Chemical and Hydrophobic Properties of PLA/HNTs-ZrO₂ Bionanocomposites

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Abstract. The utilization of biopolymers in the applications that meet demands in society for sustainability and environmental safety has been limited. That is owing to the poor mechanical and thermal properties of biopolymers. The goal of this study is to improve the limitations of the biopolymers properties. Polylactic acid (PLA) as one of the most important biopolymer was selected to investigate the effect of incorporating of natural halloysites nanotubes HNTs with different concentrations (0–8 wt%) on PLA chemical and hydrophobic properties. In the second series, Zirconium dioxide (ZrO₂) nanoparticles were added to the PLA/HNTs film with the optimum mechanical properties in the first series. The chemical structure and surface wettability were investigated for both of PLA/HNTs and PLA/HNTs-ZrO₂ bionanocomposites. The addition of ZrO₂ resulted in appearance of OH groups in the FTIR graph. In addition, the increasing of ZrO₂ loading led to increase the hydrophobicity of the PLA nanocomposites.

1. Introduction

Recently, the environmental effect of non-degradable plastic packaging wastes is raising general universal concern. These concerns caused an increased demand for biodegradable packaging materials from renewable sources (biopolymers) as an alternative to artificial plastic packaging materials. In addition to the packaging applications, biopolymers can be applied to a wide range of applications such as agriculture, electronic, outdoor furnishings, automotive industry, and construction. One such polymer is PLA, has been extensively investigated over the last several decades as a biocompatible, biodegradable, thermoplastic polyester and derived from renewable resources [1, 2]. However, PLA, like other biopolymers, exhibits some weaknesses in some properties like low impact strength, poor gas barrier, low heat resistance, and slow crystallization rate [3, 4].

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The incorporation of micro or nano-fillers into PLA is a promising method to terminate the weak properties of PLA. Different kinds of nanoparticles have been investigated to improve PLA properties such as CNT, Organoclay, Kaolinite, graphite, etc [5]. Owing to its multi-purpose features, naturally occurring tubular halloysite clay (HNTs) has attracted many interests of the researchers. These nanomaterials can be utilized as nano-filler for biopolymers. The development of thermoplastics matrices with HNTs has been investigated extremely by different research groups. HNTs can used to enhance the characteristics of polymers such as mechanical strength, thermal stability, crystalline behavior etc [6].

Unluckily, the applications of halloysite nanotubes (HNTs) in the natural situation is currently limited because of its highly hydrophilic internal and external surfaces, HNTs tend to agglomerate into clusters during the processing of nanocomposites. the interfacial adhesion of HNTs and PLA is not ideal because of the existing of hydroxyl groups only on the sides of unmodified HNTs [7, 8].

Owing to its good mechanical and biocompatibility properties, ZrO₂ is one of the most important metal oxides, which utilized extensively in different applications such as various implant devices and esthetic devices. ZrO₂ demonstrates variety of advantages like corrosion resistance, mechanical strength and fracture toughness. The enhanced properties of ZrO₂ endorsed to high and nano crystallinity of ZrO₂ which resulted to better biocompatibility and bioactivity nature [9, 10]. Recently, ZrO₂ nanoparticles have attracted the researchers in many attractive scientific and technological aspects in different research areas such as like gas sensors, solid fuel cells, high durability coating, catalytic agents, etc. This variety of applications according to the good mechanical and electrical properties, great dielectric constant, and wide band gap of ZrO₂ [11].

In this work, halloysite nanotube (HNTs) and ZrO₂ nanoparticles were used as hybrid fillers to enhance the properties of polylactic acid PLA. The hydrophilic properties and wettability of PLA/HNTs and PLA/HNTs-ZrO₂ were studied by contact angle measurements and the structure of the nanocomposites investigated by FTIR.

2. Experimental

2.1. Materials

Raw materials that used in this study are listed in Table 1. All raw materials are listed along with their functions and respective suppliers.

| Raw materials           | Function                                               | Supplier                        |
|-------------------------|--------------------------------------------------------|---------------------------------|
| Polylactic Acid (PLA)   | Biodegradable polymer used as a matrix.                | Nature Works, LLC (MN).         |
| Halloysites Nanotubes (HNT) | Enhancing the mechanical and thermal properties of polymer | Sigma-Aldrich chemicals company |
| Zirconia                | For enhancing PLA properties.                          | Merck, India Pvt. Ltd.          |
| Chloroform solutions    | solvent                                                | EM Science (NJ)                 |
| Distilled water         | Wash the beaker                                        | Labratory Unicity Alam          |

2.2. 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 (6 ml; >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) [12].

2.3. Preparation of PLA/HNTs-ZrO₂ Nanocomposites Films
PLA/HNTs-ZrO₂ films were prepared using the method of solution casting with some modifications to the method utilized by De silva et al. [13]. PLA/HNTs solutions were prepared by dissolving 3 g of PLAs pellets in 60 ml pure chloroform. Then, the solution was stirred vigorously for 4 hours. The 2 wt%, 4 wt%, 6 wt% and 8 wt% 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 the second series, the 1 and 3 wt% of zirconia (ZrO₂) concentration 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 2. Formulation of PLA/HNTs-ZrO₂ nanocomposites films. |
|----------------------|---------------|---------------|
| Sample code          | (PLA) (wt%)   | HNTs (wt%)    | ZrO₂ (wt%) |
| Neat PLA             | 100           | 0             | 0          |
| PLA/HNTs 2           | 98            | 2             | 0          |
| PLA/HNTs 4           | 96            | 4             | 0          |
| PLA/HNTs 6           | 94            | 6             | 0          |
| PLA/HNTs-ZrO₂ -1     | 95            | 4             | 1          |
| PLA/HNTs-ZrO₂ -3     | 93            | 4             | 3          |

2.4. Fourier Transform Infrared Spectrometer (FTIR)
Chemical properties for series 1 and series 2 were done by using fourier transform infrared spectroscopy (FTIR). This FTIR analysis was conducted to identify the chemical interaction occurring inside the PLA/HNTs and PLA/HNTs-ZrO₂ films and the chemical composition uniformly of the samples. All samples were examined using the Thermo Scientific IS10.

2.5. Surface Wettability
Contact angle (θ) measurements of the PLA/HNTs and PLA/HNTs-ZrO₂ films were carried out using a goniometer (Rame - Hart model 250 - Standard Goniometer- Tensiometer equipment) under room temperature. The medium was water and the droplet size was 4 µL. A total of 10 measurements at different places on the films were taken for each HNTs and ZrO₂ concentration.

3. Results and discussions

3.1. Fourier Transform Infrared Spectroscopy (FTIR)
First, ATR-FTIR analyses were carried out for the neat PLA sample. Figure 1 shows that IR spectrum of PLA has mainly five regions; the C–C stretching at 871 cm⁻¹, the C–O stretching peaks at 1265, 1180, 1129, 1090 1045 cm⁻¹, the C–H deformation peaks at 1360, 1370, 1384 1454 cm⁻¹, C=O ester carbonyl groups at 1755 and 1760 cm⁻¹, and the C–H stretching at 2995, 2944 and 2985 cm⁻¹ [14].

FTIR spectra of PLA/HNTs films revealed that some HNTs functional groups contributed to the nanocomposite film including O–H stretching of inner-surface hydroxyl groups 3695 cm⁻¹, O–H stretching of inner hydroxyl group 3621 cm⁻¹ and O–H deformation of inner hydroxyl groups 911 cm⁻¹.
In addition, the Si–O (in-plane stretching) at 1006 cm\(^{-1}\) of HNTs appeared as a shoulder to the vibration band at 1043 cm\(^{-1}\) of PLA spectra for the nanocomposite film. FTIR spectra peaks of few functional groups of HNTs such as perpendicular Si–O stretching at 1118 cm\(^{-1}\) and 750 cm\(^{-1}\) and symmetric stretching of Si–O at 799 cm\(^{-1}\) are not visible in the full range spectra of nanocomposite film due to their lower intensities compared to the other main peaks.

![FTIR spectra of neat PLA, pure HNTs, PLA/HNTs and PLA/HNTs - ZrO\(_2\) nanocomposites.](Image)

Figure 1. FTIR spectra of neat PLA, pure HNTs, PLA/HNTs and PLA/HNTs-ZrO\(_2\) nanocomposites.

The addition of ZrO\(_2\) nanoparticles to PLA/HNTs nanocomposites film, led to appearance of the vibrations of the O-H bond in the range of 3136–3857 cm\(^{-1}\). This is due to sorption of H\(_2\)O molecules on ZrO\(_2\) surface. The peaks which appear at 1764, 1634 and 1385 cm\(^{-1}\) are due to the bending vibration of Zr–OH groups [18].

### 3.2. Surface Wettability

Figure 2 demonstrates the plot of contact angle versus HNTs loadings in the PLA/HNTs nanocomposites films. The measured \(\theta\) value of neat PLA films 67.27 was close to the other reported \(\theta\) values of PLA films prepared by casting solution method. De Silva et al. revealed that the only significant difference of \(\theta\) values is between 2 and 7 wt% and it indicates that PLA/HNTs films became more hydrophobic at high HNTs loading. When adding 2 and 4 w/w% of HNTs into PLA matrix, the polarity of the composites increased due to the presence of OH groups of HNTs. Consequently, surface energy of the composite films increased and therefore \(\theta\) values tend to decrease slightly at these two concentrations compared to neat PLA film. When HNTs loading increased to 8 wt%, the contact angle values slightly increase. Owing to increase HNTs loading to high values, the surface roughness increases, the material’s surface energy reduces and becomes hydrophobic [19].

Figure 3 shows the plot of contact angle of PLA/HNTs-ZrO\(_2\) nanocomposites versus ZrO\(_2\) loading. The results revealed that the contact angle decreased with the increasing of ZrO\(_2\) loading. This result might be explained by the polarity of ZrO\(_2\). Which with the increasing of ZrO\(_2\) the film became more hydrophilic, that caused to decrease the contact angle values.
Figure 2. Plot of contact angle (θ) versus HNTs loading of PLA/HNTs nanocomposites films.

Figure 3. Plot of contact angle (θ) versus ZrO$_2$ loading of PLA/HNTs nanocomposites films.

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