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THE EFFECT OF NANOFILLERS ON THE FUNCTIONAL PROPERTIES OF PLA AND CHITOSAN BASED FILM

(Kesan Pengisian Nano Kepada Sifat Filem yang Berasaskan Asid Polilatik dan Kitosan)

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Abstract

The aim of this study was to develop poly (lactic acid) and chitosan-based films and to examine the effect of cellulose nanocrystal (CNC) as nanofillers on the properties of the films. The biofilms were prepared by solvent casting method. The physical and mechanical properties of the resulting films were examined. SEM analysis showed that the surface of PLA/Cs films smoother when 1% and 2 % of CNC were added. The results for percent of water absorption of the films increased with increasing amount of CNC in PLA/Chitosan matrix. Tensile test results indicated higher TS value by incorporation of 2% of CNC. However, the PLA/Chitosan-CNC films at 3% and 4% CNC concentration exhibited a decreased TS value. PLA/Chitosan films were improved with the addition of a small amount of CNC resulting in PLA nanocomposite, which will be further evaluated for fruit packaging applications. The data obtained through this research could contribute to the establishment of a biofilms with improved the physical and mechanical properties promising significant advantages in term of longer storage life, maintaining safety, and keeping quality of a product especially in fruit packaging.

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Keywords: polylactic acid, chitosan, cellulose nanocrystal, films, packaging

Abstrak

Tujuan kajian ini adalah untuk membuat filem berasaskan poli (asid laktik) dan kitosan dan mengkaji kesan kristal nano selulosa (CNC) sebagai pengisi nano pada sifat filem. Biofilm tersebut disiapkan dengan kaedah tuangan pelarut. Sifat fizikal dan mekanikal filem yang dihasilkan diperiksa. Analisis SEM menunjukkan bahawa permukaan filem PLA/Cs lebih licin apabila 1% dan 2 % CNC ditambah.Selanjutnya, peratus penyerapan air filem meningkat dengan peningkatan jumlah CNC dalam matriks PLA/ kitosan. Hasil ujian tegangan menunjukkan nilai TS yang lebih tinggi dengan memasukkan 2% CNC. Walau bagaimanapun, filem PLA / Chitosan-CNC pada kepekatan CNC 3% dan 4% menunjukkan penurunan nilai TS. Filem PLA / kitosan ditambah baik

dengan penambahan sejumlah kecil CNC yang menghasilkan nanokomposit PLA, yang akan dinilai lebih lanjut untuk aplikasi pembungkusan buah. Data yang diperoleh melalui penyelidikan ini dapat menyumbang pada pembentukan biofilm dengan peningkatan sifat sifat fizikal dan mekanikal yang lebih baik yang menjanjikan kelebihan yang ketara dari segi jangka hayat penyimpanan yang lebih lama, mengekalkan keselamatan, dan mengekalkan kualiti produk terutamanya dalam pembungkusan buah-buahan

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Kata kunci: asid polilaktik, kitosan, selulosa nanokristal, filem, pembungkusan

Introduction

The primary function of food packaging is to preserve the quality and safety of food products during storage and transportation, as well as to extend the shelf-life of food products by preventing undesirable factors such as spoilage microorganisms, chemical contaminants, oxygen, moisture, light, or external force. Many foods packaging currently on the market are made of synthetic polymers that were produced from fossil fuels. This is due to their high mechanical and barrier qualities, as well as their ease of processing and low price. However, there are some disadvantages to this type of material: it requires a lot of energy to recycle, and if it is not properly disposed of, this could pose a risk to the environment because it does not decompose or decomposes slowly in landfills or in the environment, releasing polluting substances. People are currently dealing with rapid climate change as well as the issue of waste disposal that comes with it. As a result, avoiding petroleum-based non-biodegradable polymers such polyethylene (PE), low-density polyethylene (LDPE), and high-density polyethylene (HDPE), as well as polypropylene (PP), which are commonly used in food packaging, is necessary. In recent years, there has been a lot of interest in developing more environmentally acceptable alternatives to the plastics that are currently utilized in the packaging sector. Many natural biopolymer materials, such as chitosan, cellulose, hemicellulose, lignin, pectin, starch, agar, *Eucommia ulmoides* gum, and natural rubbers, have been widely employed to manufacture biodegradable food packaging materials due to their environmentally friendly and biodegradable characteristics.

Chitosan

A chitosan (Cs)-based film has been chosen as an innovative film-forming content. The polysaccharide chitosan is the second most abundant in nature. It has been demonstrated to be biodegradable, non-toxic, biocompatible, and useful [1]. Chitosan is a linear polysaccharide and biodegradable copolymer made up of N-acetyl glucosamine and D-glucosamine. Chitosan is formed by chitin deacetylation, which has the structural element of crustacean exoskeleton, such as crabs and shrimps [2]. Chitosan is a deacetylated product of chitin ß-(1-4)-2-acetamido-2-deoxy-D-glucan. Chitosan has similar characteristics with chitin as the most stable anti-acid and alkali substances, and this portion is also not soluble in ordinary solvents. Most interestingly, it is microbial resistant due to its positively charged amino group, which interacts with negatively charged microbial cell membranes, causing proteinaceous and other intracellular constituents of the microorganisms to leak out [3].

However, the disadvantage of using chitosan-based film is its high cost, which makes it unsuitable for fruit packaging. As a result, it is proposed that chitosan be combined with other biopolymer to form a film in order to produce active fruit packaging [4]. Polylactic acid was chosen to combine with chitosan due to its excellent mechanical properties, which include low flammability, low moisture reversion value, low refraction index, and high UV safety index.

Polylactic acid

Polymers such as polylactic acid (PLA) have attracted the attentions of researchers due to their high strength and modulus. PLA has a proven ability either to substitute traditional petrochemical-based polymers for industrial applications or as a leading biomaterial for a wide range of applications in medicine [5][6]. PLA comes from renewable plant sources, such as starch and sugar. Degradation of PLA can be accomplished by hydrolysis of ester bonds without the need for enzymatic procedure. The use of PLA as food packaging polymer for short shelf-life products with popular applications is growing. In addition, PLA is safe and GRAS is widely

accepted as safe for use in food packages. Indeed, PLA has been known to be ideal for packaging orange juice, yoghurt and dressings [7]. Polylactic acid is a hydrophobic polymer that belongs to a class of biomaterials usually referred to as poly-a-hydroxy acids, poly-a-esters or aliphatic polyesters. It is synthesised from lactic acid (LA; 2 hydroxypropanoic acid) which is a water-soluble monomer with two enantiomeric forms, namely L-(+)-LA and D-(-)-LA. The drawbacks of PLA as it has poor thermal stability, low water vapour or gas barrier properties and inherent brittleness. In order to achieve the films as bioplastics, a filler must be added to improves the mechanical and physical properties of a film.

Cellulose nanocrystal

Cellulose nanocrystal (CNC) has sparked great attention as a potential nano-reinforcement for chitosan films due to its sustainability, abundance, high surface area to volume ratio, lightness, and high mechanical strength among the numerous nanofillers [8]. CNC is a nanometer-sized crystal rod-shaped particle that is formed as a stable aqueous colloidal suspension and is commonly separated from cellulose by acid hydrolysis [9]. Previous researchers have published numerous studies on PLA/ chitosan/CNC bio-composite films [10][11] .There are two ways to obtain nanocellulose. First is mechanical treatment and second is acid hydrolysis. In acid hydrolysis, the separation of cellulose nanocrystals (nanowhiskers) is the product of the difference in solubility between the two regions (amorphous and ordered regions) in the cellulose chain.

Cellulose is a hydrophilic polymer and therefore generally has poor compatibility with hydrophobic synthetic polymers and also poor thermoplastic properties. This constrains the use of nanocellulose, especially cellulose nano crystal, in nanocomposite fabrication [12]. However, according to Sullivan et al. CNC is easily dispersed in water, therefore it can be used as a water-based coating and films for food packaging applications [13].

The use of cellulose nanocrystal as a component in polymeric materials has received a lot of attention. Because of their high crystallinity, good processability, abundance, renewable and biodegradable nature, and outstanding mechanical properties, cellulose-based materials have been the focus of much research. In summary, the combination of cellulose-based fillers to polymer matrices improves material performance in terms of barrier, thermal, and mechanical properties. As reinforcement fillers in polymeric materials, various types of cellulose particles have been used. These cellulose particles can be distinguished by their size, morphology, crystallinity, and crystal structure [14].

Although a number of research efforts aimed at improving the film properties of biopolymer-based packaging films have shown great changes in film properties, their physical & mechanical properties are still not satisfactory and have encountered difficulties in industrial applications [15]. Blending and homogenising cellulose nanocrystals in PLA/Chitosan matrix would result in a new nanocomposite with sufficient mechanical strength suitable for use in food packaging. Therefore, the incorporation of CNC as nanofiller may be useful in improving the mechanical properties of packaging materials. This study evaluates the physical properties and mechanical properties of a new packing material of Poly-lactic acid (PLA)/Chitosan (Cs), Cellulose Nanocrystal (CNC) biopolymer film by using solvent casting technique.

Materials and Methods

Materials

Polylactic acid (PLA) resin of 4032D type used in this study was supplied by Nature Works LLC (USA) with a specific gravity of 1.24, high molecular weight and melt mass flow rate (MFR) of 7 g/10 min at 210^{o}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)

Isolation of CNC

Microcrystalline cellulose (MCC) is often derived from wood pulp and purified cotton linters. 1g of Micro Crystalline Cellulose was hydrolysed by 10 g of 64% w/w sulphuric acid at 45 °C for 45 min under constant mechanical stirring. The suspension was then diluted with cold deionised water and centrifuged at 4300xg for

15 min. Sodium hydroxide was used in the washing process to neutralize the pH value. After completion of process, the acid was moved by washing with deionized water and centrifuged first, then, 0.5 N of NaOH was applied to neutralizing the suspension followed by washing again by deionised water. The supernatant was removed, and the solid phase was diluted again with deionised water until the milky substance was form and can start to collect (Lim et al., 2021).

Films preparation

Preparation materials Polylactic acid (PLA) and chitosan (Cs) were pre-treated by drying in a vacuum oven at 50 °C for 24 h to eliminate possible absorbed water on the surface of the particles. The PLA and chitosan were dissolved separately in different solvents before blending. PLA (1% by weight) (0.3 g) was dissolved in 30 ml of chloroform and 1 g chitosan in 100 ml of 1% (v/v) acetic acid. Then chitosan solution (1% by weight) was added to the PLA solution and stir until homogenized. After stirring, the solution was modified with glycerol (1% by weight) as plasticizers and stirred for 30 minutes. Then, 1, 2, 3 and 4 wt % of CNC solution were added in PLA/CS solution and stirred until homogenized. Then the solutions were poured on a petri dish, and the solvent used was evaporated at room temperature in fume chamber for 24 h to volatilize the residual solvent. To control film thickness, the quantity of each film-forming solution poured onto a plate was calculated. After that time, films were peeled from the plates and cut to specimens of appropriate sizes for subsequent testing.[9]

Tensile properties

The tensile strength and elongation at break were assessed according to American Society for Testing and Materials (ASTM) method D882 [17]. Specimens were prepared from rectangular film strips (1 cm × 10 cm), dimensions. A universal testing machine, Instron (Model 5569) with 1kN load cell was operated at a crosshead speed of 2 mm/ min. The average value of at least three samples for each composition was reported.

Scanning electron microscopy

The microstructural analysis of the cross-sections of the films was carried out by means of a scanning electron microscope (JEOL JSM-5410, Japan). Film pieces, 0.5 x 0.5 cm^2 in size, were cryofractures from films and fixed on copper stubs, gold coated, and observed using an accelerating voltage of 10 kV. Observations were taken in duplicate for each formulation. [18]

Water absorption

Water absorption was measured using the following procedure. Films with dimensions 2cm x 2cm were placed in a desiccator for 24 h, followed by weighing to measure the dry mass. The films were then immersed entirely in the distilled water in a sealed beaker. The weight gained was monitored until equilibrium was obtained as described by previous findings [19], the percent of water absorption was calculated as follows:

$$\text{Water absorption } \% = \frac{(Ww - Wd)}{Wd} \times 100 \qquad \text{(eq. 1)}$$

Fourier transform infrared spectroscopy

The samples were dried in a desiccator for at least 1 week before analysis. A Nicolet iS10 Fourier transform infrared spectroscopy, with a spectral resolution of 1 $cm^{-1}$was used to recorded infrared spectra of samples. FTIR spectra were collected from 400 cm^{-1} to 4000 cm^{-1}[18].

Statical analysis

All data are shown as a mean ± standard deviation. Analysis of variance (one-way ANOVA; Microsoft Excel 2010) was conducted, utilising a probability level less than 5% ($p < 0.05$). A value of $p < 0.05$ was represented to be statistically significant.

Results and Discussion

Scanning electron microscopy

The results of SEM of the pure PLA/Cs films with (0% - 4%) of CNC are presented in Figure 1. SEM images showed that the surface of PLA/Cs films changed when the concentration of CNC increased. For the pure PLA /Cs film, the surface was seen to be rough and rigid, while the surface of films with CNC content up to 2% was relatively smoother than the pure PLA. For the films containing 1% and 2% of CNC, there is no agglomerations of CNC in the surface of the polymer matrix, which indicated that filler substances were homogeneously dispersed. This might have occurred

because of the processing route of films' preparation [13]. However, for the nanocomposite films with high CNC content (3% & 4%), the presence of agglomerations of CNC in the surface of the PLA matrix was observed. These agglomerations on the surface of the PLA matrix are caused by the hydrophilic nature of cellulose, which encourages strong interactions between the cellulose nanocrystals via hydrogen bonds, resulting in agglomerations on the polymer surface [14].

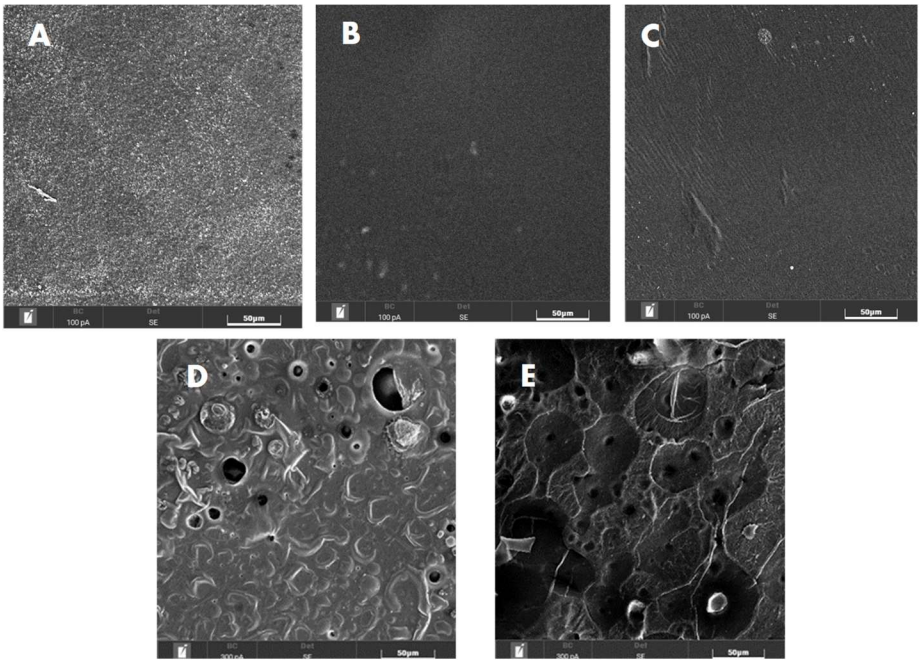

Figure 1. SEM image of the surface of (A) PLA/Cs film, (B) PLA/Cs/CNC 1% film (C) PLA/Cs/CNC 2% film, (D) PLA/Cs/CNC 3% film, (E) PLA/Cs/CNC 4% film

Tensile properties

The obtained results of tensile strength test, elongation at break and young modulus were conducted on the pure PLA/Chitosan film and the nanocomposite films with different content of CNC (0%- 4%). The comparison of the ultimate strength point of the films are presented in Figure 2, Figure 3 and Figure 4. For the pure PLA/Chitosan film without CNC, the yielded TS value (ultimate strength point) was 5.4 MPa. In the case of the film containing 2% of CNC, the TS increased significantly to 13.8 MPa in comparison with the pure PLA/Chitosan film value.

The PLA/Cs films at 3% and 4% CNC concentration exhibited a decreased TS value. The PLA/Cs films at 4% CNC load were more brittle which may be the cause for higher elastic modulus as shown in Figure 4 which is the highest value of young modulus is the films with 4% CNC [20]. The decrease in toughness in nanocomposites has been attributed to large agglomerations of nanofillers has been discussed on the SEM analysis above, the films with high CNC content (3% & 4%) showed the presence of agglomerations of CNC in the surface of the PLA/Cs matrix. Zeyad and Sullivan et al. reported similar results of the tensile strength of their cellulose nanocomposites [13, 21]. These agglomerations can act as stress concentrators, which facilitate the spreading of defects generated at the interface. These defects can grow larger than the critical crack size, resulting in film failure as can be seen on films with 3% and 4% CNC. This suggested that the film containing 2% of CNC was more ductile than the other films since the tensile strength and the elongation break is the highest compared to others [21]. Generally, the

improvement of the mechanical performance of nanocomposite films results from different factors: compatibility between the polymer matrix and the filler, aspect ratios of the filler, and the orientations of the filler. However, in this work, we can hypothesize that the improvement of the tensile strength of the nanocomposite films caused by the stiffness effect of CNC that homogeneously dispersed in the PLA matrix [22].

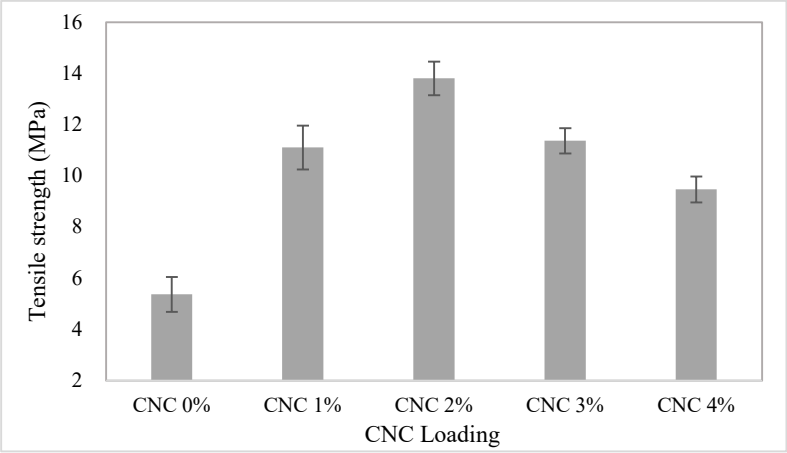

Figure 2. Effect of CNC loading on tensile strength of the film. Values in the figure were significantly different ($p < 0.05$)

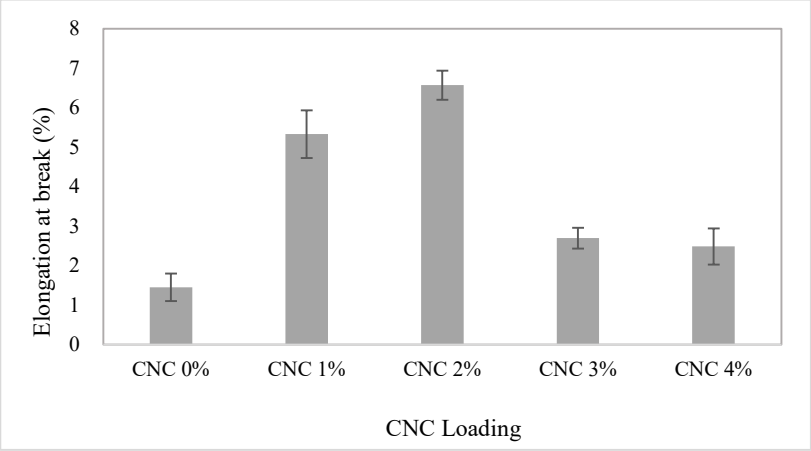

Figure 3. Effect of CNC loading on elongation break of the film. Values in the figure were significantly different ($p < 0.05$)

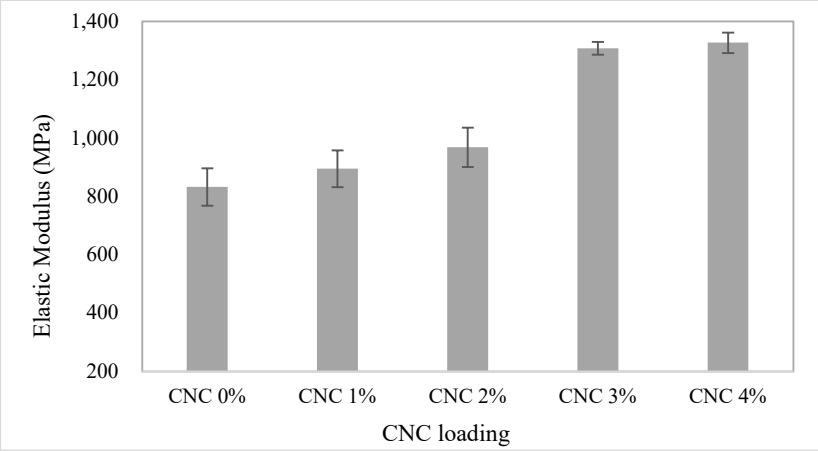

Figure 4. Effect of CNC loading on young modulus of the film. Values in the figure were significantly different ($p < 0.05$)

Water absorption

Water absorption test of pure PLA/Chitosan and PLA/chitosan/CNC films were carried out to investigate water absorption properties by calculating the percentage of water absorption. The water absorption value is shown in Table 2. It can be seen from Figure 5 that the percent of water absorption of the films increased with increasing amount of CNC in PLA/Chitosan matrix. The water absorption of all PLA/Cs/CNC films containing 0, 1, 2, 3 and 4 wt.% CNC increased to 3.02%, 3.77%, 9.82%, and 16.18% after 180 minutes of immersion, respectively. Since PLA is strongly hydrophobic [17] and CNC has hydrophilic nature [21], where hydrogen bonds easily form in water thus increased water absorption [23]. The water absorption of the films is mainly due to the CNC which affect the ability of the film to retain water. The increased water absorption of the film with CNC corresponds to the FT-IR curve, which shows a stronger intensity of the hydrophilic functional group band at 1750 cm^{-1} (reflecting C=O stretching).

Table 1. The initial weight of a films and water absorption of films containing different amount of CNCs

CNC Concentration (%)	Initial Weight (g)	Water Absorption (%)
0	± 0.0218	1.90 ± 0.50
1	± 0.0229	3.02 ± 0.39
2	± 0.0246	3.77 ± 0.29
3	± 0.0136	9.82 ± 0.45
4	± 0.0188	16.18 ± 0.36

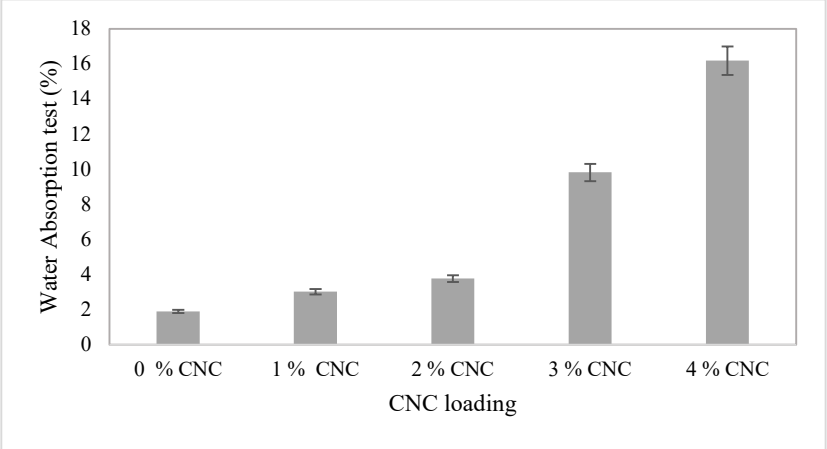

Figure 5. Water absorption test on Films with different concentration of CNC Values in the figure were significantly different ($p < 0.05$)

Fourier transform infrared spectroscopy

FT-IR spectroscopy analysis spectra were recorded to study the differences in the identifying signals of PLA/Cs/CNC films. The infrared spectra of the film with CNC as shown in Figure.6. The absorption peaks of the PLA/Cs/CNC film spectrum are mainly due to the –CH3 stretching vibration at 2,991 cm^{-1}. A strong absorption band was observed at 1,750 cm^{-1} due to the C=O stretching from keto esters [9] According to previously published research, the bending vibrations at 1,452 and 1,382 cm^{-1} are connected to symmetric and antisymmetric deformations of the CH_3 group by [24]. The band at 1261 cm^{-1} are from the antisymmetric and symmetric stretching of C–O–C in esters. The peak at 1,181 cm^{-1} can be attributed to C–O–C stretching of PLA as mentioned in previous studies [9, 12]. The peaks of the chitosan can be found at 1542 cm^{-1} (N-H bending in amide and protonated amino group) which in the agreement of previous study [25]). The peaks at 876 cm^{-1} (β-glycosidic linkage of the cellulose) were observed, associated with typical structures of cellulose [26, 27].

Conclusion

Packaging materials based on PLA and chitosan containing different amount crystal nanocellulose (CNC) were developed to improve the mechanical and physical properties of the films. Cellulose nanocrystal improved the physical properties, tensile strength, percentage elongation breaks and the water absorption. SEM images showed that the surface of PLA/Cs films smoother when 1% and 2% of CNC were added. The addition of 2% CNC enhanced the interactions (e.g., hydrogen bonds and electrostatic interactions) between the PLA/chitosan chains to perform a well-disperse film. FTIR analysis allowed characterizing the molecular interactions occurring after incorporation of Cellulose nanocrystal The set of results indicates that the films with 2% CNC were promising as a filler for PLA/Chitosan based film. However, more work is required in this area of research to maximize the effectiveness of the fillers and also bioactive incorporated agents.

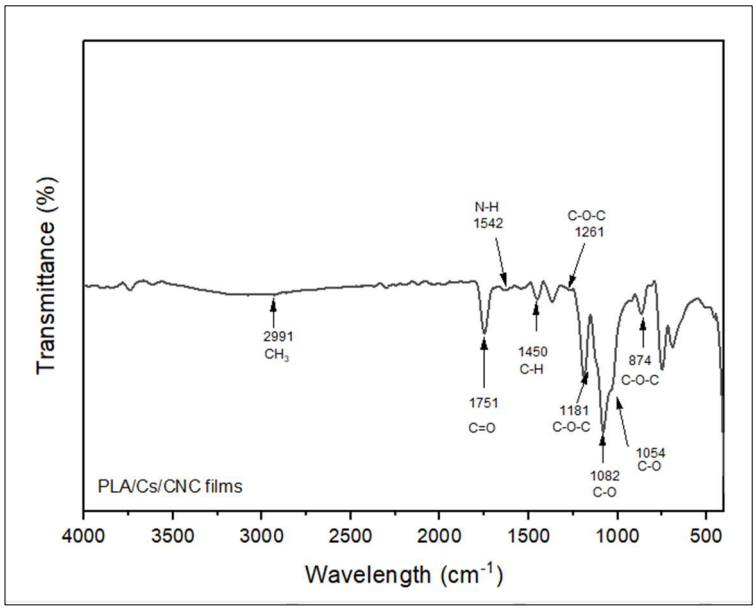

Figure 6. Fourier-transform infrared spectroscopy analysis PLA/Cs//CNC film. Scanning range from 400 to 4000 cm^{-1} is shown.

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