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Mechanical Properties of Polylactic Acid/ Graphene/ Chitin Nanowhisker Composite Film

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GRAPHICAL ABSTRACT

Pure PLA (left) and PLA/graphene film (right)

ABSTRACT

Polylactic Acid (PLA) is a thermoplastic biodegradable polyester that is widely used in various fields such as in packaging, medicine and agriculture. However, PLA has some drawbacks such as low toughness, brittleness, poor vapour barrier properties and low thermal stability that may limit its application. Properties of PLA were shown to improve when added with inorganic nanofillers such as graphene. Meanwhile organic filler such as chitin nanowhiskers (CHW) has also shown positive effect on PLA properties. In this work the effect of CHW content (1, 2, 3 and 4 phr) on mechanical and thermal properties of PLA/graphene composite films was investigated. Tensile test and thermogravimetric analysis (TGA) were carried out to study the properties of all composites. The results showed that tensile strength of PLA/graphene composites decreased with the addition of CHW at all contents. However, the tensile strength of PLA/graphene/CHW increases up to a maximum value of 3 phr. While elongation at break of all PLA/graphene/CHW composites decreases with addition of CHW fillers. Young's Modulus increases at 1 phr CHW content. The results indicate that the blending of PLA/graphene with CHW did not improve its tensile strength which showed the absence of specific interactions between PLA with both fillers as shown by Fourier transform infrared (FTIR) spectroscopy. Meanwhile TGA showed that the thermal stability of PLA did not show much improvement by addition of CHW. As a conclusion, since graphene used was at its optimum value, effect of CHW may have been more effective by using a lower graphene content.

Keywords: polylactic acid, graphene, chitin nanowhisker, mechanical properties

1. INTRODUCTION

Today, many types of petrochemical based polymers, glass, metal, paper and board were used as the main materials and polymer for packaging, medicine and agriculture. It brings great advantages such as low cost but fast production, high mechanical perfomance, good barrier properties and good heat stability. However, due to its disadvantages including declining oil and gas resources, environmental concern relating degradation, cross contamination in recycling and health concern causes urgent need to substitute this petrochemical-based polymer (Jamshidian *et al.*, 2010). Plastics are petrochemical based polymer which is non-biodegradable. It may pollute the environment if its disposal was not planned properly. Plastic such as pellets, fragments and microplastics have been shown to contain organic contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons, petroleum hydrocarbons and organochlorine pesticides (2,2′-bis(*p*-chlorophenyl)-1,1,1 trichloroethane (DDT). This toxic substance that exist in plastic can be transferred to the food chain if ingested (Mato et al., 2001). This proved that because of its non-biodegradability, plastics could endanger the environment if not properly treated. This issue has resulted in rising level of interest in product substitution of more biodegradable and sustainable as compared to petroleum-based polymer products.

PLA (Figure 1) is suitable as a substitute for this problem due to its ability to biodegrade (Grigale *et al.*, 2010). PLA was selected as a future alternative to petrochemical polymer due to its high strength, stiffness and processability. However, it has drawbacks such as high manufacture cost compared to the more commonly used plastics, low toughness, brittleness, poor vapour barrier properties and low thermal stability which making it uncertain for certain applications. Hence, many steps have been adopted such as blending PLA with other biodregadable polymer and also development of nanocomposites containing organic and inorganic nanofillers (Arjmandi *et al.*, 2015). Thus, graphene and CHW was selected as nanofiller to be reinforced with PLA. In this study, the development of PLA/Graphene and PLA/CHW/Graphene composite film by solution casting method was carried out to obtain a composite film with improved properties.

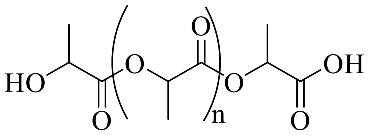

Figure 1 Structure of polylactic acid.

2. EXPERIMENTAL

2.1 Preparation of CHW

CHW was prepared by hydrolyzing 1.0 g of commercial chitin powder in 30 mL of 3M hydrochloric acid (HCl) for 3 hours in water bath. The hydrolysis was carried out at 80 ºC for 90 min under strong stirring. The hydrolysis process was continued by adding 50 mL of distilled water. The diluted suspension was centrifuged at 3200 rpm for 15 min each to obtain the supernatant. The supernatant was dialyzed in a cellulose dialysis tubing against tap water and the chitin in the tubing was further dialyzed under continuous water flow for 2 hours. After that, the tubing was immersed in a beaker of distilled water for 24 hours. The sample was transferred into small beaker and sonicated 4 times (5 min sonication and rest for 5 min). Wet CHW (Figure 2) was transferred into a bottle, weighed and kept at 4 ºC until further use (Asri *et al.*, 2017).

Figure 2 CHW in wet form.

2.2 Preparation of PLA/graphene by Solution Casting Method

The optimum formulation of PLA/graphene nanocomposites was prepared by mixing 10.0 g of PLA pellets with 0.1 wt% of graphene content in order to use as a control sample.

First, 10.0 g of PLA was dissolved in 64 mL of chloroform in a beaker with continuous stirring for 2 hours (Solution A). Then, 0.1 wt% of graphene was dispersed in 20 mL of chloroform separately by bath sonication for 30 min (Solution B). Subsequently, the solution containing dispersed graphene (Solution B) was transferred into PLA mixture (Solution A) and further subjected to bath sonication for 15 min and 30 min (Solution C).

Finally, the PLA/graphene solution was casted over a clean glass plate with spreader. The film (Figure 3) was dried at room temperature 48 hours to allow the solvent to evaporate. The film produced was carefully removed and the mechanical properties were examined. The film was kept in a desiccator before subjected to characterization using FTIR, TGA and mechanical test (Valapa *et al.*, 2015).

Figure 3 PLA/graphene film.

2.3 Preparation of PLA/GR/CHW by Solution Casting Method

The PLA/graphene/CHW composite film was produced in different CHW content which are 1, 2, 3 and 4 phr (Table 3.1). The nanocomposites were prepared by mixing 10.0 g of PLA pellet with 1.0 g of graphene and different content of CHW. CHW used was in suspension form. Solvent exchange was then carried out via centrifugation at 3200 rpm for 15 min. Water was exchanged with acetone and acetone was exchanged with 30 mL chloroform. Then, the CHW was sonicated for 5 min using bath sonication to ensure homogenous dispersion into the chloroform. The dispersed CHW was transferred into reaction flask containing PLA. The mixture was dissolved in 34 mL of chloroform at 60 °C for 2 hours with strong stirring. The solution was sonicated for 5 min using bath sonication. Separately, 1.0 g of graphene was dispersed with 20 mL chloroform in bath sonicator for 45 min. Both of the PLA + CHW mixture and graphene mixture was mixed together and sonicated for 45 min. After that, the mixture was immediately casted on a clean glass plate. The film was dried at room temperature for 48 hours to allow the solvent to evaporate. The thickness of the cast film is approximately 100 ηm and noted as PLA/graphene/CHW1, PLA/graphene/CHW2, PLA/graphene/CHW3, and PLA/graphene/CHW4. The film produced was carefully removed and the mechanical properties were examined. The film was kept in a desiccator before subjected to characterization using FTIR, TGA and mechanical test.

Table 1 Polylactic acid composite formulation

Designation	PLA (%)	CNW (phr)	Graphene (wt%)
NEAT PLA	100	0	0
PLA/GR	100	0	0.1
PLA/Graphene/CHW1	100	1	0.1
PLA/Graphene/CHW2	100	2	0.1
PLA/Graphene/CHW3	100	3	0.1
PLA/Graphene/CHW4	100	4	0.1

3. RESULTS AND DISCUSSION

3.1 Preparation of PLA/graphene and PLA/graphene/CHW Composite Film

Figure 4 and 5 shows PLA/graphene and PLA/graphene/CHW composite films, respectively that was prepared by solution casting method. The film can be described as black in colour and was uniformly dispersed as no bubble present on the film. However, as the CHW content (phr) increases, black spots appears and become noticeable. This outcome was expected to be CHW aggregates in the PLA matrix.

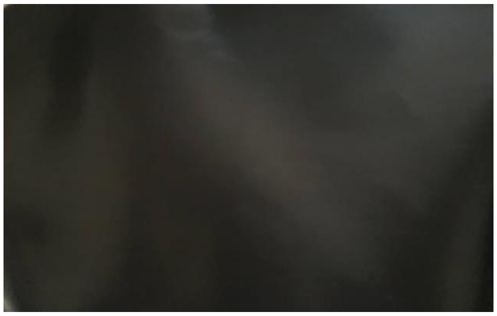

Figure 4 PLA/graphene film.

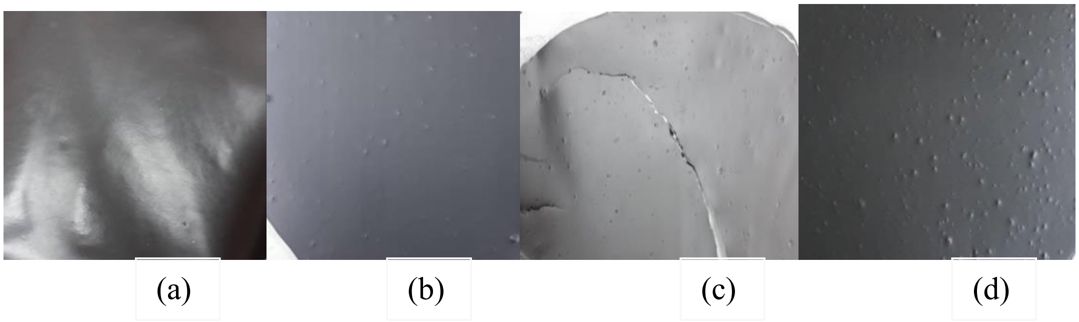

Figure 5 PLA/graphene/CHW films with different CHW content (a) 1 phr (b) 2 phr (c) 3 phr (d) 4 phr.

3.2 Analysis of IR Spectrum

All samples for PLA/graphene/CHW and PLA/graphene were analysed through IR absorption spectroscopy. FTIR spectroscopy was used to observe possible interfacial interaction between PLA matrix with both graphene and CHW. The IR spectrum of PLA/graphene is shown in Figure 6. As can be seen from Figure 6, peak at 2997.74 cm^{-1} was assigned to the asymmetric stretching vibration of -CH. Stretching vibration of carbonyl groups (C=O) appeared at 1750.84 cm^{-1} and the peak at 1082.54 cm^{-1} was assigned to the stretching vibration of C-O. The peak at 1453.87 cm^{-1} is ascribed to the -CH bending. The peak taken was only the significant peak for PLA/graphene.

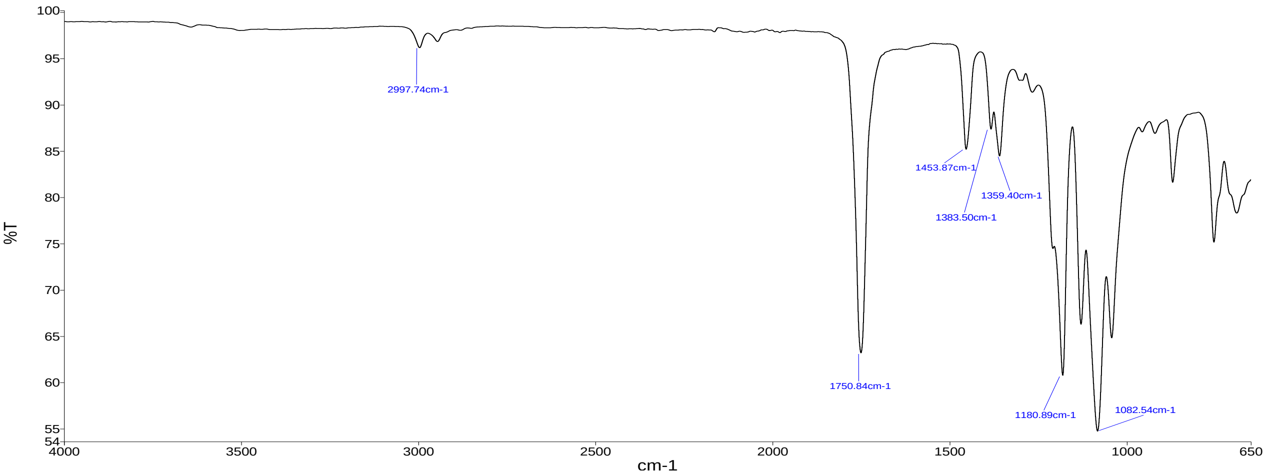

Figure 6 IR spectrum of PLA/graphene film.

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Meanwhile, Figure 7 shows the IR spectra of the PLA/graphene/CHW with different amounts of CHW (1, 2, 3 and 4 phr). The IR absorption band of PLA/graphene/CHW film displays similar absorption peak as PLA/graphene as in Figure 6. This may due to majority of the graphene still exist in aggregate structure as the solution casting method did not fully separate the graphite layers. Although the amount of CHW added is different, all samples show similar absorption bands. The O-H, C=O and C-O stretching peak were shifted slightly to higher frequency. This indicates that there is good interaction between the hydroxyl group of CHW and carbonyl group of the PLA. The spectrum did not show any difference in new peak for various amounts of CHW (1, 2, 3 and 4 phr) which indicates only physical interaction occurred between the PLA with graphene and CHW hybrid fillers.

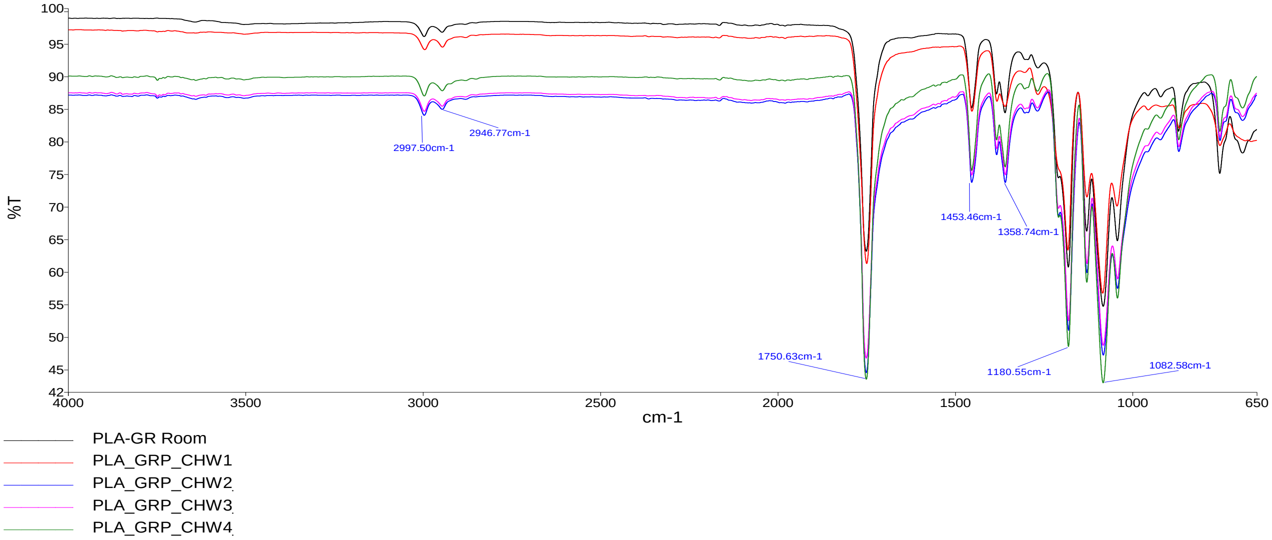

Figure 7 IR spectra of the PLA/graphene/CHW with different loadings of CHW (1, 2, 3 and 4 phr).

3.3 Thermogravimetric Analysis (TGA)

PLA/graphene and PLA/graphene/CHW composite film were carried out under nitrogen atmosphere at heating rate of 10 °C min^{-1}. The data was summarized in Table 2.

Based on the results (Figure 8), the addition of CHW as another filler affect the thermal stability of PLA matrix. As can be seen from Table 2, PLA/graphene/CHW1 is thermally stable than PLA/graphene by small increment of only 1 ºC. This improvement in thermal stability could be due to uniform dispersion of the CHW in the PLA matrix. Uniform dispersion of the nanofillers can retard the diffusion of oxygen into polymer matrix and barrier effect against the volatile pyrolized products of PLA which lead to retarding thermal degradation of polymer nanocomposites (Liu *et al.*, 2013).

Despite that, the thermal stability of the filler starts to decrease which is similar to the previous observation reported by Arjmandi *et al.*, 2015. The decrease in thermal stability happened because the fillers start to agglomerate and the presence of excess protein that might still attached to the CHW. The residual weight of PLA/graphene/CHW1 was lower than PLA/graphene. This is probably due to the presence of lower amount of crystallinity due to CHW that limits it intrinsically flame resistance property. However, there is not much change in temperature with the addition of CHW to the composite. In conclusion, thermal stability of PLA did not improve much with the addition of CHW.

Table 2 Summary of TGA result

Samples	**Degradation Temperature, T_{10}**	**T_{50} (ºC)**	**DTG peak temperature, T_{max} (ºC)**	**Residual weight (%)**
PLA/graphene	332.00	361.00	359.00	0.46
PLA/graphene/CHW1	334.00	360.00	360.00	0.31
PLA/graphene/CHW2	336.00	360.00	359.00	0.74
PLA/graphene/CHW3	324.00	334.00	358.00	0.51
PLA/graphene/CHW4	329.00	353.00	357.00	0.47

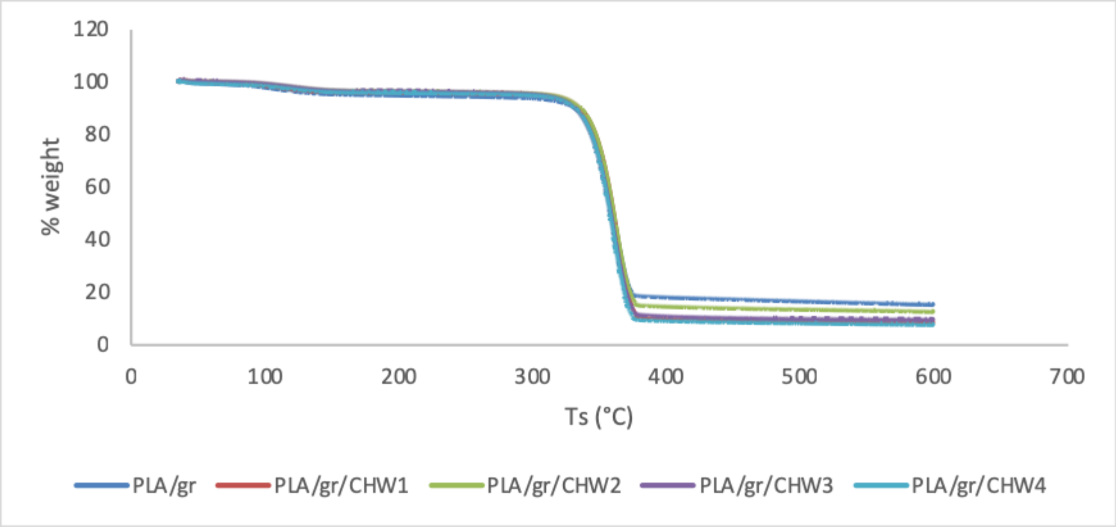

Figure 8 TGA curve of all polymer composites.

3.4 Mechanical Properties of PLA Composite Film

From the mechanical test, tensile strength, elongation at break and Young`s Modulus of elasticity were obtained and summarized in Table 3.

Table 3 Tensile Strength, Elongation at Break and Young’s Modulus of PLA/graphene/ and PLA/graphene/CHW composite film

Samples	Tensile Strength (MPa)	Elongation at Break (%)	Young’s Modulus (MPa)
PLA/graphene	16.97 ± 1.83	9.21 ± 3.23	9.73 ± 2.76
PLA/graphene /CHW1	13.69 ± 2.46	5.21 ± 1.24	12.02 ± 3.22
PLA/graphene /CHW2	13.94 ± 1.89	3.55 ± 0.72	10.75 ± 2.51
PLA/graphene /CHW3	14.03 ± 1.79	3.09 ± 0.52	9.6 ± 2.76
PLA/graphene /CHW4	10.74 ±1.96	2.9 ± 0.50	5.91 ± 2.34

The tensile strength of the PLA/graphene composite is found to be the highest at 3 phr content of CHW (14.03 MPa) when compared with PLA/graphene/CHW1 (13.69 MPa) and PLA/graphene/CHW2 (13.94 MPa). However, tensile strength of the composite was lower than PLA/graphene (16.97 MPa) upon addition of CHW. Unfortunately, there are no concrete reason to explain why the addition of CHW decrease the tensile value because no constructive data to support the reason. Based on the Figure 9, all types of composites shown increasing trend of tensile strength. Increasing in tensile strength specify that there is good interfacial adhesion between fillers and PLA matrix which promoted to good stress transfer between the matrix and fillers. The decrease in tensile strength trend was probably due to aggregation of CHW and graphene particles as a result of formation of hydrogen bonding between CHW-CHW molecules. The aggregation of the fillers gave negative impact to the system as it could act as stress-centralized point which reduced the surface area of interaction between fillers and matrix resulting in an inefficient transfer of stress from matrix to fillers. The increase of filler content into PLA matrix promote filler-filler interaction which reduce the level of filler-matrix interaction leading to low tensile strength value. Similar observation has been reported by Haafiz *et al.* (2013).

The addition of CHW into PLA matrix gives negative impact to the elongation at break of the composites (Figure 10). It can be seen that as CHW was added, the elongation at break of the composite decreases. The decreasing in elongation at break shows enhancement in brittleness of the composites. The reason for the decreasing in elongation at break was due to stiffening action of the filler by limiting the segmental chain movement of PLA during tensile testing (He *et al.*, 2011). The addition of CHW promote higher tendencies for the particles to agglomerate leading to poor interaction and dispersion in PLA matrix consequently reduction in elongation at break.

The effect of CHW on Young`s Modulus are shown in Figure 11. Young’s Modulus increases with increasing amount of CHW but start to decrease at 2 phr content of CHW. The increasing value most probably due to reduced polymer chains mobility that stiffen the structure of the PLA composite with addition of CHW content. The stiffness was due to increase in hydrogen bonding and stiffening effect of the filler (Hassan *et al.*, 2013). Similar observation has been reported by Haafiz *et al.* (2016). The Young’s Modulus increase because the modulus is measured at low strain. However, the Young’s Modulus decrease at 2 phr CHW loading. This is most probably because the sample was not fully dry and the volatile content such chloroform (solvent used in the experiment) affected the Young’s Modulus of the PLA composites in conjunction with filler agglomeration.

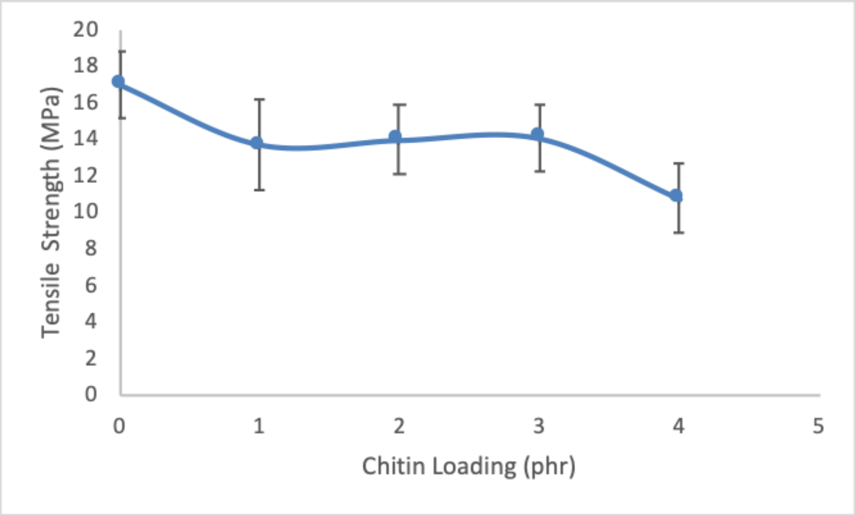

Figure 9 Tensile strength of PLA/graphene and PLA/graphene/CHW (1, 2, 3 and 4 phr).

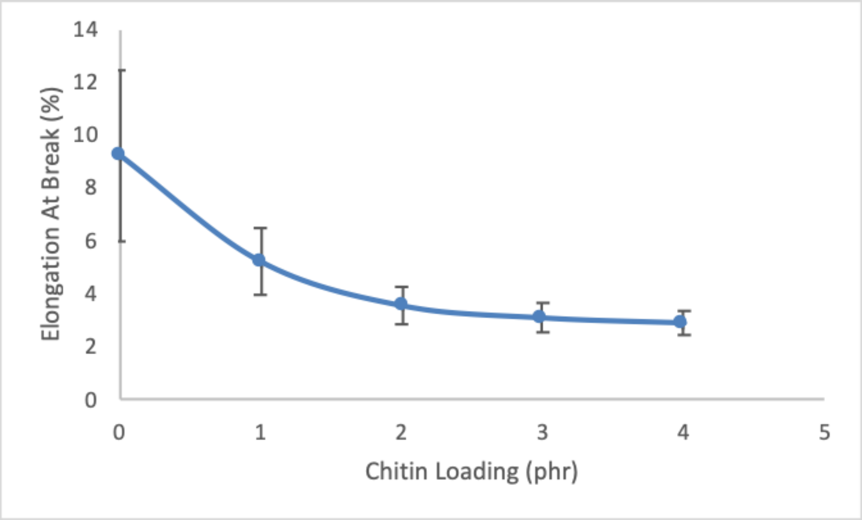

Figure 10 Elongation at break of PLA/graphene and PLA/graphene/CHW (1, 2, 3 and 4 phr).

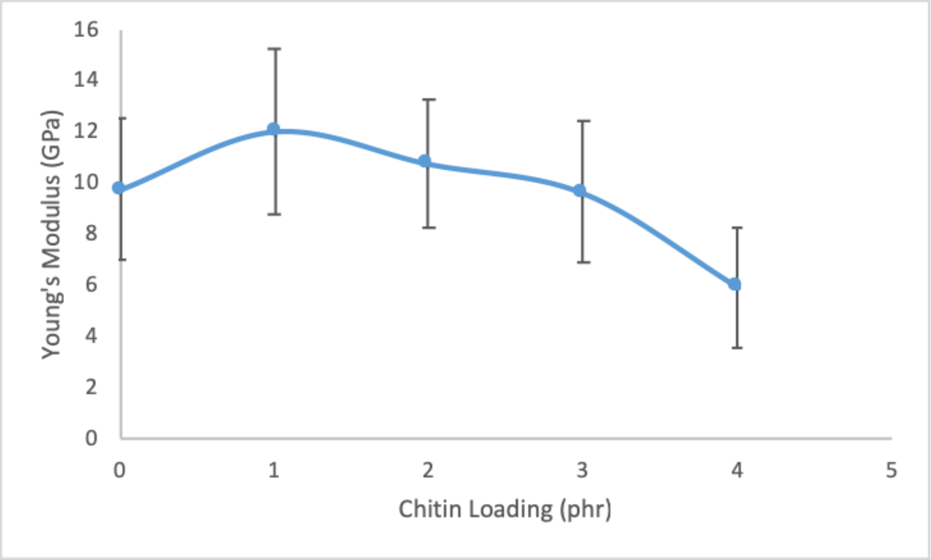

Figure 11 Young's Modulus of PLA/graphene with PLA/graphene/CHW (1, 2, 3 and 4 phr)

4. CONCLUSION

As a conclusion, PLA/graphene and PLA/graphene/CHW film synthesized using solution casting method provide different effect on mechanical strength and thermal properties. The tensile strength of PLA/graphene/CHW composite film is lower than PLA/graphene alone (16.97 MPa). The tensile strength of PLA/graphene/CHW composites increases with addition of 1 (13.69 MPa), 2 (13.94 MPa) and optimum at 3 phr CHW content (14.03 MPa) but decreases at 4 phr content (10.74 MPa). Young's Modulus also increasing at 1 phr CHW content (12.02 GPa) while elongation at break of all PLA/graphene/CHW composites decreases with addition of all CHW content. TGA showed that addition of CHW at all content does not give significant effect to the thermal stability of PLA. Thus, since graphene was used at its optimum value, effect of CHW may have been more effective when using a lower graphene content in between 0.05 to 0.1 wt %.

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