

## Mechanical strength properties of Chitin/Polylactic Acid biocomposite film

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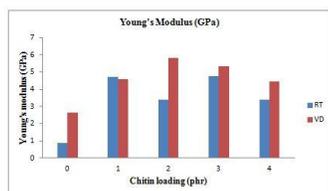
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### Article history :

Received September 2016

Accepted November 2016

### GRAPHICAL ABSTRACT



Effect of Chitin Loading on Young's Modulus (Room temperature and Vacuum Dried)

### ABSTRACT

Polylactic acid (PLA) is a biodegradable polyester that can be used for many applications such as packaging, medicine and agriculture. However, several disadvantages including brittleness, poor water vapour barrier properties and high cost production limits its application. Hence, this study focuses on developing PLA by introducing commercial chitin into PLA with the purpose of obtaining chitin/PLA biocomposite film characteristics. The chitin/PLA film was prepared at various commercial chitin contents (1, 2, 3, and 4 phr) by solution casting method to investigate the effect of commercial chitin content on its mechanical strength properties. Tensile test and Atomic Force Microscopy (AFM) analysis were carried out to study the properties of chitin/PLA composites. The results showed that the tensile strength and elongation at break of PLA decreased with the addition of chitin. The elastic modulus of the biocomposite films increased upon addition of chitin into PLA. From mechanical properties revealed that chitin and PLA blends were incompatible and supported with the results of Fourier Transform Infrared (FTIR) analysis that showed the absence of specific interaction between chitin and PLA. Likewise, AFM showed the surface morphology of PLA was changed upon addition of chitin, with increased tendency for agglomeration of chitin at high loading which indicated poor filler dispersion in the matrix.

*Keywords: Commercial chitin; Polylactic acid; Mechanical properties*

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## 1. INTRODUCTION

Nowadays, there are many research contribute a high interest in biodegradable films made from natural polymer. Such interest is due to severe environmental pollution caused by plastic food packaging. These packaging films are made up of usually synthetic polymers that are non-biodegradable which can lead to serious ecological problems. Thus, the current research has been motivated to employ biodegradable material instead of petroleum based synthetic polymer commonly used [1].

Polylactic acid (PLA) is a biodegradable polyester, suitable for many applications such as packaging, medicine and agriculture [2]. However, the major disadvantages of PLA are due to its brittleness, poor water vapour barrier properties and high production cost that limit large-scale commercial applications as packaging materials [1, 4]. Hence, to overcome these problems, PLA may require incorporation of organic or inorganic fillers [3].

Due to the growing environmental awareness towards the production of 'green materials' derived from natural resources such as plant or animal, studies on bio-composites based on chitin fibre as fillers that is renewable, biodegradable character and non-toxicity have been carried out [4].

Chitin has plays remarkable reinforcement in many bio-based polymer matrixes since it has good biodegradability and non-toxic properties which makes it suitable as filler in PLA films to enhance the properties of PLA [4,5] The functional films can be applied in many applications especially in bio-plastic production and packaging of food, as well in agriculture product. Therefore, the development of good quality chitin film will benefit both industry and environment as it will reduce solid pollution and generate income to seafood industry [5].

## 2. EXPERIMENTAL

### 2.1. Materials

PLA (Nature Work TM PLA 3001D) in pellet form was obtained from Nature Work LLC (Minnetonka, MN USA). Commercial chitin powder was purchased from Sigma Chemical Company at Iceland. The reagent used was chloroform that was purchased from Merck, Malaysia.

## 2.2. Preparation of PLA and Chitin/PLA biocomposite film

A 10 wt% solution of PLA pellets (NatureWork LLC) in Merck chloroform was prepared by stirring at 60°C until the pellets were fully dissolved. The PLA solution was immediately casted on a clean glass plate and left for 48 h in room temperature and vacuum dried at 31 °C. The thickness of the cast solution was approximately 100µm and noted as pure PLA. The chitin/PLA film was prepared by adding different amounts of commercial chitin powder (1, 2, 3 and 4 phr) with PLA pellets and dissolved in the chloroform. Then the solution was stirred till dissolved using the double-boiling method. The solution was sonicated for 5 min and immediately casted over a clean glass plate and dried using different drying methods, namely at room temperature and vacuum oven for 48 h. The film produced was carefully removed and designated as PLA/C1, PLA/C2, PLA/C3 and PLA/C4 for each method respectively. The film was tested for tensile properties and characterized using SPI 3800 Atomic Force Microscopy (AFM) and Infrared spectroscopy (IR) on Perkin Elmer 1600.

## 2.3. Mechanical Test

Mechanical test was done using the Instron 4400 Universal Tester to measure the tensile strength at the point breakage for each sample. Tensile tests were carried out at room temperature, according to the ASTM D882. A fixed crosshead rate of 10 mm/min was utilized in all cases and the results were taken as an average of 5 tests.

## 3. RESULTS AND DISCUSSION

In a previous study, the incomplete drying of the solvent (chloroform) resulted in the low tensile strength of PLA reinforced chitin nanowhiskers (CNW) [6]. The incomplete drying resulted from the method of drying in which the film was dried at room temperature for 48 hours. In order to give a better result of tensile strength, alternative drying method has been proposed. As a result, PLA film dried at vacuum dryer have the greater tensile strength compared to the room temperature.

### 3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The chitin/PLA film also was characterized using IR spectroscopy. Even though the amount of chitin added was different (1, 2, 3 and 4 phr), the spectra did not show any new peaks. It showed in the Figure 1, where the pure PLA, 1 and 3 percent of weight chitin was combined together to observe the differences among them. The different color of band shows the different amount of chitin in the PLA film. There is a small difference in wavelength obtained but the peak shown was similar. It shown that, the IR band is always same if the amount of the chitin is different. The absence of new peak indicated that the lower amount of filler was used to produce the composites film while only interactions between PLA and chitin were physical rather than chemical interaction. When the percentage of chitin was increased it was shown that the peak at  $1759.50\text{ cm}^{-1}$  became broader due to interactions between C=O of PLA and the O-H groups of chitin [7].

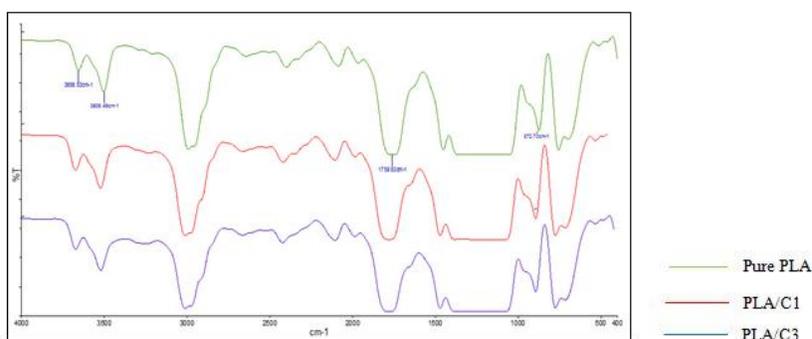


Fig. 1 Spectrum of pure PLA with different amount of commercial chitin.

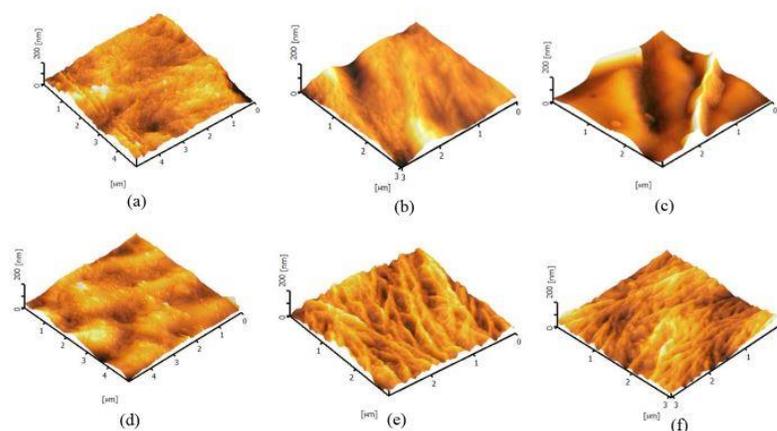
Table 1 IR band of chitin/PLA film

Types of Absorption	Frequency, $\text{cm}^{-1}$
O-H (bonded)	3503.49
C-H (alkanes)	2992.77
C=O	1759.50
C-H (alkanes)	1448

Only spectra of PLA/C1 and PLA/C3 showed similarities in shape and peaks produced. The reason both spectra were chose was due to the significant amount of chitin powder content in PLA film that may give different shape and peak of spectrum. However, the findings revealed otherwise such outcome may be due to difference in the amount of added chitin as well as physical interactions. Thus, the significance difference in spectrum cannot be observed [7].

### 3.2 Atomic Force Microscopy

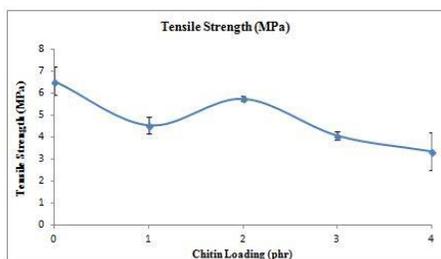
Figure 2 shows the surface morphology of PLA and chitin/PLA biocomposite corresponding to various contents and drying method. The natures of interactions between PLA and chitin powder in the biocomposites were examined by AFM. The pure PLA are relatively smooth as can be seen in (a) and (d) for both conditions which are commonly for an unfilled matrix material. With the incorporation of chitin filler, the surface of neat PLA become rough due to uneven filler dispersion within the matrix when the chitin contents are increased. The rough surface can be explained by the large sized chitin particles, that caused agglomeration into bigger size clumps [7]. This condition affects the tensile strength by reducing it to lower values than pure PLA itself. Based on (e) and (f), the surface of PLA/C1 and PLA/C3 prepared in vacuum dryer were observed as thread-like structures as compared to films dried under room temperature. This can be explained with low humidity conditions, but as a greater number of smaller domains, aggregates that are evenly distributed to lead to small increase of tensile strength in PLA composite film as compared to film that was exposed to high humidity [8].



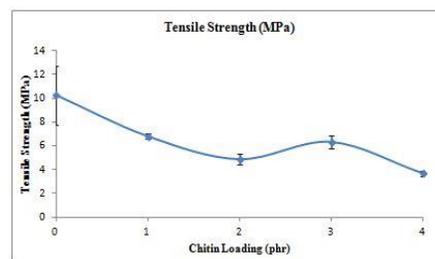
**Fig. 2** AFM images of PLA composites with addition of chitin powder in different drying method (a) PLA-RT b) PLA/C1-RT c) PLA/C3-RT d) PLA-VD e) PLA/C1-VD f) PLA/C3-VD (3 x 3  $\mu\text{m}$ ).

### 3.3 Mechanical Test

The effect of chitin loading on the tensile properties of pure PLA and chitin/PLA composites in different drying method are shown in Figure 3 and Figure 4. Generally, the incorporation of chitin powder into the PLA matrix did not give any improvements in both tensile strength and elongation at break of PLA composites compared to pure PLA. This was probably caused by less interaction of the matrix itself as the presence of bigger particles of chitin which give great effect and prevents the interaction force between the particles of matrix itself [7]. The addition of chitin into the PLA matrix has decreased the tensile strength which contributed to aggregation of chitin particles due to Van der Waal's forces. Such filler-filler interaction becomes more significant as compared to filler-matrix interaction. This because the increased amount of filler into matrix would lead to poor interfacial adhesion between chitin and PLA matrix. Hence, the decreased recorded in the tensile strength, corresponding by such changes are consistent with the observed results in microscopy analysis.



**Fig. 3** Effect of Chitin Loading on Tensile Strength (Room temperature)



**Fig. 4** Effect of Chitin Loading on Tensile Strength (Vacuum dried)

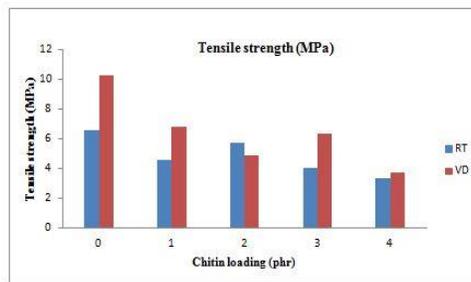


Fig. 5 Effect of Chitin Loading on Tensile Strength (Room Temperature and Vacuum Dried)

Based on Figure 5, the difference of drying method utilized to form the films has gave significant changes in tensile properties. The study found the film dried in vacuum dryer has higher tensile strength and elongation at break compared to the room temperature. It can be seen that the tensile strength of composite film in vacuum drying method was higher than dried at room temperature. The complete drying of chloroform could have higher higher tensile strength of film compared with the incomplete drying of the solvent at afforded room temperature. Besides, the decrease in moisture contributed to the higher in tensile strength. This was due to the complete drying of chloroform and reduced in humidity of the environment rather than in room temperature. The tensile strength of pure PLA and chitin/PLA composites film for different in drying method were shown in Figure 5.

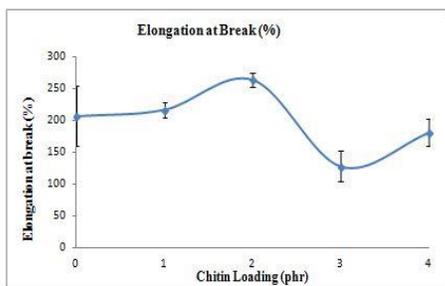


Fig. 6 Effect of Chitin Loading on Elongation at break (Room temperature)

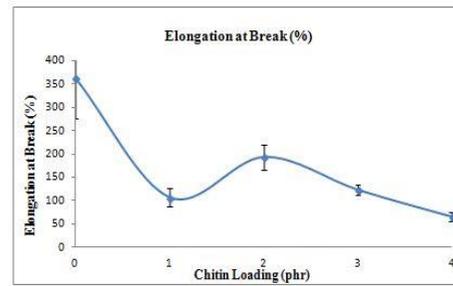


Fig. 7 Effect of Chitin Loading on Elongation at break (Vacuum Dried)

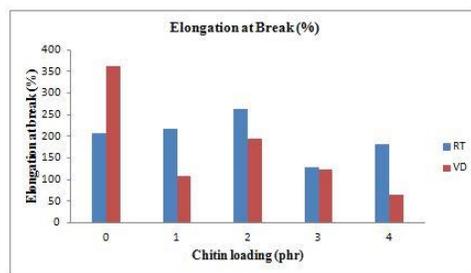


Fig. 8 Effect of Chitin Loading on Elongation at break (Room temperature and Vacuum Dried)

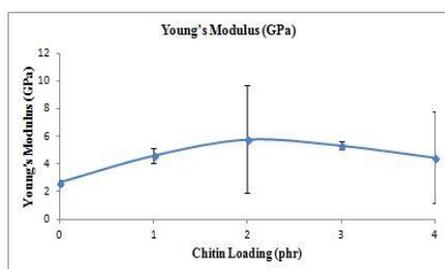


Fig. 9 Effect of Chitin Loading on Young's Modulus (Room Temperature)

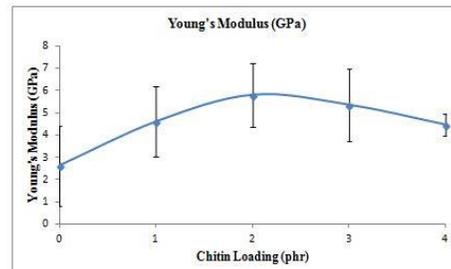


Fig. 10 Effect of Chitin Loading on Young's Modulus (Vacuum Dried)

The addition of chitin into the PLA matrix has given a negative impact to the elongation at break for composites. The result indicated that the elongation at break of chitin/PLA decreased as the amount of chitin was increased. The reduction in elongation may have resulted from the stiffening action of the filler by limiting the segmental chain movement of PLA during tensile testing [7]. The elongation at break was also affected by the amount of added fillers, dispersion of the fillers in the

matrix and interaction between fillers and the matrix. Chitin displayed poor interaction and dispersion in PLA matrix due to higher tendency to agglomerate following reduction of elongation at break. Since there were two different drying methods involved in this research, the elongation at break obtained for both condition may be varied due to the effect of incomplete drying of solvent and humidity of environment (Figure 8).

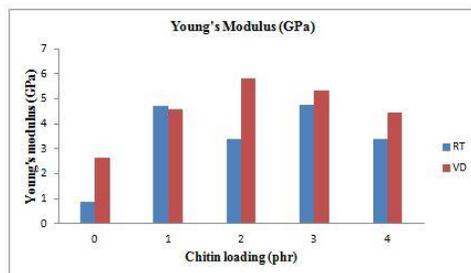


Fig. 11 Effect of Chitin Loading on Young's Modulus (Room temperature and Vacuum Dried)

#### 4. CONCLUSION

Chitin/PLA biocomposite film was successfully produced using solution casting method. AFM showed the poor dispersion of chitin particles in the composites which contributed to the decrease in tensile properties of chitin/PLA composites. While for Young's Modulus showed an increase with increasing chitin content as compared to pure PLA. It was found that the vacuum drying method gave better tensile properties of the film as compared to that dried at room temperature.

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