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INFLUENCE OF CHITOSAN NANOPARTICLES ON CELLULOSE ACETATE FILM FROM DURIAN RIND

RACHAPORN KUDISRI and TANAT UAN-ON*

Department of biotechnology, Faculty of Agro-Industry, Kasetsart University,
Bangkok, Thailand.
**E-mail: fagitnu@ku.ac.th*

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ABSTRACT

Cellulose acetate (CA) from durian rind and Chitosan nanoparticles (CSNPs) films were prepared in this study. The synthesis of CA from durian rind in a rapid process by a transesterification reaction. The structure of CA was characterized by FTIR. CSNPs were prepared by ionic gelation method with different concentrations of sodium tripolyphosphate (TPP). The particle size gradually decrease significantly when TPP concentration increases from 0.3% to 0.6%. The influence of the CSNPs on CA films was determined by measuring the tensile strength, whereby increases in the tensile strength and load at break were seen, with values of 4.38 ± 0.20 N/mm^2 and 21.29 ± 0.98 N/mm^2, respectively. At the optimum ratio of 0.975/0.025 (CA/CSNPs) the particle size was 338 nm. Therefore, the influence of the CSNPs in the CA film could be explained, whereby increasing the size of the CSNPs, the adhesion is increased through the highly agglomerated fillers, which will be strongly bonded within the matrix. The CA/CSNPs films which could be reduce agricultural waste and increase the values. In the future, these nanocomposite films can be developed in the membrane to use wastewater treatment.

Key words: Cellulose acetate, chitosan nanoparticles, ionic gelation, nanocomposite film

INTRODUCTION

Natural biopolymers have several advantages over synthetic polymers, including that they are biodegradable and renewable as well as edible. Composite films based on proteins and polysaccharides are efficient oxygen and carbon dioxide barriers. Most of these films also have desirable mechanical properties, making them useful for improving the structural integrity of fragile products (Jong & Perry, 2007). Cellulose is the most abundant natural polymer produced from a renewable source, as well as being biodegradable and non-toxic. The primary structure of cellulose is represented by a linear polymer of β-glucopyranoside residues, linked by 1,4-β-glycoside bonds (Lavoine *et al.*, 2012). Cellulose derivatives with various properties obtained by introducing different substituent groups are being developed for a broad range of applications. Durian is the most popular fruit in Southeast Asia. For the commercial production of durian is concentrated mostly in Thailand followed by Malaysia and Indonesia. It is also grown in the Philippines and other ASEAN nations but at much smaller levels. Petpen *et al.* (2014) has reported to synthesis natural fibers from durian rind with yield of 31–45% when compared with bamboo cane fiber at 26–43%. The properties of cellulose from durian rind can be used as reinforcement elements in composite materials to enhance mechanical properties.

Cellulose acetate (CA) is widely applied in bioplastics and membrane materials as the polymer matrix due to its good mechanical strength. CA is produced by the reaction of cellulose with corresponding acids or acid anhydrides as a catalyst, but this reaction suffers from a long reaction time. For developing a new reaction system, an efficient reaction system involving dimethyl sulfoxide (DMSO), aqueous NaOH, and vinyl acetate was introduced for the rapid synthesis of cellulose acetate (Xuefei *et al.*, 2013).

Chitosan (CS) is a biopolymer obtained from the conversion of seafood processing waste into high-value produce by the alkaline deacetylation of chitin. CS, as an adsorptive material for wastewater treatment, was used as a functional polymer with cellulose acetate to prepare a membrane by introducing a reactive site (amino and hydroxyl

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* To whom correspondence should be addressed.

group) in the membrane material (Seyed *et al.*, 2014). Nanoparticles represent strong colloidal particles with diameters ranging from 1-1000 nm. The word "nano" alludes to one thousand millionth of a meter (Abdulhussien & Tamadhur, 2014). Chitosan nanoparticles (CSNPs) can be prepared by an ionotropic gelation method with chitosan and sodium tripolyphosphate (TPP). This method is based on the interaction between positively charged amino groups on chitosan and negatively charged tripolyphosphate ions through either intermolecular or intramolecular linkages of the anionic counterions. A previous study into the synthesis of chitosan nanoparticles by the ionotropic gelation method reported the minimum particle size of chitosan nanoparticles was around 100 nm and the size distribution was in the range 100–400 nm (Sivakami *et al.*, 2013). The size property of chitosan in nanoparticles can influence their thermal and mechanical properties and can reinforce and improve the polymer film applicability in film packaging. Márcia *et al.* (2011) has reported about carboxymethyl cellulose (CMC) and chitosan nanoparticle films; chitosan nanoparticles can reduce the interactions between the biopolymer and water molecules, thus decreasing the solubility. Also, chitosan nanoparticles have a better interfacial adhesion with polymer matrices, when compared to their respective micro/macro counterparts (Seyed *et al.*, 2014).

The aim of this research was to study the influence of chitosan nanoparticles on cellulose acetate from durian rind for the production of nano-composite films. The synthesis of cellulose acetate from durian rind was performed using a rapid system process, and the resulting product was characterized by its degree of substitution (DS) and the functional groups using FTIR. For the synthesis of chitosan nanoparticles, the effect of the TPP concentration on the size of the chitosan nanoparticles was studied. Additionally, to enhance the mechanical properties, the chitosan nanoparticles were added into CA films made from durian rind and tensile testing was performed to investigate the mechanical properties of the resulting films.

MATERIALS AND METHODS

Materials

Durian rind was collected from a local market in Thailand. Cellulose acetate (CA) with a molecular weight (MW) of 30,000, Chitosan from crab shells with a molecular weight (MW) 190,000–310,000 ($\geq$80% deacetylated), Vinyl acetate and highly viscous sodium tripolyphosphate (TPP) were purchased from Sigma-Aldrich (USA). Dimethyl sulfoxide (DMSO), glacial acetic acid, and acetone were obtained from RCI Labscan (Thailand). All the chemicals were of analytical reagent grade.

Extraction of cellulose from durian rind

The durian rind was cut into small sizes of 1 cm × 1 cm and then dried in a tray dryer at 60°C. Then, 200 g of the samples were prepared using a streaming explosion machine (Nitto Koatsu, Japan) at a temperature of 210°C and pressure of 16 bar for 4 min, and then rinsed with water. Next, double water extraction was performed with fiber/water at a ratio of 1:10 at 80°C in 30 min. The lignin was removed from the washed fiber by soaking in 30% sodium hydroxide at 80°C for 30 min, and then separated using distilled water until the pH of the sample became neutral. Then, the fibers were treated with sodium chlorite and 10% acetic acid at 70–80°C until the fibers turned a white color. Finally, the cellulose was filtered, washed, and then dried overnight.

Synthesis of cellulose acetate

The cellulose from durian rind was placed in a 50 mL Erlenmeyer flask equipped with a magnetic stirrer. Then, 20 mL of dimethyl sulfoxide (DMSO) and 2 mL of aqueous sodium hydrate (200 g/L) were added into Erlenmeyer flask in order to activate the hydroxyl group. After that, the mixture was stirred at room temperature for 5 min. Next, the mixture was moved to immerse into an oil bath at temperature of 100°C immediately and stirred for 2 min. Next, 2.67 mL of vinyl ester (0.03 mmol) was poured into the flask with stirring for 5 min. Then, distilled water was poured into the mixture. The cellulose acetate was filtrated and washed with water and then dried at room temperature. The cellulose acetate was kept in a desiccator at room temperature for further testing (Xuefei *et al.,* 2013).

Characterisation

The degree of substitution (DS) of the cellulose acetate was determined by titration combined with saponification reactions (Samira *et al.*, 2013). The DS recorded was the average value of the percentage of acetyl groups (%AG), which replaced the hydroxyl groups in the glycosidic units. The titration method was repeated in triplicate as follows: 0.1 g of cellulose acetate 5 mL NaOH (0.25 mol/L), and 5 mL of ethanol were added to a flask, and the mixture was left to stand for 24 h. After that, 10 mL of HCl (0.25 mol/L) was added to the mixture and allowed to stand for 30 min. A standard 0.25 mol/L NaOH solution and phenolphthalein were used as the titration solution and indicator, respectively. Next, the percentage of acetyl groups (%AG) was calculated using equation (1):

$$\%AG = \frac{[(Vb_i + Vb_t)\mu_b - V_a]43\cdot 100}{M_{ca}} \tag{1}$$

Where,
Vb_i = NaOH volume added to the system.
Vb_t = NaOH volume spent in titration.
μ_b = NaOH concentration.
V_a = HCl volume added to the system.
43 = Molar weight of AG.
M_{ca} = Weight of CA sample.

The acetyl content (%AG) was calculated the DS according to the following equation (2):

$$DS = \frac{(162\cdot 1AG)}{43\cdot 100-(43-1)AG} \tag{2}$$

162 = Molecular weight of anhydroglucose unit.
43 = formula weight of AG.
1 = atomic mass of hydrogen.

Fourier Transform Infrared (FTIR) analysis

FTIR spectra of the cellulose acetate were recorded using a Fourier transform infrared spectroscopy instrument (Bruker Tenser 27, Germany) with the ATR mode. FTIR spectral analysis was performed within the wavenumber range 4000–400 cm^{-1}.

Preparation of the chitosan in nanoparticles

The chitosan nanoparticles were prepared by inotropic gelation between the chitosan and sodium tripolyphosphate (TPP). Chitosan solution (1% (w/v)) was obtained by dissolving chitosan in acetic acid solution (1% v/v) at 25°C. TPP solution was added in 5 different concentrations: 0.2, 0.6%, 0.8, 1.0, and 1.4%. The TPP was dropped into the CS solution under vigorous stirring via a magnetic stirrer for 30 min. The chitosan solution was then centrifuged at 9000 rpm for 30 min. The supernatant was separated and the chitosan nanoparticles were collected and washed several times with distilled water. The ice bath was used for 30 min to freeze the chitosan nanoparticles. Next, the suspension was lyophilized at -105°C for 24 h using a freeze dryer.

Particles-size analysis

The particle-size distribution and the mean particle size of the chitosan nanoparticles were obtained using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK). The chitosan nanoparticles were dispersed in dimethyl sulfoxide (DMSO) by ultrasonication for 20 min. The samples were diluted and placed in a cuvette with a square aperture for analysis by dynamic light scattering (DSL). The scattering intensity was measured at 25°C.

Table 1. Ratio of preparation cellulose acetate (CA) and chitosan nanoparticles (CSNPs) films

CA (mg)	CSNPs (mg)
1000	0
975	25
950	50
925	75
0	100

Film preparation

The cellulose acetate and chitosan nanoparticles films were prepared by dispersing the chitosan nanoparticles at different concentrations of 25, 50, 75, and 100 mg in 49 mL acetone for 30 min. Cellulose acetate was added into the solution with a different ratio (Table 1). The solution was stirred with a magnetic stirrer for 1 h. to obtain a homogeneous polymer matrix. The homogeneous solution was poured onto a glass plate and dried at room temperature.

Mechanical properties of nanocomposite films

The film thickness (mm) was obtained with a digital micrometer (Mitutoyo, JAPAN). Measurements were taken at 10 points on each film. The mechanical properties of the nanocomposite films were analyzed by a tensile testing machine (Testometric, UK) equipped with a 50 N load cell to study the tensile strength (TS), elongation at break (EAB), load at break (LAB), and percentage of elongation according to the ASTM D882 standard method for assessing the tensile properties of thin plastic sheeting. Film strips of 80 × 20 mm with an initial grip separation were tested, with a crosshead speed of 50 mm/min. For each type of film, four replicates were tested.

RESULTS AND DISCUSSION

Degree of substitution (DS)

The DS of cellulose is the average number of hydroxyl groups that may be substituted on the glycosidic unit. In this research, the percentage of the acetyl groups (%AG) of cellulose acetate from durian rind was calculated to be 22.57% and the DS was 1.09. Assigning the value of DS from 0 to 3, then DS = 0 is the mean value for cellulose with insoluble components and DS = 3.0 is the mean value for completely substituted cellulose (Samira *et al.*, 2013).

Previously, the DS effects on various characteristics were studied, such as the polymer crystallinity and solubility in different solvents, and it was found that with increasing the DS of cellulose through the formation of acetate esters or other derivatives, the solubilities in different types of solvents change (Guimes *et al.*, 2008).

FTIR analysis

FTIR spectroscopy was performed on the cellulose and cellulose acetate from durian rind to evaluate their chemical structures. Figure 1 shows the FTIR spectra of cellulose and cellulose acetate synthesized from durian rind. The cellulose showed characteristic OH group stretching at 3334 cm^{-1}, with the band at 2901 cm^{-1} assigned to the C-H and CH_2 groups. Cellulose acetate showed a decrease in intensity of the stretching band at 3334 cm^{-1} due to the free OH groups being replaced by the acetyl group, with the appearance of a band at 1737cm^{-1} corresponding of C=O bonds of carboxylic ester, which is present in the structure of the acetyl groups. The CH_3 groups at 1366 cm^{-1} and the C-H bond at 1207 cm^{-1} in the structure of acetyl groups and C-O bond at 1030 cm^{-1} is responsible for the link between cellulose and acetyl groups (Candido *et al.*, 2016). The results confirmed that synthesis of cellulose acetates from durian rind was successful.

Particle size analysis

The particle sizes of the chitosan nanoparticles were determined by DSL technique. Figure 2 shows the effect of the TPP concentration on the chitosan nanoparticles sizes following adding different concentrations of TPP from 0.2 to 0.6, 0.8, 1.0, and 1.4%. With increasing the TPP concentration from 0.2% to 0.6%, the size distribution of the chitosan nanoparticles with a mean diameter of 245.80 ± 9.19 nm gradually decreased to 181.48 ± 15.97 nm, then the particles size increased when the TPP concentration was above 0.6%, showing particle sizes of 253.76 ± 4.76 nm, 282.08 ± 14.85, and 338.51 ± 30.73 nm for the 0.8, 1.0, and 1.4% TPP concentration, respectively in a narrow size distribution (Polydispersity index <1). From statistical analysis, at a significance level of 0.05, the results can be split into four groups by particle size, with the 0.2% and 0.8% TPP concentrations in the same group. These results indicated that when increasing the TPP concentration to more than 0.6%, the mean particle size of the chitosan nanoparticles was larger. It could thus be concluded that the TPP concentration is an essential factor that affects the formation of the nanoparticles (Al-Nemrawi *et al.*, 2008).

Mechanical properties of the nanocomposite films

The influence of the addition of chitosan nanoparticles (CSNPs) to cellulose acetate (CA) films on the mechanical properties of the films can be observed in Table 2, where it can be seen that the effect of the chitosan nanoparticles on cellulose acetate from durian rind depend on the load at break (LAB), elongation at break (EAB), tensile strength (TS), and percentage of elongation. The film thickness was measured on average as 230–270 µm to obtain the homogeneous films, strict control of the ratio between the amounts of dry mass of the film solution. Therefore, nanoparticles mixed into the films did not affect the thickness of the film. Because of the less difference in thickness of CA/CSNPs films, the homogeneous solution was poured onto a glass plate and dried at room temperature when evaporates of acetone take a long time the dense of films became thicker. The TS of the control (without adding CSNPs) was 1.07 ± 0.87 N/mm^2, increasing to a maximum value at F13 of 4.38 ± 0.20 N/mm^2 when the particle size was 338 nm. The LAB increased to 21.29 ± 0.98 N at F13.

From the TS and LAB results, it can be observed that increasing the particle size enhanced the interaction between CSNPs and CA in the matrix. The addition of CSNPs had a reinforcing effect,

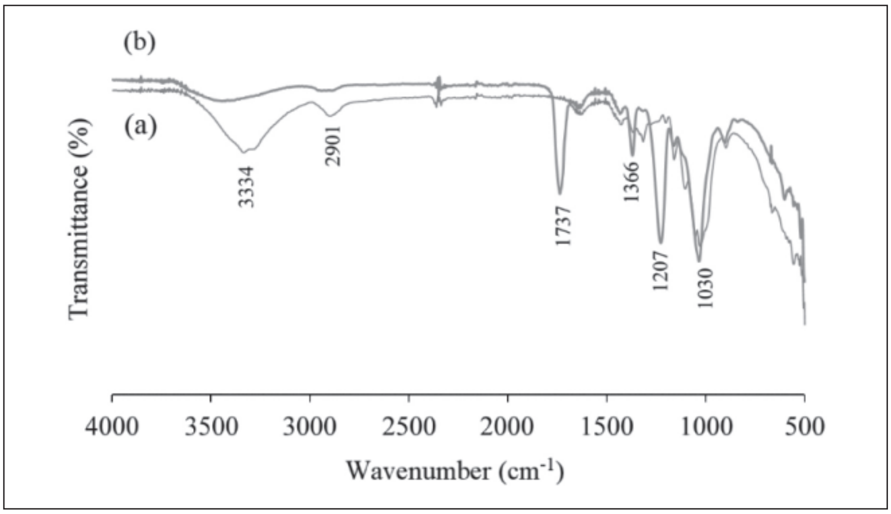

Fig. 1. FTIR spectra of (a) cellulose and (b) cellulose acetate synthesis from durian rind.

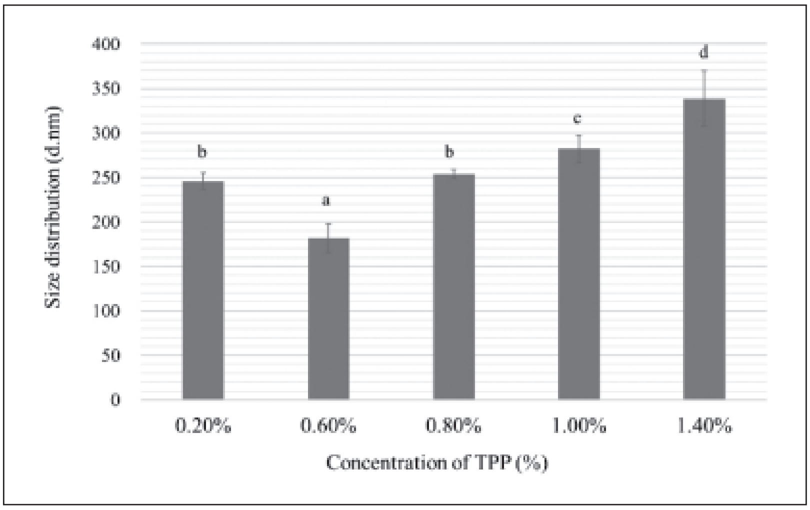

Fig. 2. Effect of TPP concentration.

Table 2. Influence of chitosan nanoparticles on cellulose acetate films from durian rind in load at break (LAB), elongation at break (EAB), tensile strength (TS) and percentage of elongation

Treatments	Nano chitosansize (nm)	Ratio (CA/CSNPs)	Thickness (µm)	Load at Break (N)	Elongationat break (mm)	Tensile Strength (N/mm^2)	Elongation (%)
Control	–	1.000/0.000	250 ± 0.01	5.45 ± 4.44^{abd}	0.65 ± 0.15^{ad}	1.07 ± 0.87^{abd}	1.62 ± 0.38^{ad}
F1	181	0.975/0.025	270 ± 0.00	0.70 ± 0.82^{ad}	1.50 ± 1.35^{ad}	0.12 ± 0.15^{ad}	3.75 ± 3.39^{ad}
F2		0.950/0.050	260 ± 0.00	7.24 ± 7.66^{ad}	0.65 ± 0.21^{ad}	1.38 ± 1.46^{ad}	1.63 ± 0.54^{ad}
F3		0.925/0.075	230 ± 0.00	0.99 ± 0.19^{ad}	0.67 ± 0.12^{ad}	0.21 ± 0.04^{ad}	1.68 ± 0.30^{ad}
F4		0.900/0.100	240 ± 0.00	0.31 ± 0.05^{ad}	3.52 ± 1.53^{ad}	0.06 ± 0.01^{ad}	8.81 ± 3.83^{ad}
F5	253	0.975/0.025	250 ± 0.00	4.13 ± 2.96^{abcd}	0.63 ± 0.01^{ad}	0.80 ± 0.57^{abd}	1.57 ± 0.03^{ad}
F6		0.950/0.050	250 ± 0.00	10.51 ± 7.07^{abcd}	0.67 ± 0.07^{ad}	2.05 ± 1.38^{abd}	1.67 ± 0.17^{ad}
F7		0.925/0.075	240 ± 0.00	6.79 ± 9.72^{abcd}	1.54 ± 1.52^{ad}	1.44 ± 2.01^{abd}	3.85 ± 3.81^{ad}
F8		0.900/0.100	270 ± 0.00	3.96 ± 5.26^{abcd}	1.33 ± 1.12^{ad}	0.72 ± 0.96^{abd}	3.33 ± 2.81^{ad}
F9	282	0.975/0.025	260 ± 0.00	7.68 ± 7.88^{bcd}	0.80 ± 0.12^{ad}	1.53 ± 1.57^{abd}	2.01 ± 0.30^{ad}
F10		0.950/0.050	250 ± 0.00	11.93 ± 9.43^{bcd}	0.57 ± 0.20^{ad}	0.94 ± 0.18^{abd}	1.43 ± 0.51^{ad}
F11		0.925/0.075	250 ± 0.00	4.22 ± 1.87^{bcd}	0.60 ± 0.09^{ad}	0.90 ± 0.40^{abd}	1.50 ± 0.24^{ad}
F12		0.900/0.100	230 ± 0.00	14.74 ± 3.16^{bcd}	0.63 ± 0.13^{ad}	3.16 ± 0.67^{abd}	1.58 ± 0.33^{ad}
F13	338	0.975/0.025	240 ± 0.00	21.29 ± 0.98^{cd}	0.80 ± 0.00^{ad}	4.38 ± 0.20^{bd}	2.01 ± 0.01^{ad}
F14		0.950/0.050	240 ± 0.00	17.35 ± 13.83^{cd}	0.76 ± 0.18^{ad}	3.48 ± 2.77^{bd}	1.90 ± 0.45^{ad}
F15		0.925/0.075	23 ± 0.00	5.53 ± 2.41^{cd}	0.68 ± 0.05^{ad}	1.05 ± 0.45^{bd}	1.70 ± 0.14^{ad}
F16		0.900/0.100	240 ± 0.00	7.50 ± 1.25^{cd}	0.67 ± 0.07^{ad}	1.53 ± 0.25^{bd}	1.68 ± 0.19^{ad}

Average ± standard deviation.
Average in columns followed by the same letters do not different from each other ($p > 0.05$) by Duncan test.
^{a,b,c} Effect of size nano chitosan, ^{d,e} Effect of ratio.

which was consistent with previous reports. The highest EAB was 3.52 ± 1.53 mm, following a percentage of elongation of 8.18 ± 3.83 at F4. The observed higher EAB and percentage of elongation at the lower nano-sized loading was due to the excellent dispersion of nanoparticles within the matrix (Sanaz *et al.*, 2012). Comparing the tensile treatment at F13 and F4, which had different values of mechanical properties, it could be seen that F13 had higher values of TS and LAB with the larger nanoparticle size, while F4 had a higher value of EAB and percentage of elongation with the lower nanoparticle sizes. The TS greatly depends on the interfacial adhesion between the matrix and the fillers (Chafidz *et al.*, 2014). With increasing the CSNPs content, there is greater adhesion so that the highly agglomerated fillers are strongly bound within the matrix and help bear the external stress, leading to a lower EAB and percentage of elongation. Here, with increasing the size of CSNPs, a larger degree of agglomeration becomes more apparent, due to the high surface energy of the CSNPs, thus contributing to the EAB and percentage of elongation being lower (Sanaz *et al.*, 2012).

CONCLUSION

In this research, the synthesis of cellulose acetate from durian rind using a rapid system was successfully achieved. FTIR analysis confirmed the replacement of free OH groups by acetyl groups in the synthesis of cellulose acetate (CA) films. For preparation of the chitosan nanoparticles with adding different TPP concentrations of 0.2%, 0.6%, 0.8%, 1.0%, and 1.4%, the mean chitosan nanoparticles sizes were measured by DSL as 181, 246, 254, 282, and 339 nm respectively. When increasing the TPP concentration to more than 0.6%, the particle size of the chitosan particles was larger. It can be concluded that the TPP concentration is an important factor affecting the formation of the nanoparticles. The chitosan nanoparticles were used to improve the mechanical properties of cellulose acetate films from durian rind, which was investigated by tensile testing. The results indicated that the chitosan nanoparticles had a positive impact on the structure of the CA films. When increasing the particle size to 338 nm, the enhanced interaction between CSNPs and CA in the matrix gave the film good strength. Therefore, the addition of CSNPs in CA films from durian rind resulted in a reinforcement of the film and an enhancement of its mechanical properties.

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