Mechanical properties of Tungsten Tri-oxide (WO$_3$) reinforced poly (lactic-acid) (PLA) nanocomposites

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Abstract. In this paper, Tungsten trioxide reinforced poly (lactic acid) (PLA) blend nanocomposites were prepared using twin screw extrusion and injection moulding with different nanofillers concentrations (0.5 wt%, 1 wt%, 3 wt%, and 5 wt%) together mixed into a PLA matrix. Mechanical properties such as tensile and flexural properties were investigated. The tensile and flexural results indicate a noticeable enhancement in the mechanical strength of the PLA material. The WO$_3$/PLA nanocomposites were compared with neat PLA to identify the attributes and loading effects on the mechanical behaviour of the nanocomposites. A high content of tungsten led to a brittle, fragile, and inelastic composite, while a lower content resulted in a high elastic modulus and stiffness of the composite. The composites reinforced with 3wt% of WO$_3$ has improved its tensile strength and flexural strength by 30.77% and 41.38% respectively. The extrusion stability and composite molten state were compromised in the presence of high concentration of tungsten while a lower percentage eased processing and injection.

1. Introduction.

Polylactic acid (PLA) is an aliphatic polyester synthetically made from lactic acid with the help of microorganisms. It has been widely used in the bio-medical and pharmaceutical fields for several decades due to its biocompatibility and biodegradability in contact with mammalian bodies[1]. Lactic acid (LA) can be frequently found naturally in animals and plants as a by-product of metabolism; therefore, PLA and its degradation products are non-toxic and harmless to the environment. Lactic acid is produced in an industrial scale by using sugar containing agricultural bi-products such as starch, sugarcane, rice husk and corn. The PLA is unable to degrade by itself but after the hydrolysis
process, it becomes biodegradable with the presence of microorganisms when it is placed in an industrial composting facility due to its high temperatures (60°C) and humidity [2]–[5].

PLA like other synthetic biopolymers is criticized for the need of high processing energy usually from fossil fuels which is needed to turn the raw materials into PLA pellets used in industries. Meanwhile, 1 kg of PLA consumes less energy than 1 kg of equivalent polymers from petrochemical feedstock. Fig. 1 shows the fossil fuel energy consumed by various polymers.

![Figure 1. Fossil energy consumed per kg of material produced [8].](image)

One of the biggest technical challenges to widespread acceptance of bio-origin polymers is difficulties in achieving barrier and mechanical properties[6]. Researchers have been developing and patenting new composites of PLA, since the discovery of this green/renewable polyester from 1980s. In 2010, PLA was the second most important bioplastic of the world with regard to consumption volume[6]. It has been intensively used after the revolution of 3D printing where it is used to print everything from models to scaffolds used in surgeries. In the recent years, governments have started encouraging industries to use this polymer for packaging due to the alarming dangers of petroleum derived plastics to the environment. Since then, PLA is being widely used as a plastic packaging from foods and beverages to cosmetics and electronic gadgets as shown in Fig. 2 [1], [4], [7]–[10]. PLA has the potential to become the most used plastic in Malaysia for packaging purposes. When the government imposed new tax in 2017 whereby the customers are required to pay 20c per plastic bag in order to preserve the environment, PLA plastic bags have become an alternative option to be used in business sectors. [11]. Apart from that, it is also being used in food and beverages packaging such as yogurt, vegetable wrappings and plastic cups. However, PLA does not meet the requirements of
some products which needs high mechanical strength and thermal stability; hence, it was necessary to reinforce it with some additives in order to enhance the properties and to replace the non-biodegradable plastics derived from petroleum base. The government of Malaysia is aiming to ban the single-use plastic by the year 2030 thus an alternative material needs to be developed [12]. In recent years, transition metal oxides gained lots of attention by industries and researchers for their unique properties. Among numerous transition metals, Tungsten oxide was of a special interest because of its distinctive characteristics which have led to numerous applications and prospective for further developments. Such applications include fire proofing fibers, optical devices, photo catalyst, gas censors and electro chromatic windows (smart windows). It is also being used as a color pigment due to its rich yellow that can be found in the formulation of paints and ceramics.

Figure 2. Common uses of Polylactic acid [7].

2. Experimental

2.1. Materials

2.1.1. Poly (Lactic acid) - PLA
PLA used in this research are solid pellets suitable for extrusion and injection moulding process. This material was manufactured by NatureWorks grade Ingeo 2003D with 1.24g/cm$^3$ and other standard characteristics reported in our previous articles. These materials were supplied by Innovative Pultrusion Sdn.Bhd., Malaysia.

2.1.2. Tungsten Tri-oxide ($WO_3$)
$WO_3$ physical and technical properties are very impressive with a melting point of 1473° C, boiling point of 1700° C and a density of 7.16 g/cm$^3$. These significant properties makes it a potential reinforcement nanoparticle to enhance the properties of PLA [13], [14].
2.2. Methods
To test the tensile stress-strain, the samples were prepared as per the ASTM D638 standards where the measurements are as follows, dumbbell shape type I model with a length of 180mm from end to end, 135mm from neck to neck, and an overall width of 20mm with a thickness of 6.5mm in average, while the gauge length of 50mm. All the samples’ measurements were carefully checked and numbered one by one, before testing or obtaining the data. The melting temperatures were chosen as per the material maker’s recommendation with an increase of 20° C because of the nanoparticle addition, which requires extra heat to infuse the particles into the polymer matrix and to attain a slender and smooth melting of the substances. Table 1 shows the material composition used in this study, and Table 2 shows the barrel temperatures chosen during the injection process.

| Sample ID | Material Composition          |
|-----------|-------------------------------|
| WPLA0     | 0wt% WO₃ 100wt% PLA           |
| WPLA0.5   | 0.5wt% WO₃ 99.5wt% PLA        |
| WPLA1     | 1wt% WO₃ 99wt% PLA            |
| WPLA3     | 3wt% WO₃ 97wt% PLA            |
| WPLA5     | 5wt% WO₃ 95wt% PLA            |

2.2.1. Material Preparation
Tungsten trioxide nano powder was weighed using a scale of high accuracy up to 0.0001grams, and a weight percentage of (0.5wt%,1wt%, 3wt% and 5wt%) was added to PLA pellets samples, after coating the pellets with a coupling agent to ease the mixing process and to increase surface adhesion. Then the material was shaken for 15 minutes in a glass container in order to ensure a homogenous dispersion of tungsten in the PLA raw material. The same process was repeated for other samples.

2.2.2. Twin Screw Extrusion
After the plastic material was mixed with tungsten nanoparticles, a twin-screw extruder was used at SIRIM Malaysia to fabricate the material under a temperature starting from 160° C to 190° C as in table 1 in the heater bands train and a pressure of 55-60bar. The molten material was then pulled using a conveyor belt and rolled manually into rolls which was later crushed in order to construct the tensile and flexural samples using injection moulding. Table 2 shows the temperature profile during the extrusion of compounds.

2.2.3. Injection Moulding
The extruded material wires were crushed and then used in an injection moulding machine (HAITAN MA600) at UNITEN labs. After trial and error, the machine was operated under a pressure of 50bars with temperatures of 162° C, 168° C, 173° C and 180° C in the heater band train, and an ASTM-D 638 standard mould was used to fabricate the specimens with dimensions of 180mm in length, 6.5±0.2mm in width and 3.1±0.2mm in thickness. The gauge length was measured to be 50mm and the limits are marked using a permanent marker.
Table 2. Distance in the barrel to feeding zone with temperature (°C).

| Distance in the barrel to feeding zone | Temperature [°C] |
|---------------------------------------|------------------|
| 0 to 90 mm                            | 160              |
| 90 to 180 mm                          | 175              |
| 180 to 270 mm                         | 180              |
| 270 to 360                            | 185              |
| 360 to 450 mm                         | 187              |
| 450 to 540 mm                         | 190              |
| From the Die                          | 190              |

During injection moulding process, the melting and moulding temperatures were set at 210°C and 40°C respectively for PLA and PLA-WO$_3$ composites based on the manufacturer’s data sheet.

2.2.4. Tensile Test
The variation of the mechanical properties of pure PLA and the reinforced PLA was determined. The tensile test was conducted using ZWICK ROEL universal tensile machine. Fig.3 shows the tensile set-up used for each specimen in the normal room temperature. The universal tensile testing machine was used to obtain the tensile properties data. Using a computerized system, the data sheet showing each specimen’s test results can be analysed. Five specimens were tested in each sample designated in the Table 1. and the average value of those tests results were analysed. The specimen stability between the machine chalks is critical to the accuracy of the tensile analysis result, hence, the specimen under testing is cautiously grasped amid the two load chalks as shown in Fig.3.

Figure 3. Tensile test set-up (ASTM-D638).
2.2.5. **Flexural Test**

The universal testing machine (ZWICK ROEL) was used to determine the flexural strength and to study the effects of the nanoparticle employed in the polymer reinforcement. As per the ASTM-D 790 standards, a 3-point flexural test was followed to determine the flexural load versus strain pattern. A computer software was used to plot the graph and analyse the data. The readings are tabulated and given in Table 3. The flexural test set-up as per the ASTMD790 standard is shown in Fig. 4.

![Figure 4. Flexural test set-up (ASTM-D790)](image)

3. **Results and Discussion**

The samples endured the analyses under diverse settings and diverse printing parameters. With regard to the Tensile strength, it is the fundamental property to be concerned about but another aspect to be taken into account is the ductility which can substantially affect by the dimension and strength of the end product. With this in consideration, the materials were assessed for competent tensile properties. The resulting values are compared and shown in Fig. 5. The outcomes of the tensile assessments indicated that all the composite samples ranging from 0.5wt%~5wt% of WO₃ reinforced PLA (WPLA0.5, 1, 3 and 5) shows greater tensile strength than the neat PLA sample with a maximum strength of 61.1MPa (WPLA3) while the neat PLA sample (WPLA0) shows the lowest tensile result of 48.0 MPa. This is attributed to the change in the reinforcement of WO₃ which has made significant improvement in the tensile strength irrespective of the loading level. Similar results were found from many previous research studies [15]–[17]. Zhang et al. (2020) reported that magnesium reinforcement in PLA showed an increase in the flexural strength compared to those neat PLA membranes [18].

![Figure 5. Tensile stress-strain graph of neat PLA and PLA/WO₃ composites.](image)
Flexural test, unlike the tensile doesn’t show much information regarding the material properties but it’s a compilation of attributes of the other properties enhanced with the nanoparticles reinforcement in PLA matrix. The results of flexural strength for all samples are summarized in Table 3. It can clearly be seen from Fig.6 that the flexural strength of the composites increased proportionally to the percentage of filler loading until 3wt%. The neat PLA (WPLA0) had the lowest flexural strength which was 85 MPa with an elongation of 5.6% while the highest flexural strength obtained from this study was exhibited by sample WPLA3 (145.0 MPa) with 4.0 % elongation. It can be observed that adding greater amount of WO3 to 5wt% resulted in decrease in the flexural strength. This could be due to agglomeration of the nanoparticles that resulted in poor integration between PLA and WO3, and subsequently caused the composite to be unable to withstand more load. The results obtained give us a proof of the enhancement in mechanical properties after being reinforced with the WO3 nanoparticles. Similar studies were done by other researchers on reinforcing nanomaterials in PLA for improvement in their mechanical strength. Ajay Kumar et al. (2020) investigated the effect of printing speeds on the tensile strength of carbon fibre reinforced PLA, and it was found that the carbon fiber reinforced PLA is of superior mechanical properties compared to neat PLA [19].

| Sample ID | Flexural Strength (MPa) | Flexural Strain (%) | Flexural Modulus (GPa) |
|-----------|-------------------------|---------------------|------------------------|
| WPLA0     | 85.0                    | 5.6                 | 1.52                   |
| WPLA0.5   | 130.0                   | 5.2                 | 2.50                   |
| WPLA1     | 140.0                   | 4.0                 | 3.50                   |
| WPLA3     | 145.0                   | 3.2                 | 4.53                   |
| WPLA5     | 102.0                   | 2.9                 | 3.52                   |

Figure 6. Flexural stress-strain graph of neat PLA and PLA/WO3 composites.

4. Conclusions
Although PLA is considered a biodegradable plastic, its setbacks could be tailored by reinforcing the polymer, using different fillers to introduce new desired characteristics. This study was conducted to identify the effects of reinforcing the neat PLA with a nanoparticle material and to verify the enhancement in mechanical properties of the renewable biodegradable material PLA that can be a potential replacement for petroleum-based plastics such as polyolefins.
This concept of reinforcing renewable bioplastics such as PLA with nano-fillers like WO$_3$ has acquired attractive mechanical properties required for various applications.

Based on the study conducted, the applied force at breaking load ratio is greater for the PLA-WO$_3$ with 3wt% of filler loading.

The results obtained showed that the reinforced composites had greater mechanical properties compared to the neat PLA.

The findings also indicated that there was good compatibility between PLA and WO$_3$ which resulted in notable improvement for mechanical properties of the composites.

Author’s contribution
M.L.M. Shaath$^1$- first draft of the paper, conduct experiment, data collection and analyses of the results, M.N.M Ansari$^{1,2}$ - Concept development, conduct experiment, advise on the manuscript writing and editing, Noor Afeefah Nordin$^2$- project management, manuscript editing and revision, M.S.H.Al-Furjan$^3$- manuscript editing and revision.

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