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EFFECT OF CHITIN SOURCE AND CONTENT ON PROPERTIES OF CHITIN NANOWHISKERS FILLED POLYLACTIC ACID COMPOSITES

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ABSTRACT:This study investigates the use of chitin nanowhiskers (CHW) from different chitin sources to develop CHW reinforced polylactic acid (PLA) nanocomposite. Chitin sources used in this study were commercial chitin (CC), fermented chitin (FC) and treated fermented chitin (TFC) whereby FC and TFC were obtained from fermentation of prawn waste. The chitin was then undergoes acid hydrolysis to produce commercial chitin nanowhiskers (CCHW), fermented chitin nanowhiskers (FCHW) and treated fermented chitin nanowhiskers (TFCHW). PLA was chosen due to several advantages such as biodegradability, good mechanical strength and in line with global pressure to improve environmental pollution aspects. Tensile strength for PLA/FCHW, PLA/TFCHW and PLA/CCHW increased with increasing filler content until it reached optimum value at 1 phr, 2 phr and 3 phr, respectively. Young's modulus for the nanocomposites increased with increasing filler content but elongation at break decreased significantly with increasing filler content for all types of nanocomposites. TGA results indicated that PLA/CHW nanocomposites displayed better thermal stability as compared to pure PLA. The biodegradability and water absorption of nanocomposites increased with increasing filler content. The overall results confirm that PLA nanocomposites from FC are not inferior than PLA nanocomposites from CC and therefore has similar potential to be used in packaging applications.

ABSTRAK:Kajian ini menyelidik penggunaan nanowisker kitin (CHW) dari sumber kitin yang berbeza untuk membangunkan komposit poli(asid laktik) (PLA) bertetulang CHW. Sumber-sumber kitin yang digunakan dalam kajian ini terdiri daripada kitin komersial (CC), kitin ditapai (FC) dan kitin ditapai yang dirawat (TFC) di mana FC dan TFC diperoleh daripada penapaian sisa udang. Kitin kemudiannya menjalani proses hidrolisis asid untuk menghasilkan nanowisker kitin komersial (CCHW), nanowisker kitin ditapai (FCHW) dan nanowisker kitin ditapai yang dirawat (TFCHW). PLA dipilih kerana kelebihannya misalnya kebolehan pereputan-bio, kekuatan mekanikal yang baik dan sesuai dengan tekanan global untuk memperbaiki aspek pencemaran alam sekitar. Kekuatan regangan untuk PLA/FCHW, PLA/TFCHW dan PLA/CCHW meningkat dengan peningkatan kandungan pengisi sehingga mencapai nilai optimum masing-masing pada 1 phr, 2 phr dan 3 phr. Modulus Young bagi komposit nano meningkat dengan peningkatan kandungan pengisi tetapi ciri pemanjangan takat putus menurun dengan ketara dengan peningkatan kandungan pengisi bagi semua jenis komposit nano.

Keputusan TGA menunjukkan bahawa komposit nano PLA/CHW memaparkan kestabilan terma yang lebih baik berbanding dengan PLA tulen. Kadar pereputan-bio dan penyerapan air komposit nano meningkat dengan peningkatan kandungan pengisi. Hasil keseluruhan mengesahkan bahawa komposit nano PLA daripada FC tidak lebih rendah daripada komposit nano PLA dari CC dan berpotensi serupa untuk digunakan dalam aplikasi pembungkusan.

KEYWORDS:*chitin; nanowhiskers; prawn waste; polylactic acid; nanocomposites*

1. INTRODUCTION

Chitin is one of the most abundant natural polysaccharides that exist in nature and is found in the outer skeleton of crustaceans such as shrimp, lobster and crab. It is known to possess many desirable properties such as biocompatible, antibacterial [1] and is found to have desirable mechanical properties due to their natural stacks of chitin nanowhiskers (CHW) [2]. Research and development on CHW sparked new interest following the successful use of nanocrystalline fractions from cellulose as fillers in nanocomposites [3-7] since both cellulose and chitin shared similar backbone structure. Natural polymers such as chitin, starch and cellulose consist of both crystalline and amorphous region. Various methods have been employed in production of CHW. One of the methods that are widely used is through acid hydrolysis [8]. The crystalline region in nanoscale size once isolated can be used as reinforcing nanofillers in polymer nanocomposites [9-10].

Synthetic polymers have become an essential part of our lives; having wide applications in various fields including in agriculture, packaging and in medical applications [11]. Although synthetic polymers have many advantages, the lack of biodegradability is one of the setbacks and has caused serious polluting effects on the environment. Therefore interests on biopolymers which are biodegradable and are synthesized from renewable resources [12] have increased among the academicians and researchers globally as indicated by the expanding literatures [13-15].

Polylactic acid (PLA) is the most promising bio-based and biodegradable thermoplastic, and is considered as a ‘green’ eco-friendly material. It is an aliphatic polyester and fulfils many requirements as a packaging thermoplastic and is suggested as a material for general packaging applications [16]. To enhance the competitiveness of PLA, many properties such as mechanical and thermalcan be further improved. In addition, the reinforcement of PLA using natural nano-fillers is interesting to be considered as it is expected to improve biodegradability besides enhancing the mechanical and thermal properties due to their nanosize crystals. Previous report mentioned that addition of chitin nanofibrils (CNs) as reinfocing fillers do not alter the other properties of PLA based materials; hence proposing that this addictive can be used in bioplastic items mainly expoliting its intrinsic anti-microbial and skin regenerating properties [17].

Several studies have reported on the use of CHW as reinforcing filler in PLA [18-19]. The earliest work was on the fabrication and characterization of melt-blended PLA/chitin composites in which the CHW was produced by an acid hydrolysis. Interestingly, the study showed that the stiffness of the composites increased with increasing chitin content while the strength decreased. In a later study, the effect of surface acetylated CHW on structure and mechanical properties of PLA was determined [20]. In the study, the miscibility between CHW and PLA was improved by surface acetylation of CHW. The acetylated CHW was incorporated into a PLA matrix by solution blending, and resulted in an increase of tensile strength and Young's modulus and they reached to the maximum value as 45 and 37% higher than neat PLA film, respectively, with the loading level of acetylated CHW reaching to 4 wt %. The enhancement could be attributed to that acetylation improved dispersion of acetylated CHW in the PLA matrix and interfacial adhesion between acetylated CHW and PLA. Recently, the effect of CHW on crystallization of triethyl-citrate-plasticized PLA has also been reported [21]. The addition of a small amount (1 wt %) of CHW to plasticized PLA significantly affected its nucleation, crystal size, and crystallization speed. In the previous study, CHW were chosen to surface modify PLA film to better utilize and combine the advantages of PLA matrix and CHW [22]. The resulting film prepared via the vertical coating method through shearing force action has significantly better strength and modulus compared to conventional solution blending. On the other study, electrospun composite nanofibers membrane of PLA and the surface grafted chitin whiskers resulted in superior tensile strength and modulus as compared to pure PLA. This is mainly due to the hydrophilicity of PLA was improved by the introduction of CHW [23]. In a recent study, it was reported that PLA based films containing CNs resulted in biocompatibility and able to stimulate the production of cell defensins, acting as an indirect anti-microbial agent [24].

In recent years, a biotechnological approach using lactic acid fermentation to purify chitin from prawn waste [25-26] provides an environmentally friendly approach as opposed to the conventional chemical method. The biological approach produces two industrially important products namely a protein-rich liquid fraction and a chitin solid fraction. Besides reducing the usage of hazardous chemicals by the conventional methods, the biological approach is able to conveniently recover the protein-rich fraction via a suitable bioreactor [25] and has been shown to be a suitable source of protein for aquaculture feed [26]. Meanwhile, finding good use to the chitin by-product fraction will give added advantage to the fermentation process.

In the present work, CHW from the chitin fraction of fermented prawn waste is investigated as nanoscale fillers to reinforce PLA. Prawn waste is widely produced from prawn processing industries and its disposal is becoming an issue due to its high perishability. Thus, its proper disposal and putting it to good use is becoming more urgent. To date, no study has been done on using CHW obtained from fermented chitin as fillers in PLA. In this study, CHW from chitin through fermentation of prawn waste is being produced as potential material for polymer reinforcement in an attempt to replace commercial chitin produced through harsh chemical treatment. The objective of this study is to compare the effects of CHW from fermented chitin with the chitin obtained through chemical method on mechanical, physical and thermal properties of CHW reinforced PLA composites.

2. EXPERIMENTAL

2.1 Materials

PLA was obtained from NatureWork^{TM} (PLA 300ID). The density of PLA is 1.25 g/cm^3, melting temperature of 145-155°C, glass transition temperature of 55-58°C, cystallinity of up to 37% and it has an average molecular weight of Mw: 220 kDa and Mn: 101 kDa. Chitin sources are i) fermented chitin (FC) produced by fermentation treatment of tiger prawn waste,ii) treated fermented chitin (TFC) which is basically an FC that undergoes an extra mild acid and alkaline treatment and iii) chitin from prawn shells purchased from Sigma Aldrich designated as commercial chitin (CC) for comparison. All types of chitin sources underwent hydrolysis and dialysis through treatment with hydrochloric acid to produce CHW. The solvent used to dissolve the PLA is chloroform, purchased from Merck Malaysia.

2.2 Production of Chitin via Fermentation of Prawn Waste

Tiger prawn (*Penaeus monodon*) waste obtained from a local prawn processing industry in Johor consisted of head, exoskeleton, and tail portion were minced through a 4.5 mm die plate using an industrial mincer (Rheninghaus Meat Mincer, model EVE/ALL 22, Italy) and were fermented using effective microorganism (EM) which has been activated with palm sugar for a week prior to use [26]. Fermentation of minced prawn waste was carried with addition of 10% (w/w) of carbohydrate sources (glucose or brown palm sugar) and 10% (v/w) activated EM in a loosely covered bottle and incubated at 37^{o}C for 72 hours. The mixture was occasionally stirred especially during the first 24 hours and pH was monitored using bench top pH meter (Hanna Instruments, Italy). The fermented product is separated into solid chitin; fermented chitin (FC) and liquid proteinaceous fraction. For the production of treated fermented chitin (TFC), FC was hydrolysed in 1M HCl at room temperature for 1 hour followed by another hour in 1M NaOH solution. Both FC and TFC were washed, dried and kept at room temperature for further use.

2.3 Preparation of Chitin Nanowhiskers (CHW)

CHW was prepared through acid hydrolysis method [8]. Fermented chitin (1.0 g) was hydrolyzed in boiling 3N HCl for 1 hour. After hydrolysis, chitin was diluted with distilled water (40 mL) and centrifuged at 3200 rpm for 15 minutes and this process were repeated thrice. The chitin extract was dialyzed in cellulose dialysis tubing against continuous water flow for 2 hours. The dialysis process was continued by immersing the dialysis tubing in a beaker of distilled water until it reaches ph 4. The chitinextractdesignatedas fermented chitin nanowhiskers (FCHW) was sealedandstored at 4°C. Similar steps were repeated using treated fermented chitin (TFC) and commercial chitin (CC) producing treated fermented chitin nanowhiskers (TFCHW) and commercial chitin nanowhiskers (CCHW) respectively. All samples of nanowhiskers were characterized using FTIR and TEM.

2.4 Preparation of PLA and PLA/CHW nanocomposites

An amount of 10 g of PLA pellets were fully dissolved in chloroform through constant stirring in a water bath at 60^{o}C for approximately 60 minutes [7]. The solution was evenly spread on a glass plate using a fabricated spreader and the film was left to dry by evaporation at ambient temperature for 48 hours. Dried film was kept in adessicator until further use. The thickness of the cast film was approximately 100 ± 0.125 µm and designated as PLA. The PLA/CHW nanocomposites were prepared by mixing PLA with different types of CHW (FCHW, TFCHW and CCHW) at different CHW contents (1, 2, 3 and 4 phr) following the same method in production of PLA film. Nanocomposites of PLA/FCHW, PLA/CCHW and PLA/TFCHW were analysed for mechanical, thermal, water absorption properties and biodegradability.

2.5 Characterizations

2.5.1 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was performed using Perkin Elmer 1600 infrared spectrometer (USA). All types of CHW were characterized using liquid method through suspension casting. All samples were recorded at 32 scans with a resolution of 4cm^{-1} and within the wavenumber range from 370 to 4000 cm^{-1}.

2.5.2 Transmission Electron Microscopy

The study of surface morphology of CNW from various sources of chitin (FCHW, TFCHW and CCHW) were evaluated using Hitachi Hd-2000 scanning transmission electron microcopy (TEM). Samples were prepared by placing 5 µL diluted suspension of

FCHW, TFCHW and CCHW on the carbon-coated grid and was allowed to dry at room temperature. The samples were negatively stained by allowing the grids to float in a 1% uranyl diacetate solution for 3 minutes. The samples were examined at an accelerating voltage of 120kV. The TEM images were obtained by using soft imagine system software.

2.5.3 Tensile Testing

Tensile test was performed according to ASTM D882 using L1oyd LRX (USA) machine under ambient condition. Rectangular specimens were cut from the obtained cast film with dimension 60 x 12.6 x 0.1 mm^3. The crosshead speed of 12.5 mm/min with 30 mm gauge length was used. Tensile strength, elongation at break and Young's modulus were determined. Seven specimens for each formulation were tested and mean value was recorded.

2.5.4 Thermogravimetric Analysis

Thermogravimetric analyses (TGA) and Derivative Thermogravimetric (DTG) were used to determine thermal stability of the PLA nanocomposites by tracking weight change during a ramp to 600°C at 20°C/min with nitrogen purge.

2.5.5 Water Absorption

Water absorption test was carried out according to ASTM D570-81. The sample (20 x 20 x 0.1 mm^3) was dried to a constant weight (Wo) in vacuum oven prior to the test and was then immersed in distilled water at ambient temperature for 2 hours and 24 hours. Wet weight after immersion (Wi) were taken and percentage weight gain was taken as the water absorption values using Equation (1),

$$\text{water absorption (\%)} = [\,(Wi - Wo) / Wo] \times 100 \qquad (1)$$

2.5.6 Soil Burial Test

Soil burial test was conducted with the purpose of studying biodegradation of composites in natural conditions using garden soil [25]. The garden soil used contained a balance of three soil materials namely silt, sand and clay with humus. It has a pH of 6-6.5 and high calcium levels because of its previous organic matter content. Rectangular samples (20 x 20 x 0.1 mm^3 dimension) were kept in a desiccator until a constant weight (W1) was achieved. The samples were buried in garden soil at a depth of 170-220 mm from the soil surface for durations of 1-8 weeks. The soils were sprayed with water every 24 hours to maintain its moisture. After selected durations, samples were washed with water to remove the soil from the surface of samples and dried at 55ºC in vacuum oven and was weighed to a constant weight (W2). The percent weight loss (WL) was calculated according to Equation (2).

$$WL\,(\%) = [(W1 - W2) / W1] \times 100 \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is an indispensable technique and relatively simple method to obtain information on any possible changes in the chemical structure of the chitin after undergoing chemical acid hydrolysis to produce CHW. FTIR spectra of various types of CHW (FCHW, CCHW and TFCHW) are shown in Fig. 1 and their vibrational assignments are summarized in Table 1.

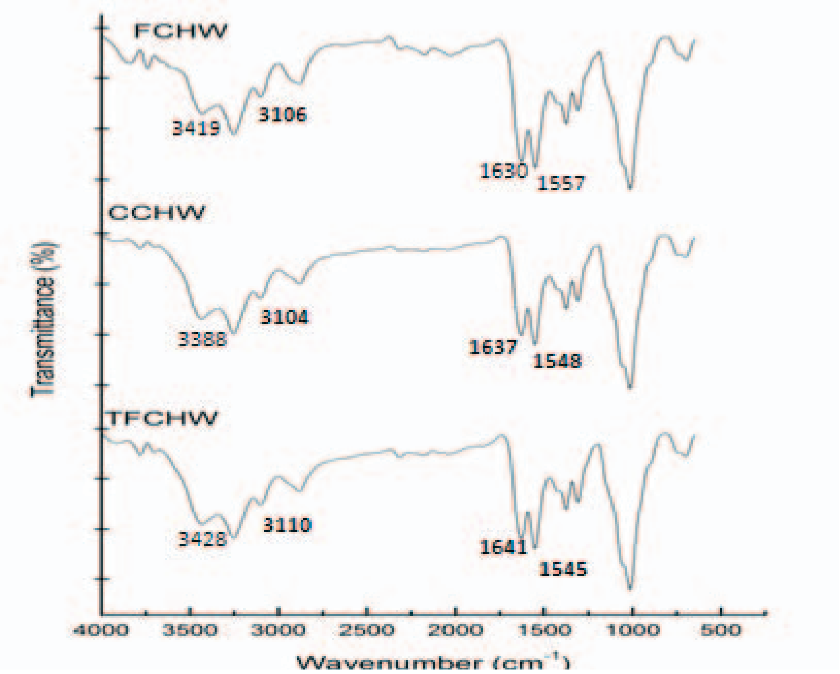

Fig.1: FTIRspectra of FCHW, CCHW and TFCHW.

Table 1:FTIR spectra peak assignments for chitin whiskers (FCHW, CCHW and TFCHW).

Peak assignment	**Peak frequency (cm^{-1})**		
	FCHW	**CCHW**	**TFCHW**
O-H groups	3419	3388	3428
N-H stretching	3106	3104	3110
C-H stretching	2923	2883	2869
C=O (Amide I)	1630	1637	1641
C=O (Amide II)	1557	1548	1545
C-H bending	1473	1380	1372
C-N groups	1384	1308	1317
C–O stretching	1112	1074	1024
N-H bending	722	762	713

Based on the FTIR spectra, all samples showed similar absorption bands at two main absorbance regions around 1600 cm^{-1} and 2800-3500 cm^{-1} indicating that all samples have similar chemical compositions. The characteristic carbonyl (C=O) stretching around 1640 cm^{-1} is attributed to the carbonyl vibrations of amide functional group. Some of the carbonyl groups (Amide I) are bonded through hydrogen bonds to the amino group inside the same chain (C=O---H-N) that is responsible for the vibration mode at around 1640 cm^{-1} while the rest creates similar bond with –CH_2OH from the side chain. This additional bond created the slightly lower peak of Amide II at around 1560 cm^{-1}. The existence of these interchain bonds is responsible for the high chemical stability of the α-chitin structure [1,28,29]. The presence of amide group was further strengthened by appearance of C-N absorption band at around 1370 cm^{-1} and N-H bending around 720-770 cm^{-1}.

In the corresponding region of the OH and NH (3600–3000 cm^{-1}) groups, all samples exhibit similar vibrational stretching peaks. This is attributed to the different packing arrangements of the macromolecules. The shoulder that appears in the spectrum at 3426 cm^{-1} is attributed to the intramolecular hydrogen bond involving the OH on carbon 6 and carbonyl oxygen (OH (6)---O=C). The band appears at 3315 cm^{-1} corresponds to the intramolecular hydrogen bond (OH (3)---O(5) from the ring). The bands at 3100-3270 cm^{-1} are assigned to the vibrational assignments of the NH of the amide (intermolecular hydrogen bond C=O—H-N and the NH groups intramolecularly bonded by H). Similar observations have been reported in the study of chitin from shrimp, prawn, king crab, squid and lobster [30].

The FTIR spectra of all samples displayed similar absorption bands denoting that there is no significant difference between theCHW from various sources of chitin and that the hydrolysis process was successful in producing CHW and did not alter the chemical structures. The hydrolysis done in a controlled condition as shown in this study was able to protect the chemical groups of chitin. On another note, it is envisaged that the milder fermentation treatment during production of fermented chitin (FC) could protect the polymeric structure of chitin which in turn will produce a higher aspect ratio chitin nanowhiskers (FCHW).

3.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was performed to confirm the separation of individual crystallites into nanowhiskers. TEM is considered a powerful technique in characterization of nanomaterials. The analysis of the suspension of FCHW, CCHW and TFCHW shown in Fig. 2 (a)-(c) revealed some changes in the morphological features of the chitin after the acid hydrolysis treatment. As anticipated, TEM images showed the typical rod-like nanoparticles for FCHW, CCHW and TFCHW confirming that the treatment used was successful in producing the individual rod-like chitin nanowhiskers. Interesting observations can be seen on the size differences of various CHW.

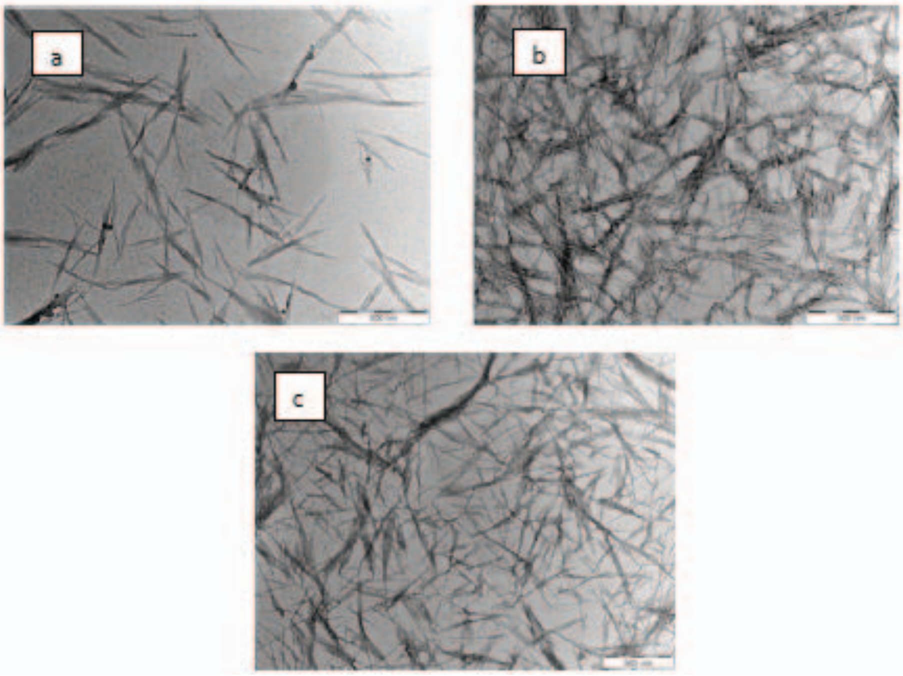

Fig.2: TEM of a) FCHW, b) CCHW and c) TFCHW.

The average sizeof FCHW was found to be more than 500 nm in length and 10 nm in width as compared to CCHW which recorded about 300 nm in length and 10 nm in width.

Meanwhile when the fermented chitin was chemically treated prior to hydrolysis to form whiskers, the width of TFCHW was found to be shorter than FCHW which is about 300 nm length and 20 nm widths in average. The extra chemical pretreatment of fermented chitin had probably shortened the polymeric chitin chain, hence producing a shorter CCHW. Based on the usual trend of the positive effect of using higher aspect ratio CHW, the slightly higher aspect ratio of FCHW is expected to give comparable if not a betterr einforcing performance as fillers in PLA compared to using CHW from commercial chitin source (CCHW). It is also interesting to note that FCHW displayed many individual whiskers as compared to aggregated and stacked whiskers in CCHW and TFCHW. This characteristic may produce a better reinforcement to the PLA matrix.

3.3 Tensile Properties of PLA Nanocomposites

The effects of FCHW, CCHW and TFCHW content on the tensile strength, elongation at break and Young's modulus of PLA/FCHW, PLA/CCHW and PLA/TFCHW composites are shown in Fig. 3, 4 and 5, respectively. Figure 3 shows that incorporation of all types of CHW showed an increase in tensile strength of the nanocomposites as compared to pure PLA (11.95 MPa). For all nanocomposite samples, the tensile strength increased until a maximum value before it started to decrease. The maximum values differ for each nanocomposite. The maximum values are 1, 2 and 3 phr for PLA/FCHW (17 MPa), PLA/TFCHW (12 MPa) and PLA/CCHW (21 MPa) respectively. The highest value is PLA/CCHW nanocomposite, which increased by 91% at 3 phr compared to pure PLA. This is followed by PLA/FCHW by 54% at 1 phr and 36% increment for PLA/TFCHW at 2 phr content. However, the trend between PLA/FCHW and PLA/CCHW were different after 2 phr, whereby the tensile strength of PLA/CCHW continued to increase until it reached the maximum value at 3 phr. The tensile strength of PLA/FCHW on the other hand decreased after 2 phr.

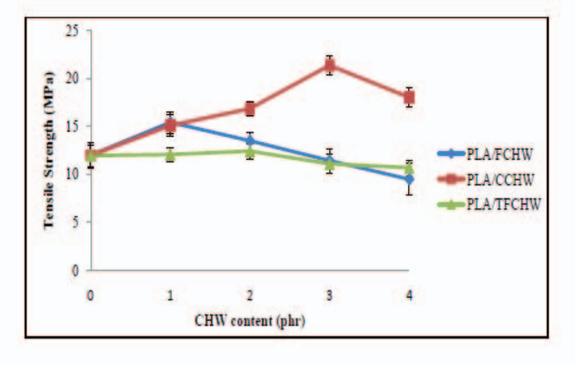

Fig. 3: Effect of FCHW, CCHW and TFCHW content on tensile strength of PLA/FCHW, PLA/CCHW and PLA/TFCHW.

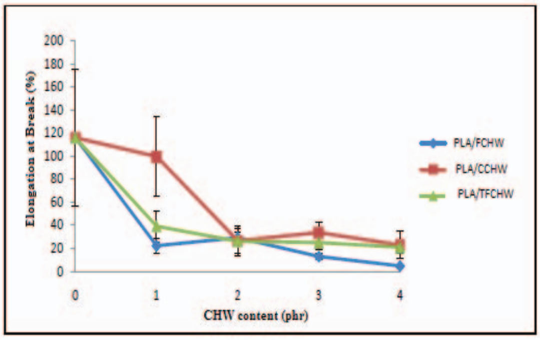

Fig. 4: Effect of FCHW, TFCHW and CCHW content on elongation at break of PLA/FCHW, PLA/TFCHW and PLA/CCHW.

The general improvement in the tensile strength of nanocomposites indicates that there is a good interfacial adhesion between the fillers (FCHW, CCHW and TFCHW) with PLA matrix leading to good stress transfer between the matrix and fillers. This is likely due to the good dispersion of fillers, stiffness of the fillers and existence of hydrogen bonding between N-H group on CHW and the lone pair of electrons on C=O of PLA matrix. In addition hydrogen bonds may also formed between terminal hydroxyl group of PLA and C=O of CHW (Fig. 6).

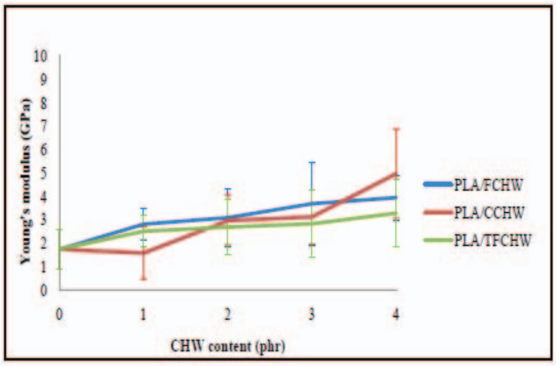

Fig.5: Effect of FCHW, TFCHW and CCHW content on Young's modulus of PLA/FCHW, PLA/TFCHW and PLA/CCHW.

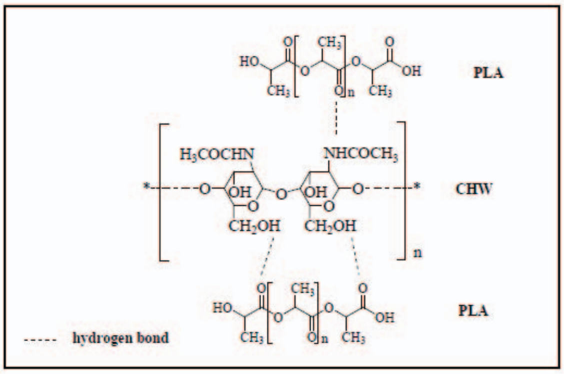

Fig. 6: Possible intermolecular interactions between PLA and CHW.

The formation of hydrogen bonding was also reported when cellulose nanowhiskers (CNW) were used as fillers in PLA nanocomposites due to the presence of polar O-H groups on CNW backbone chain [31]. Cellulose and chitin have the same molecular structure except for replacement of OH on carbon-2 with an acetyl amino (amide) group. Hence, a slightly lower intermolecular attraction between CHW with PLA is expected with CHW due to fewer amounts of OH groups on CHW.

As mentioned earlier, after the optimum filler content, the tensile strength for all nanocomposites decreased. The most likely reason is due to agglomeration among the whiskers of FCHW, CCHW and TFCHW in PLA when their content increases since hydrogen bonding between CHW-CHW molecules is more likely to form with increasing filler content. These filler-filler interactions reduce the level of filler-matrix interactions in the system. The aggregation of the filler could act as stress-centralized point and reduced surface area of interaction between filler and matrix leading in an inefficient transfer of stress from matrix to fillers resulting in low tensile strength values of PLA nanocomposites. Similar observation of reduction in strength after a certain filler content has been reported in many previous studies on PLA nanocomposites [7,32].

In terms of comparison between types of CHW from different sources, it can be concluded that CCHW had the highest increase compared to FCHW and TFCHW. CCHW is a pure chitin whereas FCHW had slight impurities of protein and minerals due to the incomplete purification of chitin during fermentation method. As for the TFCHW, it was too purified such that the polymeric chitin may have been shortened and may have affected the resulting tensile strength of the nanocomposites. Besides its poorer performance, usage of TFCHW is also not cost effective as it needed to undergo an extra chemical treatment prior to production of CHW. FCHW is a promising material for reinforcement of PLA as it does increase the tensile strength of PLA and also relatively lower cost to produce FCHW compared to CCHW since fermented chitin is a by-product of fermentation of prawn waste for the production of protein.

In Fig. 4, results of elongation at break for PLA/FCHW, PLA/TFCHW and PLA/CCHW show that the elongation at break of the nanocomposites decreased upon the addition of FCHW, TFCHW and CCHW fillers into the PLA matrix which indicates an enhancement in brittleness of the nanocomposites. It was observed that the decrease is more dramatic for PLA/FCHW and PLA/TFCHW nanocomposites at 1 phr. At 2 phr, the elongation of break values is almost similar. Overall, it can be said that PLA/FCHW nanocomposites is the most brittle with 4 % elongation at break for 4 phr fillers content. The decrease in ductility upon addition of fillers were reported previously in many studies on PLA nanocomposites [7,25]. The reason for the decrease is that stiff reinforcements of chitin nanowhiskers had probably caused substantial local stress concentrations and failure at reduced strain. The local stress concentration can be affected by volume fraction of the added reinforcement, dispersion of the reinforcement in the matrix, and interaction between the reinforcement and the matrix [33]. The other possible reason is due to the stiffening action of chitin nanowhiskers restricting the segmental chain movement of PLA.

The Young's modulus of PLA/FCHW, PLA/TFCHW and PLA/CCHW increased with increasing of FCHW, TFCHW and CCHW content respectively (Fig. 5). The increase in the modulus with increasing CHW content can be explained by increased in hydrogen bond interaction, stiffening effect and high crystallinity index of the CHW filler which are the typical characteristics of polymer/filler composites. Similar findings have been reported in the physicochemical and mechanical properties study of PLA/cellulose nanowhiskers nanocomposites [34-36].

It is noted that the modulus continue to increase with increasing filler content while the tensile strength increase to a maximum value, after which it decreased due to filler agglomeration. The continued increase in modulus can be explained by the fact that modulus is measured at low strain and weak van der Waals forces are sufficient to bond the fillers and matrix. Therefore modulus is not affected by filler agglomeration which happens at higher filler content. These weak bonds can transfer the stress between fillers and polymer; therefore showing a higher modulus at small strains[37].

The mechanical properties of nanocomposites is dependent on several factors including: i) adhesion between the PLA matrix and reinforcements, ii) stress transfer efficiency of the interface; iii) volume fraction of the fibers; iv) aspect ratio of the reinforcements; v) fiber orientation; and vi) the degree of crystallinity of the matrix [38]. The higher tensile strength of the nanocomposites compared to pure PLA can be explained based on the aspect ratio of the three CHW. All three types of the CHW possess rod-like structures or whiskers which has high aspect ratios. The high aspect ratio would increase the effectiveness of stress transfer efficiency at the interface between the matrix and the reinforcement. It is possible in cases where the adhesion is relatively poor, effective stress transfer can still occur due to high aspect ratio of the reinforcement.

3.4 Thermogravimetric Analysis

The addition of fillers into PLA could help to increase the temperature region where PLA can be used. The TGA and DTG curves reveal the weight loss of material as it is heated. Figure7(a)-(c) shows the TGA and DTG (derivative thermograms) of pure PLA and its nanocomposites with various FCHW, CCHW and TFCHW content. The TGA and

DTG curves of neat PLA and all PLA nanocomposites show a similar decomposition pattern of one-step degradation process represented by a single peak in DTG curve. It can be observed that all samples showed initial weight loss at approximately 100°C. The weight loss was a result of evaporation of moisture and was previously reported in the study of PLA-cellulose whiskers composites [5,36].

Table 2 summarized the thermal stability PLA and nanocomposites based on T_{20} and T_{max} values. T_{20} is the temperature at which 20% of the nanocomposites has decomposed while T_{max} is the temperature at which the rate of decomposition is highest. Both T_{20} and T_{max} can be used to determine the thermal stability of the nanocomposites. Interestingly based on T_{20} and T_{max}, thermal stability of PLA nanocomposites for all types of CHW were seen to be significantly higher than pure PLA. Based on T_{20} values, all the three nanocomposites have almost similar values with PLA/TFCHW at 3phr being the highest at 355°C, which is 15 degrees higher than PLA. This can be considered a significant improvement due to the incorporation of CHW and is effective in enhancing the thermal stability. PLA/FCHW and PLA/CCHW havesimilarhighest values at 353°C, which is slightly lower than PLA/TFCHW.

Meanwhile for T_{max}, the highest was obtained at 371^{o}C by PLA/FCHW4, 13 degrees higher than pure PLA which is also quite significant. For the CCHW, the maximum values are slightly lower at 367^{o}C and T_{max} reaching maximum values at 3 phr CHW content. However, the maximum values for PLA/TFCHW occurred at 1phr CHW content.

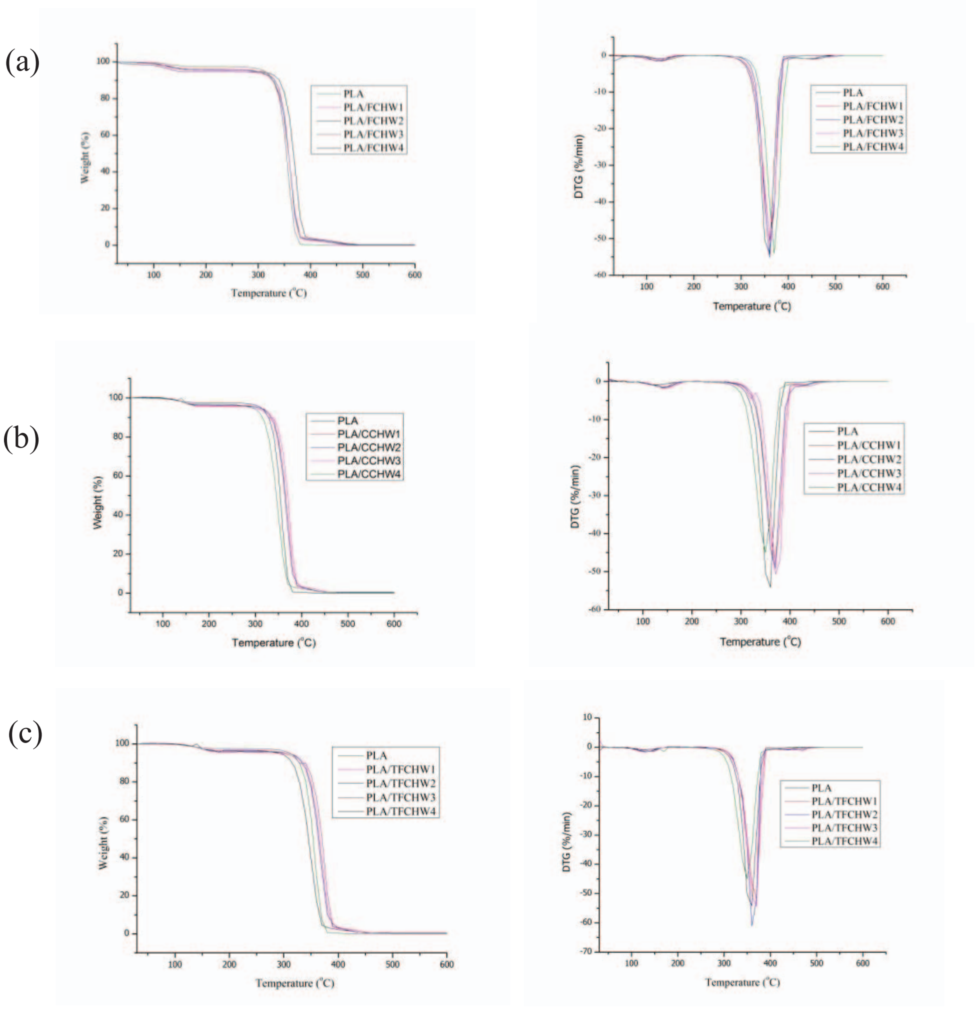

Fig.7: TGA and DTG curve of a) PLA/FCHW, b) PLA/CCHW and c) PLA/TFCHW.

From the TGA of PLA and the PLA/CHW nanocomposites, it can be concluded that all the three CHW types are effective in enhancing thermal stability of PLA nanocomposites. This improvement can be due to the good physical interaction between the PLA and CHW.

Beside that, the improvement in thermal stability could also be attributed to the uniform dispersion of the CHW in PLA matrices resulting in an increase in tortuous path for the [39-40] transfer-outmigration of degraded volatiles to the surface, thus retarding the decomposition rate [41]. Previous studies on cellulose/MMT nanocomposites also reported similar results [41-43]. From the overall results, it is difficult to conclude which type of CHW is the most effective in enhancing the thermal stability of PLA/CHW nanocomposites. It can however be said that the CHW from the fermented chitin are not inferior compared to the CHW from commercial chitin.

Table 2:Effectof CHW on thermal stability of PLA nanocomposites

Formulation	**Degradation temperature (°C)**	
	T_{20}	T_{max}
PLA	340	358
PLA/FCHW1	342	363
PLA/FCHW2	345	362
PLA/FCHW3	342	362
PLA/FCHW4	353	371
PLA/CCHW1	348	363
PLA/CCHW2	347	359
PLA/CCHW3	353	367
PLA/CCHW4	328	360
PLA/TFCHW1	353	367
PLA/TFCHW2	315	363
PLA/TFCHW3	355	365
PLA/TFCHW4	341	366

3.5 Biodegradability and Water Absorption Properties

An increase in biodegradability and mechanical strength at lower cost are advantage for the application of PLA/CHW as packaging materials. The effects of CHW source and content on biodegradability and water absorption properties of PLA/CHW nanocomposites are discussed together in this section since both properties are interrelated.The biodegradability of PLA, PLA/FCHW, PLA/CCHW and PLATFCHW were conducted using soil burial test. The weight loss of PLA, PLA/FCHW, PLA/CCHW and PLA/TFCHW were collected for duration ranging from 14 to 56 days and are shown in Table 3.

It can be seen that the biodegradability as indicated by the weight loss of all nanocomposites samples were higher than pure PLA at all durations. This is attributed to the presence of chitin materials on the surface of the samples which attract the microorganisms such as fungi to consume this material as nutrient source. It was also noted that prolonging the burial time lead to higher weight loss, which is as expected. Pure PLA hardly showed any weight loss after 14 days unlike the nanocomposites which had started to show some weight loss, especially PLA/CCHW and PLA/TFCHW. It was reported that the degradation of pure PLA in soil is slow and it takes a long time for degradation to start, probably because of the low temperature and water content and the relative scarcity of PLA degrading organisms [44]. However, in a composting environment, the pure PLA is able to be hydrolyzed into smaller molecules after 45-60 days at 50-60°C.

It was also observed that biodegradability increased with increasing in the filler content for all types of nanocomposites. The highest weight loss was recorded at 4 phr CHW content for all types of nanocomposites with PLA/CCHW4 having the highest at 3.29% and PLA/FCHW4 the lowest at 2.28%. The increasing CHW content will increase chances for chitinolytic microorganismsto consume the CHW as well as increasingthe interaction of CHW with water, thus increasing the biodegradation process. Therefore the ability of water to diffuse into the polymer matrix has a strong influence on the rate of degradation of PLA [45]. The degradation occurs by firstly water being diffused into the material followed by hydrolysis of C-O ester bonds and lowering of molecular weight. Rates of hydrolysis increase with water content and temperature and are catalyzed by free carboxyl groups of the hydrolyzed PLA ends. Hydrolysis occurred faster in the interior of a thick sample since carboxylic acid concentration is higher than the exterior due to leaching of the acidic PLA oligomers into the surrounding aqueous medium [46].

Table 3:Water absorption of PLA nanocomposites (%)

Formulation	**Water Absorption (%)**	
	2 Hours	**24 Hours**
PLA	0.00 ± 0.09	0.30 ± 0.09
PLA/FCHW1	1.90 ± 0.10	3.03 ± 0.09
PLA/FCHW2	3.40 ± 0.10	3.59 ± 0.03
PLA/FCHW3	3.60 ± 0.10	3.74 ± 0.07
PLA/FCHW4	4.70 ± 0.64	5.86 ± 0.18
PL/CCHW1	2.00 ± 0.10	2.97 ± 0.05
PLA/CCHW2	3.17 ± 0.15	3.20 ± 0.12
PLA/CCHW3	4.04 ± 0.25	4.84 ± 0.27
PLA/CCHW4	7.07 ± 0.52	9.35 ± 0.37
PLA/TFCHW1	1.38 ± 0.06	1.94 ± 0.07
PLA/TFCHW2	2.27 ± 0.10	2.68 ± 0.02
PLA/TFCHW3	2.51 ± 0.03	2.73 ± 0.03
PLA/TFCHW4	2.77 ± 0.11	5.15 ± 0.24

In a study by Rosdi and Zakaria [48] on the effect of chitin particles on degradation of PLA by soil burial test for duration of 10 weeks showed weight losses of 7.5% at 56 days which is higher compared to using CHW from the present study. However the study showed that addition of chitin particles did not improve the mechanical properties of PLA [47] as compared to the increase of strength with the incorporation CHW in the present study.

From the soil burial test, it can be concluded CCHW is more effective than FCHW in promoting the degradation of PLA but not significantly higher. The plausible reason is the purity of CCHW as compared to FCHW which was derived from fermented chitin. In the previous study on PLA and PLA/cellulose nanowhiskers from oil palm empty fruit bunch, it was also found that the incorporation CNW promotes the biodegradability of PLA [36]. For 5 phr of CNW, the weight loss after 56 days of soil burial is 2.1% which is less than PLA/CCHW4 reported in this study which is 3.3%. Overall it can be concluded that CHW has the potential to degrade PLA faster compared to cellulose nanowhiskers.

The water absorption of PLA, PLA/FCHW, PLA/CCHW and PLA/TFCHW after 2h and 24h immersion in distilled water at ambient temperature are shown in Table 4. As expected, amount of water absorption increased with time for PLA and all PLA/CHW nanocomposites. It was also observed that the amount of water absorption increased with increasing filler content for all types of CHW. Similar to the biodegradability results, PLA/CCHW again showed the highest water absorption at 9.35% after 24h which is around 80% higher than PLA/FCHW and PLA/TFCHW.

Materials with higher water absorptivity displayed better biodegradability mainly due to the fact that hydrophilic material will allow micro-organism to penetrate into the material, further accelerate the breakdown of polymer matrix and increased the degradation process [27]. Higher water absorption will also enable micro-organisms such as fungi and bacteria to use the CHW as their nutrient source. From both studies, it can be seen the higher the water absorption the faster the biodegradation of the composites. Comparing the PLA/CCHW and PLA/FCHW provides new knowledge on their potential as biodegradable packaging materials.

Table 4: Weight loss of PLA nanocomposites (%)

Formulation	**Weight Loss (%)**			
	14 Days	**28 Days**	**42 Days**	**56 Days**
PLA	0.02 ± 0.01	0.267 ± 0.01	0.34 ± 0.01	0.88 ± 0.02
PLA/FCHW1	0.05 ± 0.03	0.337 ± 0.03	0.838 ± 0.03	1.47 ± 0.02
PLA/FCHW2	0.36 ± 0.01	0.783 ± 0.01	1.375 ± 0.06	1.67 ± 0.03
PLA/FCHW3	0.42 ± 0.06	0.955 ± 0.06	1.61 ± 0.05	1.98 ± 0.03
PLA/FCHW4	0.44 ± 0.01	1.32 ± 0.02	1.87 ± 0.03	2.28 ± 0.03
PLA/CCHW1	0.87 ± 0.02	1.10 ± 0.02	1.44 ± 0.02	1.77 ± 0.03
PLA/CCHW2	1.15 ± 0.02	1.33 ± 0.02	2.13 ± 0.03	2.57 ± 0.10
PLA/CCHW3	1.48 ± 0.01	1.67 ± 0.03	2.34 ± 0.01	2.85 ± 0.02
PLA/CCHW4	1.83 ± 0.02	2.09 ± 0.09	2.77 ± 0.03	3.29 ± 0.01
PLA/TFCHW1	0.88 ± 0.02	1.17 ± 0.01	1.54 ± 0.02	1.85 ± 0.03
PLA/TFCHW2	1.33 ± 0.02	1.33 ± 0.01	1.75 ± 0.02	2.07 ± 0.07
PLA/TFCHW3	1.48 ± 0.02	1.88 ± 0.02	2.02 ± 0.01	2.30 ± 0.05
PLA/TFCHW4	1.77 ± 0.03	2.36 ± 0.06	2.75 ± 0.05	2.89 ±0.01

4. CONCLUSION

The objective of this study is tocompare the properties PLA/CHW nanocomposites in which the source of CHW are different, which are commercial chitin and fermented chitin. Tensile strength for all nanocomposites increased with increasing filler content until it reached a certain maximum value while Young's modulus increased with increasing filler content. However, elongation at break decreased with increasing filler content for all types of nanocomposites. TGA results indicated that the all nanocomposites displayed better thermal stability as compared to pure PLA. The addition of FCHW, CCHW and TFCHW into PLA improved the biodegradability of PLA. The water absorption of all nanocomposites also increased with increasing filler content.The overall results confirm that PLA nanocomposites from FC are not inferior than PLA nanocomposites from CC and therefore has similar potential to be developed into eco-friendly packaging materials. The future areas of investigation are to further improve the mechanical properties. The ductility can be improved by using plasticisers and hybridization with other nanofillers such as graphene will help to enhance the modulus and strength.

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