

Tensile Properties of Poly Lactic Acid (PLA)– Tungsten Trioxide (WO₃) Nano Composites for 3D Printing Process

M.L.M Shaath, M.N.M. Ansar, A. Atiqah, A. Hamdan

Abstract: Poly Lactic Acid (PLA) is one of the most crucial aliphatic polyesters which is considered as one of the favourable options in environmentally friendly thermoplastic polymers since it could be biodegraded in certain conditions. PLA has been extensively used in the packaging, electronic industries, and household applications. As a result, the improvement of mechanical properties of PLA is necessary, which can be achieved through heat resistant materials such as Tungsten trioxide (WO₃). The objective of this research was to investigate the tensile properties of PLA-WO₃. The 3D printing process was employed to fabricate PLA-WO₃ (3wt% WO₃) and Neat PLA (control sample). The tensile test was conducted to investigate the effect of WO₃ to the PLA. The results show that the tensile properties of PLA-WO₃ were improved up to 75% as compared to Neat PLA. This result shows positive indication to the PLA-WO₃ for many industrial applications.

Keywords: Biodegradable; PLA, Tungsten Trioxide; 3D Printing; Tensile Properties.

I. INTRODUCTION

Poly (L-lactic acid) (PLA) is a biodegradable polyester which is created from renewable bio origin raw ingredients such as corn-starch and have been developed in commodity as well as biomedical applications [1]. PLA has attracted serious attention from researchers to build new biopolymers application. In this perspective it is likely that novel high-tech advances will lead to the great invention of new reinforced materials, including in packaging, transportation, automotive and electronics industry, as well as biomedical field and many others [2]. Moreover, in correlation with the vital demand for bioplastics, it is expected that global production capacities will soon be higher than before to more than 7.8 million tonnes in 2019.

Meanwhile the bio-based/non-biodegradable and biodegradable polymers will represent about 84% and 16%, respectively. The quick rise of biodegradable plastics is one of the significant discoveries of the last decade. However, it's only used for specific requests and industries such as packaging or engineering areas, and the bio-based polymers still can't replace and be fully competing with petrochemical polymers from the category of goods or engineering thermoplastics.

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PLA has very low heat resistance, with less than 10% elongation at break [3]. These properties will limit its application in certain industries that need plastic deformation under high stress. Therefore, a nano composite is proposed to increase the properties of this bioplastic structure. In addition, blending PLA with other materials and composites, which have desired mechanical and thermal properties are needed to penetrate in 3D Printing industry. It involves thermoplastic polymer materials such as polyamide (PA) [5], acrylonitrile butadiene styrene (ABS), polycarbonate (PC) [6] Poly (L-lactic acid) (PLA) [4] and lastly thermosetting polymer materials like epoxy resins. Figure 1 shows the schematic of 3D printing machine.

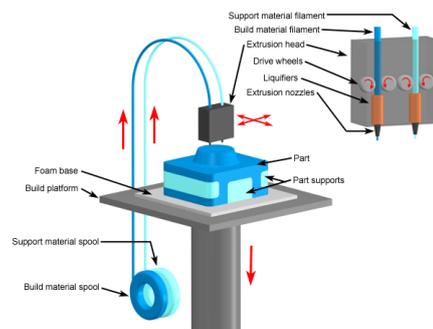


Fig. 1 3D printing extrusion process [7]

In this research, a Malyan M180 3D printer with a double nozzle was used to prepare the test samples as per the ASTM D 638 standards.

Hybridisation of PLA will improve its properties such as thermal, flexural, and dynamic rheology. Addition of nanoparticles derived from metal oxides, such as WO₃, TiO₂, ZnO, MgO, and SiO₂ into different polymer matrices are in recent times being studied for their possible usage as a packaging material [8]. It changes the micro-structural properties such as glass transition, crystallization, cross-linking, phase separation and orientation as well as Viscoelastic behavior of blends. Furthermore, it enhances the flammability, thermal stability, and thermo-mechanical behavior, as well as mechanical properties [9]. Therefore, a hybridization of PLA with tungsten trioxide (WO₃) nanoparticles was proposed. Tungsten trioxide is used for numerous applications in daily life. It is regularly used in engineering to develop tungstates used for X-ray screen phosphors, for fireproofing fabrics [10], in gas sensors [11] and paints. Thus, the objective of this paper is to investigate the effect of WO₃ on the tensile properties of PLA- WO₃ nanocomposites with different processing temperature.

II. METHODOLOGY

i) Materials

Commercially available, medical-grade PLA of melting temperature of 160-185 °C in the form of small pellets is to be used in this research. The green color Nano powder of 231.08 g/mol molecular weight is not very easy to mix with PLA particles, that’s why a synthetic oil was used as a coupling agent; however this coupling agent is unrelated to the experiment. In other words, this coupling agent doesn’t react with either of the materials, the only use is to make the surface of the particles oily, and to attract the nano-particles of WO₃ to the PLA surface, which guarantee a firm yet fair distribution of the nano-particles in the sample, the bottom line is, the oil worked perfectly well in the experiment, and a greenish, uniformed color was seen in the material prior melting, as seen in Figure 2. A green color powder of WO₃ nano sized particles is going to be mixed with the PLA pellets, in addition to that, the materials mixed will be extruded and then made into a 1.75 mm filament ready for 3d printing purposes.



Fig. 2 Tungsten trioxide PLA mixture

ii) Fabrication of PLA-WO₃ composites

The new method of fabrication of PLA-WO₃ involves several steps. Firstly, the composition of WO₃ (3wt.%) in powder form was added and melted down the raw PLA pellets together with WO₃ using co-rotating twin screw extruder. The melting temperature of which the extruder disperses would create chemical bonds between the two materials. The filament with a diameter of 1.75mm is extruded at range of 170 °C, 185 °C via extruder machine. Then, it employed in 3D printing (MALYAN M180) to produce samples as shown in Figure 3. Besides that, a Neat PLA samples were fabricated as well as a control sample in experiment. The formulation of the composite is given in Table 1.

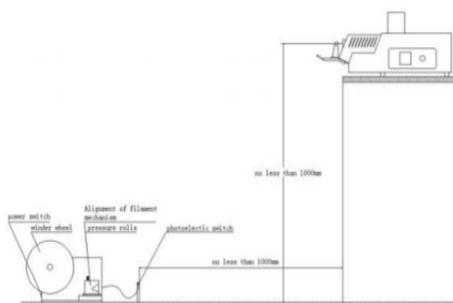


Fig. 3 The alignment of extruder and winder

Table. 1 Material Composition

Sample ID	PLA (wt.%)	WO ₃ (wt%)	Temp (°C)
Neat PLA	100.0	0	185
PLA-WO ₃ T1	97.0	3.0	185
PLA-WO ₃ T2	97.0	3.0	175
PLA-WO ₃ T3	97.0	3.0	165

iii) Characterization

The tensile properties of specimens were tested using a universal testing machine. Three samples were prepared following the ASTM standard for each Neat and nanocomposite sample. The size of each specimen was measured to be 140 X14 X 2mm as in Figure 4.



Fig. 4 Tensile specimen fabricated via 3D printing machine following ASTM D638 standard.

III. RESULTS AND DISCUSSION

Figure 5 shows the tensile strength graph of the pure PLA, the maximum strength was 21.7 MPa, when added with 3 wt. % of tungsten trioxide (WO₃), the tensile strength was improved by 25% as compared by neat PLA. Previous work done by Xin Wang et al. [12], have shown that with the incorporation of nanoparticles or nanomaterials reinforcements into polymer matrix permits the fabrication of polymer nanocomposites can exhibit the good mechanical properties.

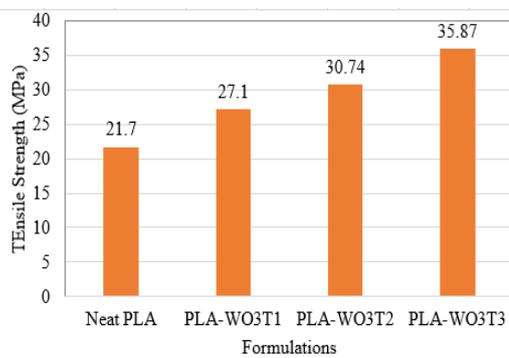


Fig. 5 Tensile strength of Poly Lactic Acid (PLA) – Tungsten Trioxide (WO₃) Nanocomposites



Furthermore, with the new fabrication method of printable filament, properly adding suitable nanoparticle could enhance the mechanical properties of the targeted polymer. This strategy is mainly effective in yielding a high performance composite when the filler is uniformly distributed, the matrix in return changes which lead to noticeable enhancements in properties, and the nanoscale filler is substantially different from the pure or original matrix [13].

The effect of reducing temperature of extrusion process, the tensile strength was increased with 13.4% and 32.4% for PLA-WO3T2 and PLA-WO3T3. The suitable temperature is 165° C for processing the PLA-tungsten trioxide nanocomposites.

Figures 6 and 7 show that the stress-strain curve for neat PLA and PLA-WO3T3 also confirmed and showed that, with the addition of tungsten trioxide the tensile strength improved as well. This phenomenon is due to the nanoparticles are well mixed with the proper extrusion alignment with winder.

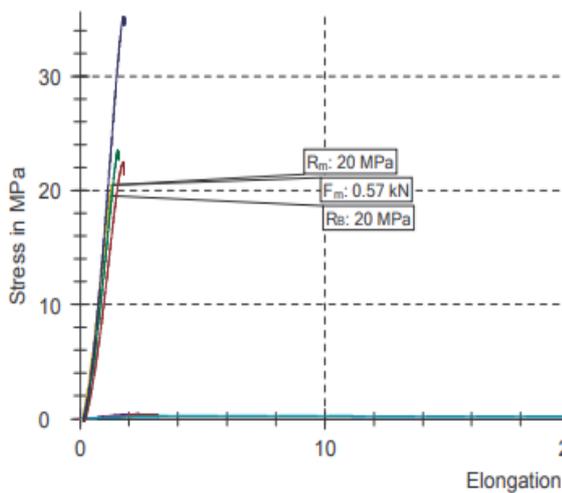


Fig. 6 Tensile strength of Neat PLA

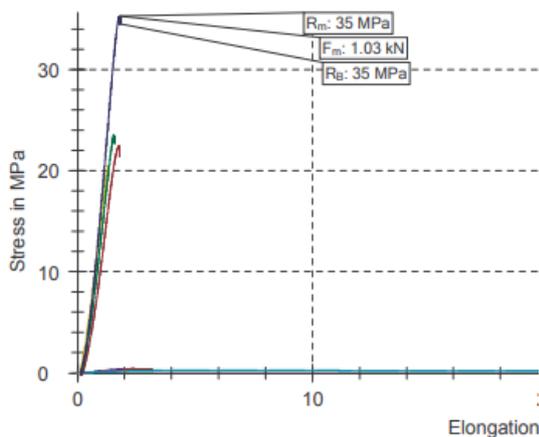


Fig. 7 Tensile strength of PLA- WO3T3 nanocomposite

IV. CONCLUSION

From the research done, the addition of 3wt. % of tungsten trioxide has enhanced the tensile properties of PLA-WO3 nanocomposites successfully. The tensile strength of PLA-WO3 nanocomposites with the variation of processing temperature showed that 165°C is the preferable processing temperature of extrusion alignment with winder

machine. This may attribute to new method was employed to fabricate this PLA-WO3 nanocomposites that can be proposed to other applications. Moreover, the addition of nanoparticle of tungsten trioxide could also solve other issues such as flame retardancy, conductive electrical characteristics, anti UV degradation, the reinforcing of PLA matrix with inorganic nano-materials, the addition of micro and nano-fillers related with selected additives, is well-thought-out as a great technique leading to discover new characteristics and significant improvements of properties of nanocomposites. The future research work needs to be done to investigate the morphology and thermal properties of PLA-WO3 nanocomposites.

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REFERENCES

1. Tsuji H. Poly (lactic acid) stereocomplexes: A decade of progress. *Adv Drug Deliv Rev* 2016. doi:10.1016/j.addr.2016.04.017.
2. Murariu M, Dubois P. PLA composites: From production to properties. *Adv Drug Deliv Rev* 2016. doi:10.1016/j.addr.2016.04.003.
3. Marei NH, El-Sherbiny IM, Lotfy A, El-Badawy A, El-Badri N. Mesenchymal stem cells growth and proliferation enhancement using PLA vs PCL based nano fibrous scaffolds. *Int J Biol Macromol* 2016. doi:10.1016/j.ijbiomac.2016.08.053.
4. Wang X, Jiang M, Zhou Z, Gou J, Hui D. 3D printing of polymer matrix composites: A review and prospective. *Compos Part B Eng* 2017. doi:10.1016/j.compositesb.2016.11.034.
5. Wróblewska AA, Lingier S, Noordijk J, Du Prez FE, De Wildeman SMA, Bernaerts K V. Polyamides based on a partially bio-based spirodiamine. *Eur Polym J* 2017. doi:10.1016/j.eurpolymj.2017.08.056.
6. Durante M, Formisano A, Lambiase F. Incremental forming of polycarbonate sheets. *J Mater Process Technol* 2018. doi:10.1016/j.jmatprotec.2017.11.005.
7. Source of figure <https://www.aniwaa.com/3d-printing-technologies/>
8. Williams DE, Aliwell SR, Pratt KFE, Caruana DJ, Jones RL, Cox RA, et al. Modelling the response of tungsten oxide semiconductor as a gas sensor for the measurement of ozone. *Meas Sci Technol* 2002. doi:10.1088/0957-0233/13/6/314.
9. Giita Silverajah VS, Ibrahim NA, Md Zin Wan Yunus W, Hassan HA, Woei CB. A comparative study on the mechanical, thermal and morphological characterization of poly(lactic acid)/epoxidized palm oil blend. *Int J Mol Sci* 2012. doi:10.3390/ijms13055878.
10. Singla RK, Zafar MT, Maiti SN, Ghosh AK. Physical blends of PLA with high vinyl acetate containing EVA and their rheological, thermo-mechanical and morphological responses. *Polym Test* 2017. doi:10.1016/j.polymertesting.2017.08.042.
11. Lassner E, Schubert W-D, Lassner E, Schubert W-D. Tungsten Compounds and Their Application. *Tungsten*, 2011. doi:10.1007/978-1-4615-4907-9_4.
12. Wang X, Jiang M, Zhou Z, Gou J, & Hui D. 3D printing of polymer matrix composites: A review and prospective. *Composites Part B: Engineering*, 2017, 110, 442-458.
13. Manias, E. Nanocomposites: Stiffer by design. *Nature Materials* 2007, 6(1), 9