PCM composites tensile and hardness test samples were printed on the 3D printer and the experiments were conducted. Based on the results obtained, this study concludes that the mechanical properties of the PLA improved. The results obtained also confirm the predictions which were done by Jonoobi, which clearly state that CNF has an excellent potential as a strengthening material as it improves the mechanical properties of the parent material (PLA).

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