The Effects of Tensile Properties of PLA/HNTs-ZrO$_2$
Bionanocomposites

A M Alakrach$^1$, N Z Noriman$^1$, Omar S Dahham$^1$, R Hamzah$^1$, Mohammed A Alsaadi$^2$, Z Shayfull$^{3,4}$, S Z Syed Idrus$^5$

$^1$Center of Excellence Geopolymer and Green Technology (CEGeoGTech), Faculty of Engineering Technology (FETech), Universiti Malaysia Perlis (UniMAP), Level 1 Block S2, UniCITI Alam Campus, Sungai Chucuh, Padang Besar, 02100, Perlis, Malaysia
$^2$Nanotechnology & Catalysis Research Centre (NANOCAT), University of Malaya, 50603 Kuala Lumpur, Malaysia
$^3$School of Manufacturing Engineering, Universiti Malaysia Perlis, Arau, 02600, Malaysia
$^4$Green Design and Manufacture Research Group, Center of Excellence Geopolymer and Green Technology (CEGeoGTech),Universiti Malaysia Perlis, Kangar, 0100, Malaysia
$^5$School of Human Development and Techno-communication (iKOM), Green Advanced Computing and Technology (GREAT) Research Group – CEGeoGTech, Universiti Malaysia Perlis (UniMAP)

Email: niknoriman@unimap.edu.my

Abstract. The applications of biopolymers that are requested in the society for sustainability and environmental safety have many limitations. That is can be attributed to the limited mechanical and thermal properties of biopolymers. The aim of this study is to diminish the limitations of the biopolymers properties. Polylactic acid (PLA) as one of the famous biopolymers was selected to investigate the effect of incorporating of hybrid fillers, natural halloysites nanotubes HNTs and Zirconium dioxide (ZrO$_2$) nanoparticles. In the first stage, HNTs was added to PLA matrix in different loading (0, 2, 4, 6 and 8 wt%). In the next stage ZrO$_2$ was incorporated to PLA/HNTs in two loadings (1 and 3 wt%). The mechanical properties (tensile strength, elongation at break and Young’s modulus) were investigated for both of PLA/HNTs and PLA/HNTs-ZrO$_2$ bionanocomposites. PLA films incorporated with 4 wt% loading of HNTs resulted in optimum mechanical properties due to the homogenous distribution of halloysite nanoclay, which increased the tensile strength and elongation at break by 70% and 27% respectively. Unfortunately, the addition of ZrO$_2$ reduced the mechanical properties of PLA/HNTs-ZrO$_2$.

1. Introduction
Polylactic acid (PLA) is one of the promising biodegradable polymer material, owing to its unique properties such as high modulus, high strength, good biocompatibility and compatibility, and high optical transparency. Consequently, PLA is undoubtedly one of the good candidates for the replacement of petroleum based polymer in a lot of applications. Recently, various industrial applications started using PLA such as food packaging, automotive parts, and medical devices.
However, PLA exhibits low thermal stability and poor resistance properties. Thus, the conception of a bionanocomposite has been initiated as one of the solutions to improve the properties of the biopolymers [1-3]. Bio-nanocomposites usually are produced by the combination between a biopolymer and a nanofiller. The good distribution of nanofiller into the biopolymer matrix plays a vital role in the improvement of the biopolymer properties, such as physico-chemical mechanical, thermal, and barrier properties [4]. Numerous kinds of nanofiller have been incorporated to prepare PLA bio-nanocomposites, these includes organoclay [5], CNT [6], and graphitic nanofiller [7], etc.

Natural Halloysite nanotubes (HNTs) with the chemical structure (Al2Si2O5(OH)4.2H2O) is a 1:1 layered silicate clay mineral where each tube consists of an outer tetrahedral (Si–O) sheet and an outer octahedral (Al–OH) sheet. Recently, Halloysite nanotubes (HNTs) have engaged the researchers’ attention as a new category of nanofiller for reinforcing the mechanical, thermal, crystallization, fire and other polymers properties such as PP, PS, PA6, PA12 and epoxy resins, etc. [8, 9]. HNTs are compatible and durable in the high levels of shear mixing. In addition, they are available in huge amounts, as a result, halloysites are much more affordable than CNTs and graphene [10]. On the other hand, HNTs tend to be agglomerated during the preparation of polymer/HNTs nanocomposites, that is because of the negative charge on the outer surface and the large surface energy of HNTs [11].

Surface modifications to HNTs may give the chance to expand the basal spacing of HNTs by the intercalation of inorganic and organic additives either on the outer surface or in their interlayers, which may help in the producing of homogeneous mixture of HNTs with polymers during the preparation. Furthermore, precipitating of suitable nanoparticles on the HNTs surface also provide good wetting and bonding of HNTs with polymers [12].

Zirconium dioxide or Zirconia (ZrO2) material has unique characteristics such as excellent thermal stability, high refractive index and high hardness. The nanoparticles zirconia has been utilized successfully nanocomposite industry with high refractive index, high hardness, and improved scratch resistance. ZrO2 nanopowder was employed to decrease the thermal expansion coefficient of PES to be able for using in the connector of optical fiber. However, most of the studies that utilized ZrO2 nanoparticles in the fabrication of polymer/ZrO2 nanocomposites focused on the thermal stabilities and infrequently on the surface mechanical properties of the polymer/ZrO2 nanocomposites [13].

In this study, ZrO2 nanoparticles was prepared from zirconium isopropoxide (ZrIP) by sol-gel method, and incorporated into PLA/HNTs mixture to prepare a homogeneous PLA/HNTs-ZrO2 nanocomposites. Moreover, PLA/HNTs-ZrO2 thin films were fabricated using solution casting at different PLA/HNTs-ZrO2 compositions.

2. Experimental

2.1. Preparation of ZrO2 Nanoparticles

Zirconium isopropoxide (ZrTIP), acetic acid glacial, and deionized water were used to synthesize ZrO2 via the sol-gel method. Initially, a ZrTIP (2.8 ml; 97%) solution was mixed in concentrated/pure acid acetic acid glacial (6ml; >90%). After that, ZrTIP was titrated slowly into the acetic acid glacial solution. Next, DI water (36 ml) was slowly added under vigorous stirring at an ambient temperature and mixing/rate of 350 - 500 rpm for 5 hours. Once a clear solution was obtained (sol – transparent solution), the mixture was stirred for another hour at 80 °C. To keep the reaction temperature constant, the beaker was covered with an aluminum foil and a thermometer was placed near the surface of the mixture. The solution was subsequently converted to a gel mixture at a reaction temperature of 60 °C. The continuation of the reaction will eventually result in a white suspension, which was subsequently dried overnight (12 hours at 80 °C) until it is amorphous (to obtained smallest crystal size structure from drying process), resulting in dried ZrO2 nanoparticles (yellowish color). Next, the ZrO2 nanoparticles was manually grounded using an agate mortar. ZrO2 powder (0.70 g) was calcined for 5 hours at 500 °C, and directly stored in a controlled humidity and temperature conditions. This method was utilized by Amir et al. (2015) [14].
2.2. Preparation of PLA/HNTs-ZrO$_2$ Nanocomposites Films

PLA/HNTs-ZrO$_2$ films were prepared using the method of solution casting with some modifications to the method utilized by De Silva et al. [15]. PLA/HNTs solutions were prepared by dissolving 3 g of PLA pellets in 60 ml pure chloroform. Then, the solution was stirred vigorously for 4 hours. The 2 wt%, 4 wt%, 6 wt% and 8wt% of HNTs were added to the PLA/chloroform solution and stirred for 24 hours. After that the solutions were sonicated for 30 minutes. The mixture was then poured into petri dishes and left for 24 hours to dry and evaporate. The obtained PLA/HNTs nanocomposites were named as PLA/HNT0, PLA/HNT2, PLA/HNT4, PLA/HNT6 and PLA/HNT8. Once the mixture had evaporated, the plastic film was removed and collected from the petri dish. For series 2, the 1 and 3 wt% of zirconia (ZrO$_2$) loading were prepared by dissolving them in the solution of optimum value of PLA/HNTs formulation. The solution was stirred for 24 hours to allow the dispersion and then sonicated it for 30 minutes. The mixture was then poured into petri dishes and left to evaporate. When the mixture had evaporated, the plastic film was removed and collected from the petri dish.

Table 1. Formulation of PLA/HNTs-ZrO$_2$ nanocomposites films.

| Sample code       | PLA (wt%) | HNTs (wt%) | ZrO$_2$ (wt%) |
|-------------------|-----------|------------|---------------|
| Neat PLA          | 100       | 0          | 0             |
| PLA/HNTs2         | 98        | 2          | 0             |
| PLA/HNTs4         | 96        | 4          | 0             |
| PLA/HNTs6         | 94        | 6          | 0             |
| PLA/HNTs8         | 92        | 8          | 0             |
| PLA/HNTs-ZrO$_2$1 | 95        | 4          | 1             |
| PLA/HNTs-ZrO$_2$3 | 93        | 4          | 3             |

2.3. Tensile Testing

Tensile strength (TS), modulus of elasticity (E) and elongation at break (ε) of PLA/HNTs (series 1) and PLA/HNTs-ZrO$_2$ (series 2) were measure with TA TX Plus Texture Analyzer (Stable Micro System, UK) based on the ASTM D 882-02 standard. Strip of films (10.0 x 1.0 cm) were clamped between the manual grips (without sharp edge). Five strips of each HNTs loading and another five strips of each ZrO$_2$ loading was used.

3. Results and discussions

3.1. Tensile Properties of PLA/HNTs

Figure 1 shows the TS of PLA films at different loadings of HNTs nanoclay. Tensile strength measures the highest stress value that a film can resist being stretched before cracking. Figure 1 exhibits that TS increased with the increasing of HNTs up to 4 wt%, and thus decreased slightly from 4 to 8 wt%. The optimum value of TS was 37 MPa at HNTs loading of 4 wt%, which the tensile strength increased by 43% compared to the neat PLA. However, the TS values of the PLA/HNTs bio-nanocomposite films were still high compared to the neat PLA films. The enhancement in tensile strength of PLA/HNTs bio-nanocomposites was attributed to the reinforcement provided by the good dispersion of halloysites nanotube. Better dispersed nanoclay may promote higher tensile strength due to an increase contact surface area and interaction between HNTs and the PLA matrix [16].

Similarly, to the tensile strength, Fig. 2 exhibits that the elongation at break (EAB) was increased up to 4 wt% of HNTs loading, therefore, the values of elongation at break started decreasing. This results can be explained as a Small quantity of HNTs could work as plasticizer of PLA, which dispersed the impact energy during the break. In addition, the reduction in toughness values of the PLA/HNTs nanocomposites with relatively high HNTs loadings should be attributed to the weakened interfacial interactions at high loadings of nanofillers [17].
The young’s modulus (YM) or modulus of elasticity is the slope of the linear section of the stress-strain curve during the film undertakes the elastic deformation. The aim of measuring the YM is to determine the resistance deformation, which can be utilized to reflect the stiffness and strength of the film [18]. Figure 3 illustrates a similar trend with tensile strength (TS) which YM increased with the increasing of HNTs loading up to 4 wt%, thus decreased with increasing loading of HNTs from 4 to 8 wt%.

![Figure 1. Tensile strength of PLA bionanocomposite films with different HNTs loadings.](image1)

![Figure 2. Elongation at break of PLA bionanocomposite films with different HNTs loadings.](image2)

3.2. **Mechanical Properties of PLA/HNTs-ZrO$_2$**

The effect of the addition of ZrO$_2$ on the mechanical properties (tensile strength, elongation at break and young’s modulus) were shown in table 2.

The tensile strength (TS) of optimum 4 wt% PLA /HNTs film is the highest compared to 1 and 3 wt% of ZrO$_2$ loading film. In addition, with the increasing of ZrO$_2$ loading, the values of TS decreased. This reducing in TS values could be attributed due to the poor interfacial interaction between ZrO$_2$ and PLA.
The results exhibit a decreasing in the elongation at break with the increasing of ZrO$_2$ loadings, as shown in Table 2. Which the lowest value of elongation at break was measured at 3 wt% HNTs loading. The decreasing of elongation at break of PLA/HNTs-ZrO$_2$ with the increasing of zirconia loading can be explained by the increasing of the film rigidity.

Finally, the young’s modulus of PLA/HNTs-ZrO$_2$ nanocomposites values also decreased with the increasing of ZrO$_2$ loadings. This could probably be attributed to the effect of stiffening of the ZrO$_2$ filler inside the PLA/HNTs film.

Table 2. Mechanical properties of PLA/HNTs-ZrO$_2$

| Sample              | Tensile Strength (MPa) | Elongation at Break (%) | Young’s Modulus (GPa) |
|---------------------|------------------------|-------------------------|-----------------------|
| PLA/HNTs            | 36                     | 4.3                     | 1.10                  |
| PLA/HNTs-ZrO$_2$-1  | 28                     | 3.6                     | 0.82                  |
| PLA/HNTs-ZrO$_2$-3  | 24                     | 1.5                     | 0.75                  |

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