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Physico-mechanical Properties of Nano Bio-films For Application in Food Packaging

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ABSTRACT

Petroleum-based packaging has long dominated the packaging industry, raising environmental concerns. As a result, the packaging industry has started using nano bio-plastics. Incorporating nanoparticles, nano bio-plastic packaging helps in prolonging product shelf life. Additionally, packaging manufactured of nano bio-plastic is made of biodegradable polymers. Nano bio-films made from polylactic acid (PLA) and nanoclay were produced using a solvent casting process. 1.0%, 3.0% and 5.0% (wt.) of nanoclay were added to the PLA solution. The mechanical, chemical, morphological and transparency properties of nano bio-films were investigated. To improve their suitability for food packaging applications, tensile test, Fourier-transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM) and UV-barrier test were performed. With tensile strength (TS) of 30.36 MPa and elongation at break (EAB) of 7.05%, respectively, nano bio-films with 3.0 wt. % nanoclay demonstrated higher mechanical properties than pure PLA film with about 35% of increment. In aspects of FTIR analysis, no significant differences were found with both nano bio-films and pure PLA film. The SEM morphology shows that adding nanoclay at 3.0 wt. % improves the adhesion between the PLA matrix and the nanoclay. The addition of nanoclay had a minimal impact on the PLA film's transparency, and it was interesting to see that nanoclay concentration of 1.0 wt. % and 3.0 wt. % had roughly the same light transmission values of 84.86% and 83.95%, respectively. According to the findings of this study, the PLA nano bio-film with 3.0 wt% nanoclay exhibits the optimum physico-mechanical properties.

Keywords: Biodegradable Polymer, Food Packaging, Nanoclay, Thin Films

1. INTRODUCTION

The pervasive practice of utilizing synthetic food packaging has massively increased pollution. These materials, which have a difficult time being disposed of, are typically manufactured from petroleum-based substances [1]. According to a MESTEC (2018) statistic, the waste sector's Greenhouse Gases (GHG) emissions increased by 29% between 2005 and 2014, and Malaysia released a net 50, 479, 060 tonnes of GHG in 2014. The waste sector was the second largest contributor to national GHG emissions in 2014 (9%) after the energy sector, which responsible for 80% of GHG emissions. According to Rammak et al. [2] , waste generated by the use of petroleum-based plastics has become a severe concern around the world. Besides that, handling of packaging waste is also a serious problem even for developed countries [3]. Aligned with Malaysia's National Energy Policy (2022), packaging industries and consumers should benefit from the use of biomaterials in their businesses and daily lives. As a result, using biomaterial as biodegradable packaging will change customers' and packaging industries' awareness of environmental benefits in the food business [4]. Recent studies indicated that integrating

recycling and replacing fossil fuel-based plastics by biodegradable/compostable/biobased plastics is a promising approach to reduce GHG emissions from plastics [5].

To resolve this concern, an important and current element must be applied to ensure long-term development, even in the face of global pandemics and armed conflicts. Therefore, biodegradable polymers like polylactic acid (PLA) have been the focus of research to develop biodegradable packaging due to the increasing pollution of landscapes and water bodies by plastics worldwide [4]. Due to its renewable and biodegradable properties, PLA is seen as an environmentally friendly and long-term alternative to petroleum-based polymers [5]. Furthermore, PLA has excellent processing performance and can be processed through extrusion, injection moulding, and film blowing, which has been approved by the US Food and Drug Administration (FDA) to meet Generally Recognized As Safe (GRAS) standards for food packaging [8]. Several research have gathered fundamental knowledge regarding these biopolymers with high transparency when compared to other biopolymers [9]. However, PLA is well known as a brittle material and this has been an urgent to modify in improving its properties [6].

Therefore, adding nanomaterials prove to increase the properties of PLA-based polymer compared to PLA alone as food packaging [9]. Additionally, the packaging industry has taken considerable use of the addition of nanoparticles to biodegradable polymers. In comparison to the control film, research reveals that adding cellulose nanofibers to polyvinyl alcohol food packaging strengthened the bio-nano composite's strength and elongation [7]. Nanoclay is the most used nanomaterial in packaging because it improves barrier, thermal, and mechanical properties, as well as having antimicrobial activity. Adding nanoclay to polyethylene/thermoplastic starch exhibited good antimicrobial activity which suggests an active packaging material to inhibit microbial spoilage [8]. Although nanoclay is commonly used to incorporate nanoclay into other petroleum-based polymers such as polyethylene terephthalate (PET), polyacrylic acid (PAA), and low-density polyethylene (LDPE), there has been a lack of study incorporating nanoclay in biopolymer matrix to improve its properties [12]. There are a few research stated and justified that, adding nanoclay into the biopolymer matrix has improved the tensile strength about 14% in comparison to pure PLA [9].

The aim of this study is to develop nano bio-films with enhanced properties for food packaging where PLA is used as polymer matrix and nanoclay as filler to enhance their final properties. The mechanical, chemical, transparency and morphological properties were characterized by tensile test, FTIR, UV transmitter and SEM.

2. MATERIAL AND METHODS

Polylactic acid (PLA) granules (Nature Works LLC, product name Ingeo™ biopolymer, white in colour 100% corn based; density: 1.25 g/cm^3) and chloroform are obtained from Merck, USA. Nanoclay (Nanomer® 1.28E, montmorillonite clay surface modified with 25-30 wt. % trimethyl stearyl ammonium) was acquired from Nanocor, USA respectively.

2.1 Film preparation and production

The solvent casting method is used to create nano bio-films. 2g of PLA granules are dissolved in 40 ml of chloroform using a magnetic stirrer at room temperature (23°C) for 45 minutes, or until fully dissolved. The PLA solution is then added with various amounts of nanoclay varying from 1.0%, 3.0% and 5.0% (wt.), followed by 5 minutes of sonication with an ultrasonic probe. The solution is then placed into a petri dish (15 × 15 cm). The solutions were evenly dispersed with a

bent glass rod and allowed to dry at room temperature one for about 48 hours. Finally, the nano bio-films are peeled for further analysis.

2.2 Characterisation of Films

2.2.1 *Mechanical Properties*

Tensile tests were performed on films using an Introns Universal Testing Machine in accordance with ASTM D882-97. Triplicate samples were cut into 13 cm × 64 cm lengths. At the end of each film, the samples were taped together using cardboard. The cardboards were clamped between the grips, and the experiment was carried out at a crosshead speed of 5 mm min^{-1} with an initial gauge separation of 50mm.

2.2.2 Fourier-transform infrared spectroscopy (FTIR)

The samples were tested for FTIR spectra using a spectrometer. The films are cut into small pieces with the same size (1 cm × 1 cm). Film samples were scanned between 4000 cm^{-1} and 600 cm^{-1} after being applied directly to the diamond tip. For 16 successive scans, all samples were scanned at 4 cm^{-1}.

2.2.3 Morphological Properties

The films are cut into identically sized (1 × 1 cm) pieces. Double-sided adhesive tape is used to secure the specimen to the stubs. The surface was then sputtered with a conductive gold coating for 45 seconds prior to SEM investigations.

2.2.4 Transparency analysis

A UV-double beam was used to analyse the transparency of the film. The light transmittance of the nano bio-films was tested in the visible region (400-700 nm) using ASTM D1746. For a clear comparison, light transmittance at 240 nm was measured.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

Nano bio-films were analysed for tensile strength (TS), Young's modulus (YM) and elongation at break (EAB). Based on table 1, the TS of pure PLA films is 30.36 MPa, which is in the range of PLA tensile strength as reported by previous researchers [9; 10; 11; 12]. Generally, adding up to 5.0 wt. % nanoclay resulted an increment on the film's strength. The TS of 1.0 wt. % nanoclay increased slightly to 36.12 ± 2.04 MPa. The film was improved about 18% from pure PLA film. At 3.0 wt. % nanoclay, the TS increased to 36.12 ± 2.04 MPa with improved by about 35% from pure PLA film. Then, at 5.0 wt. % nanoclay, the TS recorded at 34.25 ± 2.44 MPa with 12% higher as compared to pure PLA film.

The nano bio-film with 3.0 wt.% nanoclay had the greatest TS value, which could be attributed to the dispersion pattern. A good dispersion of nanoclay can result in a rise in TS value, resulting in a strong interface between nanoclay and PLA. This strong interface is known as interfacial adhesion, and it contributes to the strong bonding that keeps the interfaces between two nano

bio-film phases together, resulting in good mechanical performance. Figure 3 (c) shows that the nanoclay and PLA matrix are well dispersed, allowing for a greater contact area of nanoclay and PLA. Because of the large contact surface area, the nanoclay and PLA molecules formed strong interfacial hydrogen bonds [7]. The interaction is important to facilitate the transfer of stress generated in the PLA matrix to the nanoclay [9]. The higher the TS of the packaging film, the more resistant it is to external forces encountered during food handling, shipping, and transportation [13].

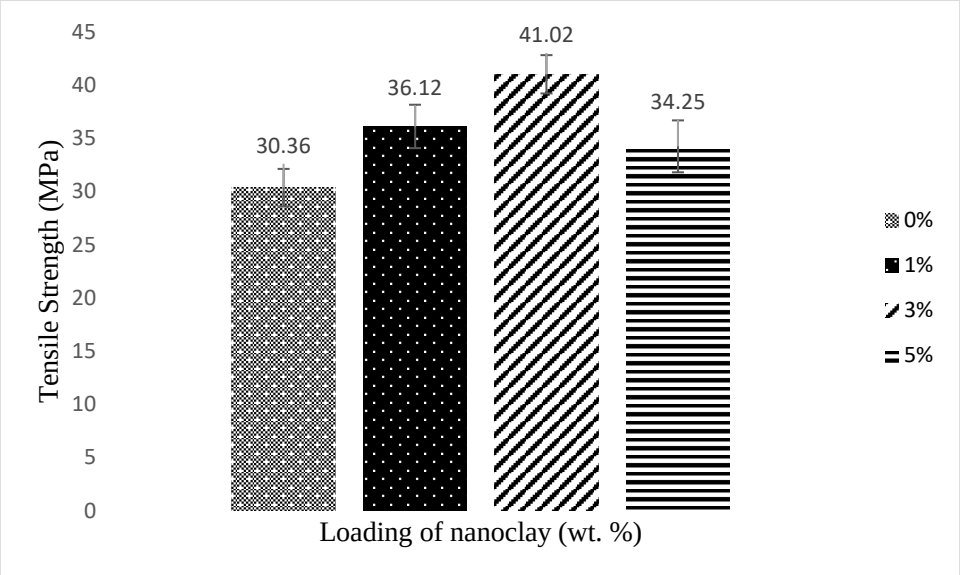


Figure 1 Tensile Strength of pure PLA film and nano bio-films

Table 1 Tensile Strength (TS), Young's modulus (YM) and Elongation at Break (EAB) of pure PLA film and nano bio-films

Loading of nanoclay (wt. %)	Tensile strength, TS (MPa)	Young's modulus, YM (MPa)	Elongation at break, EAB (%)
0.0	30.36 ± 1.77	1164 ± 137	3.93 ± 0.11
1.0	36.12 ± 2.04	1817 ± 60	7.05 ± 0.52
3.0	41.02 ± 1.80	2147 ± 203	10.40 ± 0.73
5.0	34.25 ± 2,44	2178 ± 64	8.30 ± 1.01

The decrease in TS of the nano bio-films at 5.0 wt.% nanoclay was attributed to excessive nanoclay loading, which generated poor nanoclay dispersion and a poor distribution layer into the PLA matrix. The bad distribution was caused by poor nanoclay dispersion, which resulted in agglomeration of the nanoclay particles [14]. This can be seen in Figure 3 (d) when white spots are seen on SEM microscopic images of 5.0 wt. %. Agglomerates are made up of a large number of primary particles that are kept together by a weak force. Agglomeration occurs when nanoclay is not consistently distributed, causing cracks (weak spots) to propagate inside the agglomeration. If a stress is applied to the weak area, it can be readily broken [15]. A higher loading of nanoclay used often results in poor dispersion of the nanoclay, resulting in agglomeration. It can be concluded that nanoclay dispersion is an important component that can have a direct impact on the mechanical properties of the generated nano bio-films. Othman et al.,

(2016) observed a similar finding, with the TS decreasing by roughly 7% from pure PLA films when 4.0 wt.% nanoclay was introduced to the PLA matrix [12].

The pure PLA film's Young modulus (YM) was determined to be 1164 ± 137 MPa. The YM of the nano bio-films seemed to have risen as the nanoclay loading increased. The nano bio-film containing 5.0 wt. % nanoclay has the greatest YM value of 2178 ± 64 MPa. The value rose by 87% as compared to the pure PLA film (1164 ± 137 MPa). Meanwhile, the addition of 3.0 wt. % nanoclay resulted in an 84% increase.

According to Table 1, the EAB of pure PLA is 3.93 ± 0.11%. The EAB values increased as the nanoclay loading increased from 0 to 3.0 (wt.%) and then reduced with the addition of 5.0 wt.% nanoclay, which may be due to uniform dispersion of nanoclay or nanoclay agglomeration, respectively. The reduction in EAB indicates an increase in the brittleness of the nano bio-film, which may be desired and advantageous for biodegradable packaging material because it is directly related to the film's biodegradability[16]. Nevertheless, the EAB value of 5.0 wt. % nanoclay (8.30 ± 1.01 %) is still higher than pure PLA film. Based on the results, 3.0 wt. % nanoclay has the highest EAB values (10.40 ± 0.73%), showing an improvement of 10.40 ± 0.73%.

3.2 FTIR

Figure 2 illustrated the FTIR spectra of pure PLA film and nano bio-films. All films exhibited the same spectra, indicating that there was no significant chemical change on the film. C-H stretching (CH_2 and/or CH_3) was assigned to the peak approximately 2900 cm^{-1}[2]. The IR band identified at around 1700 cm-1 could be C=O stretching, whereas the bands observable at 1300-1500 cm^{-1} could be symmetric and asymmetric deformational vibrations of C-H in CH_3 of PLA [17]. According to Rimoli et al. [19], the peak at 1181 cm^{-1} can be explained to PLA C-O-C stretching. Finally, IR bands identified at 860 cm-1 and 750 cm-1 can be assigned to the amorphous and crystalline phases of PLA, respectively [17]. A similar observation was made with biodegradable nanocomposites reinforced with cellulose nanofibers derived from coconut industry waste, which were designed to replace synthetic plastic food packaging [7]. Considering that there was no conformational change inside the PLA structure, the band was observed nearly unchanged from the spectra of the pure PLA film. However, the pure PLA film has a little higher peak position at 866cm^{-1} than the other nano bio-films, which vary between 753cm^{-1} and 755cm^{-1}. This shows that the materials were efficiently absorbed into the films via chemical bond (hydrogen bond) formed between the compounds and the PLA molecules [19].

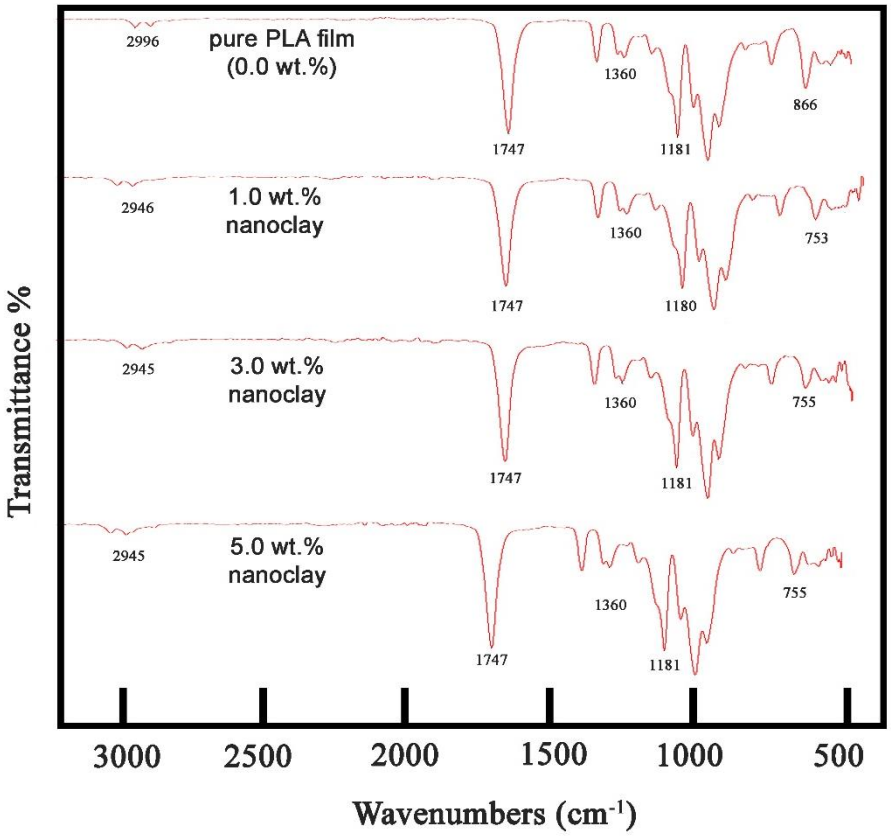
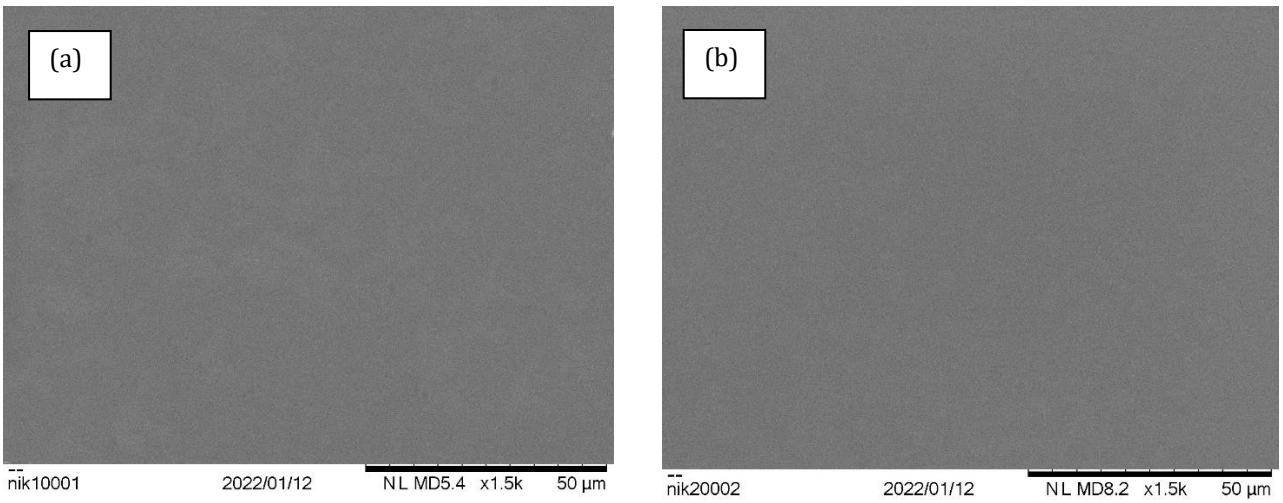


Figure 2 FTIR spectra of pure PLA film and nano bio-films

3.3 Morphological Properties



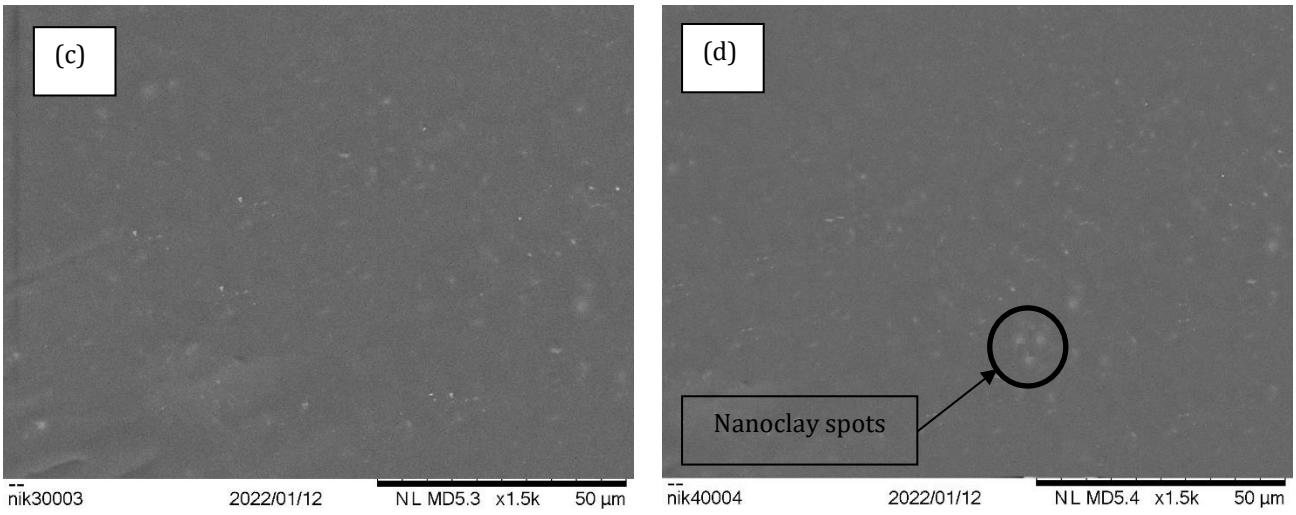


Figure 3 Surface morphology structure of (a) pure PLA film and nano bio-films with (b) 1.0 wt. %, (c) 3.0 wt. % and (d) 5.0 wt.%

Figure 3 shows SEM microscopic pictures of pure PLA film and nano bio-films. Figure 3(a) illustrates a pure PLA film with a smooth surface. Similar with Figure 3(b) shows a smooth surface despite adding 1.0 wt. % nanoclay to the PLA matrix. This could be due to a low amount of nanoclay loading in the PLA matrix. When compared to other nano bio-films, both of these films have a relatively fragile structure. It was described as having a loose surface structure. [20].

As the number of loading increase, the nano bio-films exhibited a course film surface with the present of white spots. The surface become more compact with the increasing of nanoclay. This can be seen in figure 3(c) and figure 3(d). For nano bio-film at 3.0 wt. %, the nanoclay were proportionally dispersed and gave good dispersion. Good dispersion of nanoclay may help improve mechanical strength of the film [9] which resulting in a strong interaction of nanoclay and PLA. This can be seen at mechanical properties when the TS value for 3.0 wt. % was the highest. Both of these nano bio-films are still uniformly dispersed. Nevertheless, Figure 3 (c) shows a good distribution of nanoclay and the size of the distribution is smaller and does not tend to agglomerate compared to Figure 3 (d). The homogenous distribution of nanoclay in the PLA matrix is due to the high affinity of PLA and nanoclay, which results in the creation of a hydrogen bonding contact between them [21].

However, since the white spots in Figure 3 (d) are larger and therefore the nanoclay may have clumped, this could indicate that the 5.0 wt. % nanoclay layer has agglomerated to a small extent. The nanoclay has agglomerated because it was present in high concentration and was not subjected to dispersion treatment. Agglomeration of nanoclay can created a weak force between PLA which causes decreasing amount of TS value. Similar result showed by Abdul Majid et al. [22] that the TS value decreased when higher value of napier cellulose nanowhisker were added to PLA matrix.

3.4 Transparency Analysis

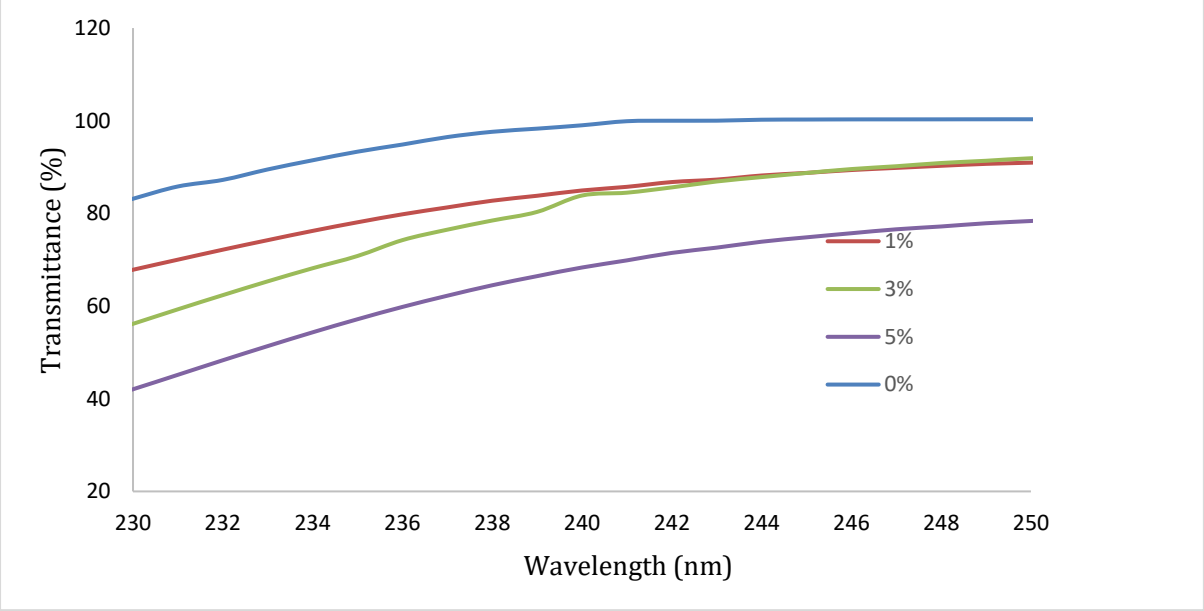


Figure 4 Graph of transparency of pure PLA film and nano bio-films

Figure 4 shows a graph of transmittance (%) vs. wavelength (nm) for nano bio-films. For a clear comparison, the light transmittance was determined in the range of 240 nm. Pure PLA film has the highest light transmittance of 100%, followed by 1.0 wt. %, 3.0 wt. % and 5.0 wt. % nanoclay with 84.86%, 83.95% and 68.32%, respectively. In these studies, it should be noted that the higher the percentage of permeability, the better the transparency of the films.

In general, as the concentration of nanoclay was increased, the percentage of transmittance reduced. Pure PLA films were proven to be the most transparent. There were substantial changes in the percent light transmittance of nano bio-films containing 1.0 wt. % nanoclay, which were around 17% lower than pure PLA film. Meanwhile, the difference between pure PLA film and 3.0 wt. % nanoclay were just 18%. The percent changes in light transmittance between 1.0 wt. % and 3.0 wt. % nanoclay, on the other hand, are just approximately 1.0%. This suggests that 3.0 wt. % nanoclay offers the same transparency as 1.0 wt. % nanoclay. Furthermore, the difference with pure PLA films and 5.0 wt. % is approximately 31%. As a response, it is apparent that the addition of nanoclay can influence the percentage permeability of a thin film. This implies that 5.0 wt. % is not effectively diffused, which may result in nanoclay aggregation in the films.

It has been shown that the transparency of nano bio-films decreases with increasing nanomaterial content [2]. This is because the nanoclays present are made of soil, which consists of gravel, silt, and clay [22]. In general, soils are brown in colour, and nanoclay is brownish. Thus, this may affect the percentage of permeability. Consumer perception and acceptance can be affected by food packaging materials [7]. According to [23; 7; 24], most food packaging materials are transparent and colourless. Overall, these nano bio-films are still transparent. Therefore, they are suitable and recommended for packaging purposes.

However, additional research will be made to assess the application of the nano bio-films for greater potential in fruits packaging. There are several research have included natural agents such as bacteriocins, essential oils and natural extracts for antimicrobial properties in food packaging as well as the assessments of the packaged fruits using nano bio-films.

4. CONCLUSION

The present study provides information on preparation of nano bio-films (PLA/nanoclay) with 0, 1.0, 3.0 & 5.0 (wt. %) nanoclay loading. Different instrumental procedures including the tensile test, FTIR analysis, SEM analysis and UV-barrier test, were used to characterize the films. The result from mechanical study shows an increment in mechanical strength (TS) at 3.0 wt. % nanoclay with 41.02 MPa and improvement in EAB with 10.40%. The effective dispersion of nanoclay particles in the PLA matrix was confirmed by SEM microscopy. Data obtained from FTIR confirmed the interaction among components of the nano bio-film through hydrogen bonding between 753 – 755 nm. The incorporation of nanoclay in the films decreased their transparency. Nonetheless, at optimal nanoclay loading (3.0 wt. %), the loss in light transmittance was only about 18%. Overall, nano bio-films containing 3.0 wt. % nanoclay demonstrate interesting features that should be explored further.

As the world is heading toward a more sustainable future to preserve resources for future generations and protect ecological life. Nano bio-films can help to reinforce fundamental beliefs and the need to accomplish the Sustainable Development Goals (SDGs) for a healthy and peaceful future, as specified in the United Nation's 2030 goal to reach "zero carbon emissions". Furthermore, numerous scientists have suggested the idea of "smart manufacturing," which integrates nanotechnology and biomaterials to reach "zero carbon emission" for “smart packaging”.

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