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RESEARCH ARTICLE | SEPTEMBER 21 2020

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AIP Conference Proceedings 2267, 020002 (2020)
https://doi.org/10.1063/5.0016532

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Processing, Tensile and Morphological Characteristics of Polylactic acid/ Chitosan Biocomposites Prepared by Melt Compounding Technique

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Abstract. Biodegradable polymers of polylactic acid (PLA) and chitosan (Cs) has a great potential as alternative candidates to replace conventional synthetic plastic apart to reduce the plastic waste pollution due to the unique properties of superior mechanical strength, feasible processability and rapid degradation. In this work, PLA/Cs biocomposites were prepared via melt compounding and compression moulding techniques in the absence of any plasticizer and additive. The effect of chitosan loading (2.5, 5, 7.5, 10 php) on processing, tensile and morphological characteristics of PLA/Cs were evaluated using internal mixer, universal testing machine and field emission scanning electron microscopy (FESEM), respectively. Processing characteristic indicates PLA/Cs biocomposites demonstrated higher processing torque in comparison to neat PLA due to the increase in melt viscosity and decrease in chain mobility of the polymeric materials. Tensile test results revealed that the maximum strength (54.60 ± 0.51 MPa) and tensile elastic modulus (2.67 ± 0.01 GPa) was attained by PLA/2.5Cs biocomposite. In fact, the addition of chitosan content up to 10 php results in significant decreased in tensile strength and elongation at break of 23.38 ± 0.37 MPa and 0.96 ± 0.04 %, respectively. This is supported by the electron micrograph observation of the PLA/2.5Cs tensile fractured surfaces that exhibits uniform dispersion and good interfacial adhesion between chitosan and PLA matrix which signifies higher tensile properties. However, more agglomeration and poor filler-matrix interaction was observed with further addition of chitosan content of above 7.5 php which implies deterioration in tensile properties. The results suggest that the incorporation of low chitosan loading improve the processing, tensile and polymer compatibility in PLA/Cs biocomposites.

1. INTRODUCTION

In recent years, bio-based polymers have raised a major interest among academics and industrial researchers due to the environmental concerns associated by petrochemical-based polymers. Polyhydroxyalkanoate (PHA), polylactic acid (PLA) and polycaprolactone (PCL) are among of biodegradable polymers which are derived from microorganism, conventionally synthesized from bio-derived and synthetic monomers, respectively. Among these, PLA has generated great interest as a substitute for petroleum-based plastic materials due to its remarkable properties. PLA is made up from a linear aliphatic thermoplastic polyester which exist either in amorphous or semi-crystalline state [1]. It is derived from lactic acid monomers which is acquired through the fermentation process of agricultural resources (eg: corn, sugarcane, potato, cassava) [2] and further synthesized either by direct condensation or ring-opening polymerization of lactic acid monomers [3].

3rd International Postgraduate Conference on Materials, Minerals & Polymer (MAMIP) 2019
AIP Conf. Proc. 2267, 020002-1–020002-9; https://doi.org/10.1063/5.0016532
Published by AIP Publishing. 978-0-7354-2030-4/$30.00

PLA exhibits superior mechanical strength, transparency, biodegradable and biocompatibility [4-5]. Due to the comparable properties to most petroleum-based materials, it has been applied in various applications involving food packaging (drinking bottles, food wrapping, food containers), automotive (3D printing, spare parts) and medical (wound dressing, drug delivery device, scaffold) fields [6]. However, PLA has few drawbacks which limit or restrict it usage in the wider range of application in terms of poor thermal stability and barrier properties apart poses significant embrittlement characteristics [7]. Thus, incorporating of PLA with the other natural polymers [8] possibly could provide a good strategy in order to reduce those attribute negative properties since a wide range of desirable properties could be obtained.

Chitosan (Cs) is a cationic polysaccharide that is chemically synthesized by partial alkaline deacetylation of chitin which is extracted from the cell wall of fungi or exoskeleton of crustaceans and arthropods [1]. It imparts the characteristics such as renewable, non-toxic, edible, biodegradable, biocompatible, antimicrobial and antifungal ability [9] attributed by the occurrence of amino group at C2 position which contribute an efficient usage in countless application especially in food packaging. This was due to it has been claimed as generally recognized as safe (GRAS) category under U.S Food and Drug Administration (FDA) apart has capability to preserve and prolong the shelf life of foodstuff such as fruit, vegetables, meat and seafood [7]. It fact, chitosan-based films exhibit faster degradation rates with significant weight loss after 150 days of soil burial [10]. Thus, this could be an impressive substitute to petroleum-based synthetic products which requires hundred or thousand years to be decomposed. Hence, incorporating chitosan with PLA could be an ideal combination in polymer system in order to accomplish the aforementioned applications.

To date, various preparation method such as solution casting, extrusion, electrospinning and melt compounding has been applied to prepare composite, film or mat. Among these, melt blending is a favourable processing technique with acceptable mechanical properties and environmentally friendly as compared to a conventional processing techniques. Apart from industrially oriented, melt blending offers the capability to tune the properties by manipulating the processing conditions during blending process. Based on the literature of the previous studies, melt blend of PLA with functionalized chitosan grafted with oligo(L-lactic acid) (Cs-g-OLLA) demonstrated uniform dispersion of spherical aggregates and reduction in oxygen permeability up to ~10 folds [11]. In addition, the melt blend of PLA and tributyl o-acetyl citrate (ATBC) promotes the reduction in brittleness of PLA. However, lower tensile strength and tensile modulus was exhibited by the plasticized PLA/Cs composites [12].

Thus, the aim of this present study is to investigate the feasibility of PLA/Cs biocomposites fabricated through melt blending method in the absence of any plasticizer or additive. The effect of chitosan loading on the processing, tensile and morphological properties of the resulting biocomposites were evaluated as well. In fact, a few studies have been performed on mechanical and physical properties of the compatibilized PLA/Cs biocomposites using solution casting technique [13-15]. However, limited work has been reported on the blending of PLA/Cs via melt compounding technique which are industrially oriented.

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2. EXPERIMENTAL

2.1. Materials

Polylactic acid (PLA) resin of 4032D type used in this study was supplied by NatureWorks LLC (USA) with specific gravity of 1.24, high molecular weight and melt mass flow rate (MFR) of 7 g/10 min at 210°C/2.16 kg. Chitosan (Cs) powder with a degree of deacetylation of 90.5%, molecular weight of >700 kDa, a viscosity of 62 cPs, was purchased from Cleo International Trading (Shanghai) and was used as a filler.

2.2. Preparation of Biocomposites

Melt compounding of PLA at different chitosan loading was conducted in a Thermo Haake internal mixer (Model R600/610) operated at processing temperature of 180°C and 60 rpm of rotor speed for 10 minutes. The PLA/Cs biocomposite compositions were designated as follows: PLA/2.5Cs, PLA/5Cs, PLA/7.5Cs and PLA/10Cs which represents 2.5, 5, 7.5 and 10 parts per hundred parts of polymer (php) of chitosan loading in PLA matrix, respectively. Due to hygroscopic nature, both PLA and chitosan were dried in vacuum oven overnight at 60°C and 105°C, respectively in order to remove moisture before use. The PLA resin was first added into the mixing chamber followed by chitosan addition after three minutes of mixing. The process then was continued until completion of 10 minutes

mixing time. Once the melted samples were obtained, the dumbbell sheet (ASTM D638) of neat PLA and various PLA/Cs biocomposites were fabricated using hot press compression molding machine (Model RT-7014A) with a hydraulic press at pressure of 1000 psi at 180°C for three minutes. The same conditions were applied for preparation of neat PLA sample which was used as a reference.

2.3. Investigation Methods

2.3.1. Melt processing on compounding

Processing behaviour of the PLA/Cs biocomposites were assessed by observing the curves of torque against mixing time recorded during compounding process performed on the Thermo Haake internal mixer (Model R600/610) operated at temperature of 180°C, for 10 minutes and 60 rpm as mentioned previously. The melt viscosity index, η was estimated as the ratio between processing torque to the rotor speed which was recorded in Nm/rpm.

2.3.2. Tensile properties

The tensile strength, tensile modulus and elongation at break were assessed according to ASTM D638 of approximately 1 mm thickness of the prepared dumbbell specimens. Universal testing machine, Instron (Model 3366) with 1 kN load cell was operated at a crosshead speed of 5 mm/ min. The average value of at least five samples for each composition was reported.

2.3.3. Morphology characteristics

The microstructure of the chitosan powder and tensile fracture surface of neat PLA and PLA/Cs biocomposites were observed under field emission scanning microscope (FESEM) (Model Supra 35-Zeiss VP). The samples were mounted onto aluminium stubs, sputter coated with a gold thin layer and was observed under 10 kV accelerating voltage. The morphological characteristics of the tensile fracture surface of the samples were examined at 100x magnification.

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3. RESULTS AND DISCUSSION

3.1. Processing Torque

Figure 1 illustrates the processing torque variation with respect to mixing time of the melted pure PLA and PLA/Cs biocomposites at various chitosan loadings. Similar trends of processing torque were exhibited by PLA-based biocomposites. It can be observed that upon PLA addition, the torque increased sharply at initial processing time due to higher shear force applied in order to rotate the rotors. At this stage, the gelation process occurred which involve the process of compaction, densification, fusion and elongation of the polymer [16]. After one minute, the torque begins to decrease drastically due to the melting of PLA hence promotes to the reduction in melt viscosity. Similar finding was reported by Zaaba and Ismail [17] who observed a reduction in mixing torque at initial melt processing stage of peanut shell powder-filled polylactic acid/thermoplastic corn starch biocomposites. In comparison to neat PLA, torque of PLA/Cs biocomposites showed slightly higher, due to decrease in chain mobility. This can be explained by the increment in melt viscosity upon chitosan incorporation after three minutes of mixing time, leading to higher resistance of macro molecule mobility in the melted PLA. Thus, greater shear force was required which contributes to the higher processing torque. This is in agreement with the study reported by Tee *et al.* [16] who found greater rotational force was needed as more epoxidized palm oil (EPO) and epoxidized soybean oil (ESO) were introduced into the mixing chamber containing PLA resins. The torque then reaches a constant value after seven minutes of processing which indicates the complete melting of PLA and attains full homogenization between PLA

and chitosan. This stage also known as stabilization torque which is illustrated in Figure 2. As can be seen, the higher the chitosan amount loaded into PLA, the higher was the stabilization torque as the torque increase from 0.4 Nm to 0.8 Nm with the addition of 2.5 php and 10 php of chitosan, respectively. This consequently increase the melt viscosity index of PLA/Cs samples, thus lowering its processability. However, the incorporation of chitosan does not significantly affect the processing torque due to nature of the filler as very fine chitosan particles was added. Similar findings were obtained by Al-Saleh *et al.* [18] as the increase in carbon nanofiller loadings showed insignificant increase in mixing torque.

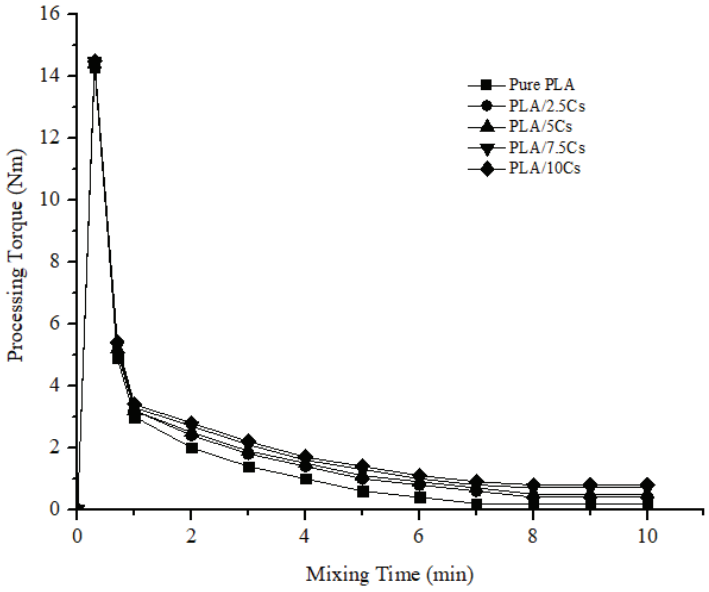

FIGURE 1. Processing torque time curve of PLA-based biocomposites at 180° C and 60 rpm

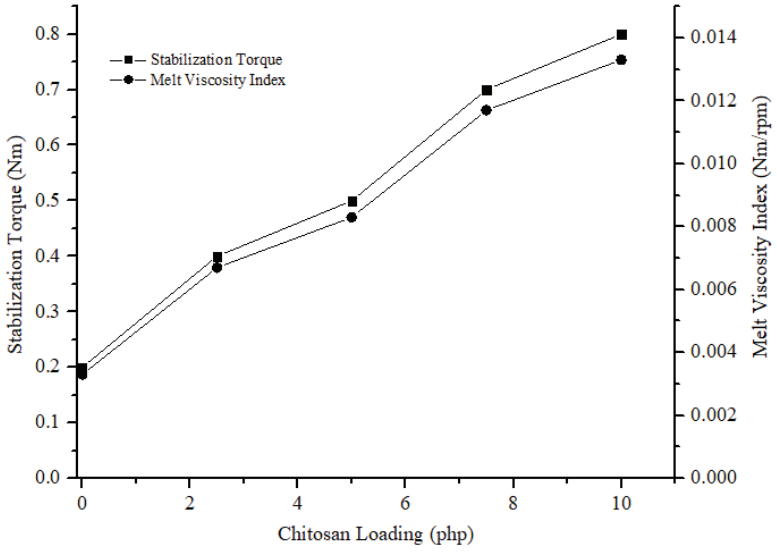

FIGURE 2. Stabilization torque and melt viscosity index (η) at various chitosan loadings of PLA-based biocomposites

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3.2. Tensile Properties

In this section, the effect of chitosan loadings on the tensile characteristics of PLA/Cs biocomposites were investigated. Figure 3 presents the tensile strength of PLA-based biocomposites as a function of chitosan content. There was a slightly increased (~2%) in tensile strength by the incorporation of 2.5 php chitosan loading in comparison to neat PLA. However, it decreased drastically with further addition of chitosan content up to 10 php. This indicates 2.5 php is the optimum concentration for this system which was attributed by a better filler dispersion and strong interfacial adhesion between chitosan particles and PLA matrix. This result was supported by morphological study that will be discussed in the next section. In fact, the addition of the chitosan could strengthen the hydrogen bonding in the materials due to the presence of hydroxyl groups, thus improve the tensile properties [19]. Nonetheless, higher filler content could promote to the flaws or failure on the prepared biocomposite. This could be due to the agglomeration of chitosan which arise internal stress concentration within the PLA matrix, thus reduces the tensile strength. Another study reported by Bonilla *et al.* [20] explained the reduction in tensile strength at higher filler content is caused by the incompatibility between polymeric materials of PLA and its filler, thus generate poor filler-matrix interaction and discontinuities in the PLA matrix. This consequently reduced the intermolecular forces in the matrix, and hence contributes to the biocomposite failure.

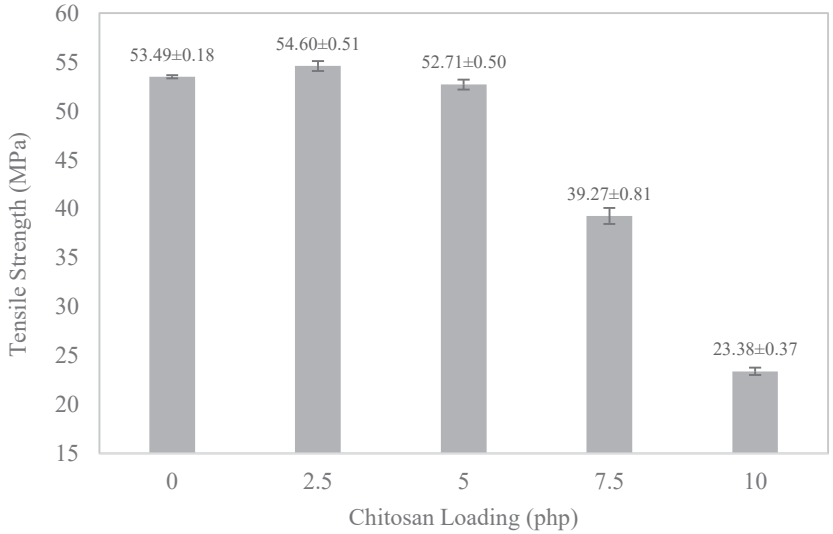

FIGURE 3. Tensile strength of PLA-based biocomposites at various chitosan loadings

The effect of chitosan loadings on tensile modulus is shown in Figure 4. From the figure, all PLA/Cs biocomposites demonstrated higher tensile modulus with respect to neat PLA with approximately ~14% increment in the PLA/2.5Cs biocomposite. This was due to the addition of chitosan could results in the formation of partially separated microspaces during the tensile loading, and hence restrict the chain mobility of the PLA which consequently increase the stiffness. Similar finding was reported by Fathima *et al.* [21] in polylactic acid/nanochitosan composite films. However, slightly decreased in tensile modulus at 10 php filler loading was due to chitosan agglomeration and thus promotes weak interfacial adhesion at the Cs-PLA interface. This claim is further confirmed by the micrograph image that will be discussed in the next section.

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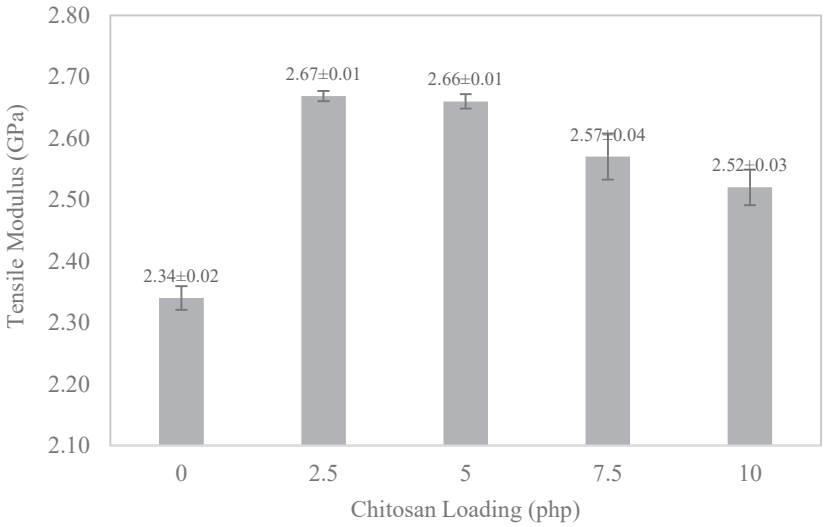

FIGURE 4. Tensile modulus of PLA-based biocomposites at various chitosan loadings

Figure 5 illustrates the elongation at break of PLA/Cs biocomposites at various chitosan loadings. As can be seen, there was a gradual decreased in the elongation at break with an increased in filler content. This may be caused by the stiffening action of the chitosan which hinders the chain mobility of the PLA during tensile testing, thus increase stretching resistance upon strain application, and hence lowering the elongation at break. Similar finding was observed by Mohd Nor and Othman [22] who found the reduction in elongation at break as the loading of palygorskite (PAL) increased in natural rubber nanocomposites. Thus, appropriate volume fraction of chitosan should be identified as it could affect the percentage of elongation at break and hence the film extensibility.

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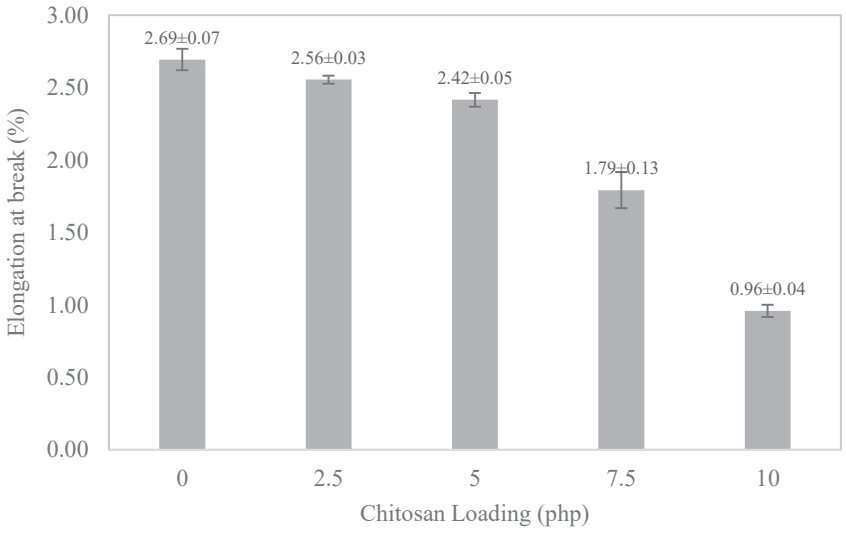

FIGURE 5. Elongation at break of PLA-based biocomposites at various chitosan loadings

3.3. Morphology

Figure 6 exhibits the SEM micrograph of the pure chitosan, pure PLA and the prepared PLA/Cs biocomposites which was observed under 100x magnification. Pure PLA (Fig. 6a) exhibited homogeneous and smooth fractured surface while rough and irregularities surface with particle size in range of ~16-72 µm was observed for pure chitosan (Fig 6b). The fractured surface of PLA/Cs biocomposites are illustrated in Figure 6(c-f). As shown in Fig. 6(c), PLA/2.5Cs demonstrated the presence of tearing effect on the surface resulted from the biocomposites fractured during tensile testing. This was associated by a strong intermolecular interaction generated between these two polymeric materials thus contributed to the higher tensile properties. However, less tearing was presence by further addition of chitosan content. In fact, through the morphological image, it was observed a uniform dispersion and well embedded of chitosan particles in the PLA matrix upon chitosan incorporation of up to 5 php (Fig. 6d). The results indicated that at this filler loading, the chitosan was well blended in the matrix and are compatible, thus increase the miscibility between Cs-PLA polymers and hence improve the tensile properties. However, at higher chitosan loading of above 7.5 php, the SEM image showed greater surface roughness, more cavities and poor filler distribution due to the excess of chitosan in the PLA matrix. This suggests that exceeding the optimal loading, chitosan could agglomerate which consequently results in the pulled out and dislodged of chitosan particles from the matrix. This is evident through the formation of micro-voids, micro-gaps and micro-cracks in the fractured surface (Fig. 6e-f) which ascribed by poor interfacial adhesion at the Cs-PLA interface. This is in agreement with Claro *et al*. [23] who found poor chitosan dispersion at higher filler proportion in a PLA/chitosan prepared by twin-screw extruder method. The result implies to the lower tensile properties at higher chitosan loading. Similar finding was reported by Azlinda *et al.* [24] who found increasing the banana fibers content promoted weaker strength of the composite due to presence of more cavities in the polymer matrix.

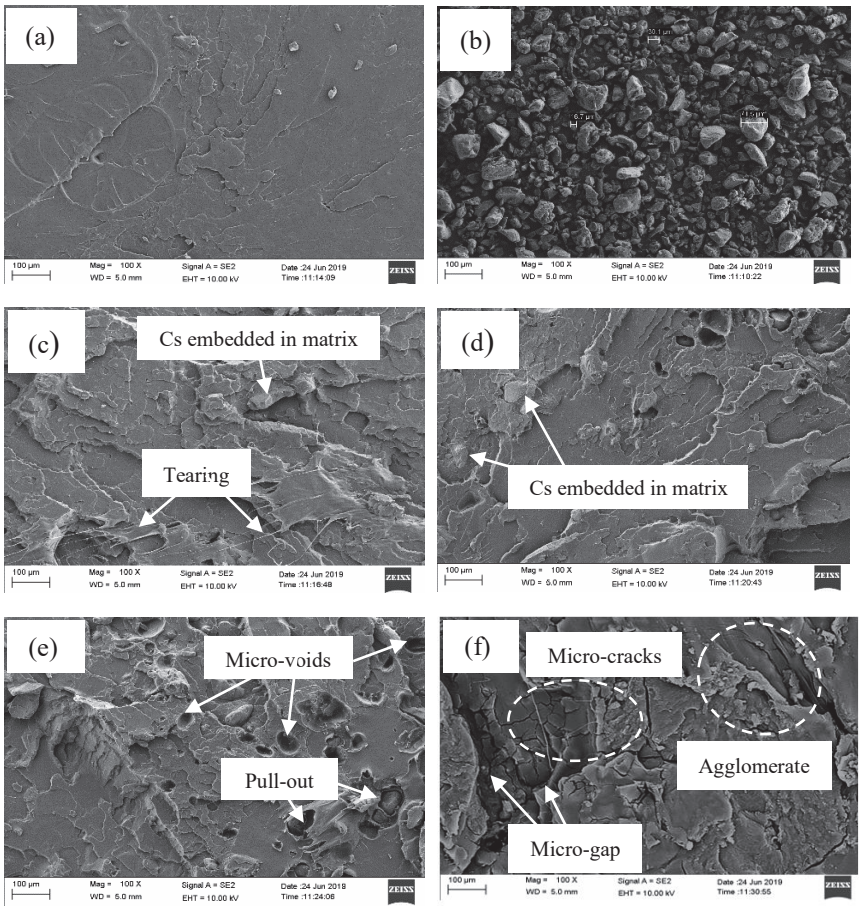

FIGURE 6. SEM images of (a) Pure PLA, (b) Pure chitosan, (c) PLA/2.5Cs, (d) PLA/5Cs, (e) PLA/7.5Cs, (f) PLA/10Cs biocomposite under 100x magnification

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CONCLUSION

PLA/Cs biocomposites were successfully fabricated using melt compounding technique by incorporating 2.5, 5, 7.5 and 10 php of chitosan. The processing torque data revealed that PLA/Cs biocomposites demonstrated higher processing torque as compared to the neat PLA due to the higher melt viscosity in polymeric material. Tensile data indicated that PLA/2.5Cs presents the optimum results; tensile strength and tensile modulus improved by 2% and 14%, respectively in comparison to neat PLA due to strong interfacial adhesion and good miscibility between chitosan and PLA polymers. However, at higher filler loading, the tensile properties were significantly dropped due to the chitosan agglomeration. SEM fracture surface exhibited higher surface roughness and more cavities with chitosan incorporation of above 7.5 php, which attributed by poor interaction at filler-matrix interface. The results suggest that the incorporation of low chitosan loading improve the processing, tensile and polymer compatibility in PLA/Cs biocomposites.

ACKNOWLEDGEMENT

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1/2018/STG01/UNIMAP/03/3 from the Ministry of Education Malaysia.

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