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ORIGINAL PAPER

Effect of nanoclay (NC) on mechanical and thermal properties of cellulose nanoparticles (CNPs) filled cornstarch bioplastic film

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Abstract

This paper explores the effect of nanoclay for improving the interfacial properties of starch bioplastic material filled with cellulose-nanoparticles (CNPs). The CNPs were prepared through acid-hydrolysis process by using acid concentration to break the amorphous region of chopped fiber to produce nano-cellulose. Various CNPs concentration (0.5 – 2.5 wt.%) were dispersed in cornstarch biopolymer matrix to form bioplastic films through solution casting method and listed for thermal and mechanical properties. Cornstarch bioplastic filled with 1.5 wt.% of CNPs showed optimum improvement in thermal and mechanical properties. Furthermore, nanoclay (NC) of varying weight percentage (0.1 – 0.5 wt. %) were added to the optimum improved 1.5 wt.% CNPs filled cornstarch bioplastic material. Hence, the hybrid cellulose-nanoparticles/nanoclay (CNPs/NC) filled cornstarch was improved both thermally and mechanically. The stiffness parameter (β_f) and confinement region (C) of the bioplastic during relaxation stage were 0.70 and 1.03 respectively for hybrid fillers at 1.5/0.3_CNPs/NC, which is an indication that nanoclay had a very good reinforcing effect on the starch polymer system. Improved tensile modulus and tensile strength of the CNPs/NC by 639% and 97% respectively were found when compared to CNPs filled cornstarch bioplastic material. Furthermore, the addition of nanoclay slow down the effect of water absorption rate. Hence, the water uptake of the bioplastic film was normalized.

Keywords Cornstarch · Cellulose-nanoparticles · Nanoclay · Bioplastic film · Interfacial properties

Introduction

In the last decade, researchers have explored significant uses of starch bioplastic material. Due to the problems associated with petroleum-based plastics, many researchers are now focusing on naturally derived plastics, such as starch-based materials. Starches are characterized as semi-crystalline biopolymer because they are mixture of amylose and amylopectin, with highly branched polysaccharide [1]. Before processing starch into bioplastic material, such starch must be plasticized by the addition of glycerol, gelatin and water, combined with the application of heat and shear forces [2]. Starch is a cheap resource material and it is well known to possess fast biodegradability, which is why it is one of the effective packing materials [3]. The demand for polymeric plastic packaging materials has increased in recent years due to its properties, such as malleability, versatility, lightness, and low cost, which confer numerous advantages to the polymers in this type of application. As a packaging material, starch main deficiencies are low mechanical properties and high permeability to water vapor, which makes its use unfeasible on a large scale [4]. The formation of a polymeric blend using the starch together with other natural additives such as cellulose has been an alternative to overcome those deficiencies and to achieve an increase in the properties that could justify the application of starch as a package material [5, 6]. This structured cellulose may be either cellulose nanocrystals (CNCs) or cellulose fibers (CFs) which are also called fibrillated cellulose (FC), bacterial cellulose nanofibers (BCNFs), and may be called cellulose nanoparticles (CNPs) [7–9]. If the mechanical properties of the bioplastic can be further improved by the addition of a small quantity of an environmentally harmless material, this polymer will find applications in more special or severe circumstances

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[10–12]. The use of cellulosic fibers (such as flax, wood, bamboo, hemp, etc.) as reinforcements in polymer matrix has helped to obtain value-added mechanical and thermal performances [13, 14].

The effect of cellulose on cornstarch bioplastic films and the concentration of cellulose fillers to enhance the mechanical and barrier properties of the bioplastic materials have been reported by several studies [11, 15–18]. Their objectives are to, evaluate the effect of the addition of different concentrations of cellulose on the mechanical, thermal, and water absorption properties [19, 20], investigate the properties of starch/gelatin/fillers (CNC) film [21], investigate the effects of ionic, for example, conduction of electrolytes with starched crystalline cellulose [22, 23], etc. All these studies are limited to improving strength, thermal properties, reducing water absorption etc. However, in the present study, a considerable novel study is to introduce nanoclay as secondary filler since nanoclay has a high aspect ratio. Hence. nanoclay exfoliation in polymer is to enhance and improve the interfacial properties of cellulose reinforced bioplastic films.

Reinforcing nanofillers have become an interesting component of nano-biocomposite due to their low thermal and mechanical properties. Likewise, increased environmental concerns regarding packaging have led to increased interest in biopolymer packaging materials. To improve some of the properties of biopolymer films, active additives such as plant extracts [24], nanofillers [25] or other biopolymers [26], are added to the film forming matrix. However, low mechanical properties, thermal stability, and barrier properties restrict its use in a wide-range application. When biopolymer was prepared with 5 wt.% of each clay and cellulose nano-reinforcement using solution casting, individual effect of layered silicates and microcrystalline cellulose as reinforcement are affected due to high percentage of clay and cellulose [27]. The results from the dynamic mechanical analysis (DMA) showed an improvement in storage modulus over the entire temperature range for both reinforcements, together with shifts in the tan delta peaks for both reinforcements to higher temperatures. In another study [28, 29], the dynamic mechanical properties of PLA/PCL blends in the presence of respective clay and microtalc. They reported a decrease in the storage modulus (E^I) of PLA because of a plasticization effect of PCL on PLA. The storage modulus, however, increased in the presence of fillers, but was still lower than that of neat PLA. This was attributed to the inherent stiffness of talc and clay, which introduced a rigid interface in the blend. For in this current study, the correlation between the mechanical and thermal properties is examined to deduce the improvement in the interfacial properties of the bioplastic films with the addition of very minute amount of nanoclay (0.1 – 0.5 wt. %) to CNPs filled bioplastic films.

Bioplastic materials on the other hand have higher shrinkage, low thermal stability, and sagging properties. These properties mainly affect the processing of bioplastics to achieve a desired product. Possibly, by improving the properties of cellulose reinforced cornstarch polymer, the drawbacks in the bioplastic polymer materials will be improved, hence, improving their performance, [30–32]. In this study, nanoclay is used as secondary filler and the effect of nanoclay addition in cellulose nanoparticles (CNPs) reinforced cornstarch polymer material was studied. It was observed that the addition of nanoclay in polymer matrix improved the thermal, mechanical and barrier properties. Hence, the interfacial property of the bioplastic film was improved.

Materials

The materials used in this experiment for the fabrication of polymer nano-biocomposite films are cornstarch, glycerol, and banana fiber prepared cellulose nanoparticles (CNPs). Dried banana fibre extracted from banana pseudo-stem was purchased from Reddcolt Enterprises in India. Cloisite® 25A nanoclay was natural montmorillonite (MMT) clay supplied by Southern Clay Products, Inc., USA. Cloisite® 25A nanoclay is an off-white additive particle for plastic and rubber, normally used to improve various physical properties, such as reinforcement, synergistic flame retardant and barrier properties. Cornstarch and nonhazardous Glycerol AR were purchased from Radchem Laboratory supplies (Pty) Ltd, Johannesburg, South Africa.

Methods

Cellulose nanoparticles (CNPs) preparation

Extraction of cellulose nanoparticles (CNPs) was prepared by chopping long banana fibers into smaller sizes varying from 1–5 mm. The chopped fibres were chemically treated using sodium hydroxide (NaOH) dissolved in water. 25 g of NaOH were dissolved in 500 ml distilled water. The chopped banana fibers were soaked in the NaOH solution for 30 min. 35 g of sodium carbonate mixed with 365 ml of distilled water solution was used as a delignification on the fibers to further remove lignin, hemi-cellulose, wax, and oils from the fibers. The fibers were then dried in an oven at 60 °C for 4 h. The dried fibres were later soaked in concentrated sodium hypochlorite (NaOCl) solution for 30 min and was rinsed in distilled water to remove impurities. The wet fiber was placed in the oven at 60 °C 4 h to dry. The steps were repeated two times for proper purification. The fiber was then treated with acid through hydrolysis process [33]. 35 ml of sulfuric acid (H_2SO_4) was mixed with 365 ml of distilled water in a beaker. The fibres were soaked into the solution using mechanical stirrer to stir for 30 min. The non-cellulosic phases were rinsed in distilled water to get rid of impurities and excess sulfuric acid in the fibres. The fibre was placed in oven and dried at 60 °C for 4 h, grinded and sieved to produce cellulose nanoparticles (CNPs).

Preparation of starch bioplastic films

Figure 1 shows the combined images of cornstarch (CS), cellulose nanoparticles (CNPs), nanoclay (NC), bio-polymer preparation process with the addition of CNPs/NC particle fillers and the resulting bioplastic film. The films are processed by solution casting method. In this method, cornstarch (12.5 g) powder was dissolved in with 210 ml of distilled water. The solution was maintained at 80 °C and stirred at 500 r/min using temperature-controlled magnetic stirrer for about 10 min. Following this, 30 wt.% of glycerol to starch powder was added to the solution as a plasticizer. The resulting mixture was stirred for about 45 min, during which a clear white solution was formed. The solution was then poured into an open-end metallic mold and left in an oven at 60 °C for about 6 h. During this process, the water molecules evaporated leaving behind a thin film on the mold. The mold was then removed from the oven and the film was hand peeled from mold at room temperature for characterization and mechanical studies. Alternate reinforced bioplastics were fabricated by addition of cellulose nanoparticles (CNPs) fillers at varying weight fraction (0.5 – 2.5 wt.%) CNPs to cornstarch (CS) powder. At the achievement of reinforced bioplastic formation with the best mechanical property, CNPs/NC bioplastic with varying weight percentage (0.1 – 0.5 wt. %) of nanoclay were also fabricated.

Morphological characterization

The structure of the cellulose nanoparticles (CNPs) cornstarch bioplastic material and CNPs/NC cornstarch bioplastic materials were studied by transmission electron microscopy (TEM). The morphology of the nanoclay dispersion was examined by Philips CM120 BioTWIN TEM operating at 120 kV. Ultra-thin transverse sections (80–100 nm) were sliced from the film specimen using an LKB/Wallac Type 8801 ultra-tome III 8802A diamond-coated control blade unit.

FTIR analysis

To analyze the intermolecular interactions within the CNPs/NC reinforced cornstarch bioplastic films, Fourier transform infrared (FTIR) Spectrometry was carried out

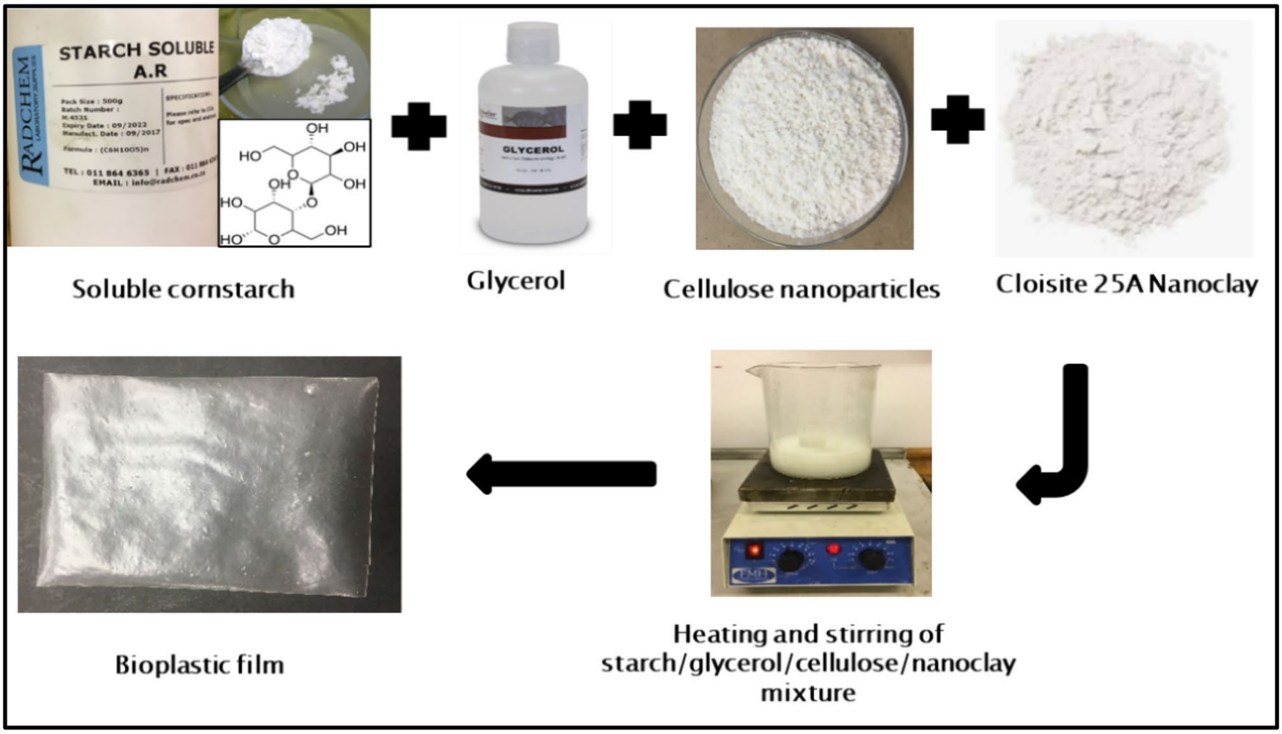


Fig. 1 Schematic preparation process of neat cornstarch bioplastic, CNPs cornstarch bioplastic and CNPs/NC reinforced cornstarch bioplastic films

using Perkin-Elmer Spectrum Two Universal ATR (model L1050242). The Spectrum 10 software compiled with FDA 21 CFR Part 11 regulation for Windows was used to manage the FTIR instrument. The characteristic peak of the FTIR spectra were recorded using an infrared spectrometer in the frequency range of 400 cm^{-1} – 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} by co-addition of scans for each spectrum at room temperature.

Dynamic mechanical analysis (DMA)

DMA test was performed on bioplastic films using TA Instruments (Model Q800 V20.6, New Castle, USA). Three specimens of each type measuring 60 mm × 10 mm × 3 mm were tested, and the average was considered. The DMA tests were performed in tensile mode at a strain amplitude of 1.0%. The testing temperature ranges from 20 to 180 °C with frequency of 1 Hz. The loss modulus, storage modulus and tan δ (damping ratio) were plotted against the temperature (°C).

Tensile properties

Tensile test sample was prepared according to ASTM Standard (ASTM D3039-76) [34]. Tensile tests were conducted on five samples each for the neat cornstarch bioplastic, CNPs reinforced cornstarch bioplastic and CNPs/NC reinforced corn starch bioplastic films. The mean values were recorded for the final strength acquired.

Water absorption

The bioplastic films samples were weighed immediately after their removal from the oven. Sample 10 mm by 10 mm in size were cut from the polymer bioplastic films sheet, weighed, and immersed in water at room temperature for 24 h. Subsequently, the cut samples were removed, wiped with a dry napkin, and weighed to determine their final weight. The increase in weight was measured on daily basis for 10 consecutive days based on their water absorption. The percentage of water absorption was calculated using the following equation.

$$\text{Water absorption } (P_w) = \frac{(W_f - W_i)}{W_i} \times 100 \qquad (1)$$

where P_w is the percentage of water absorption; W_i is the initial sample weight and W_f is the final sample weight. The average measurements were taken.

Result and discussion

Structure of morphology

The interfacial properties of the bioplastic materials were studied by transmission electron microscopy (TEM) analyses. TEM micrography was performed to investigate the dispersion of both cellulose nanoparticles (CNPs) and effect of nanoclay (NC) inclusion in the bioplastic material. Figure 2 reveals dispersion of CNPs in the starch polymer matrix. Result of the TEM images shows that

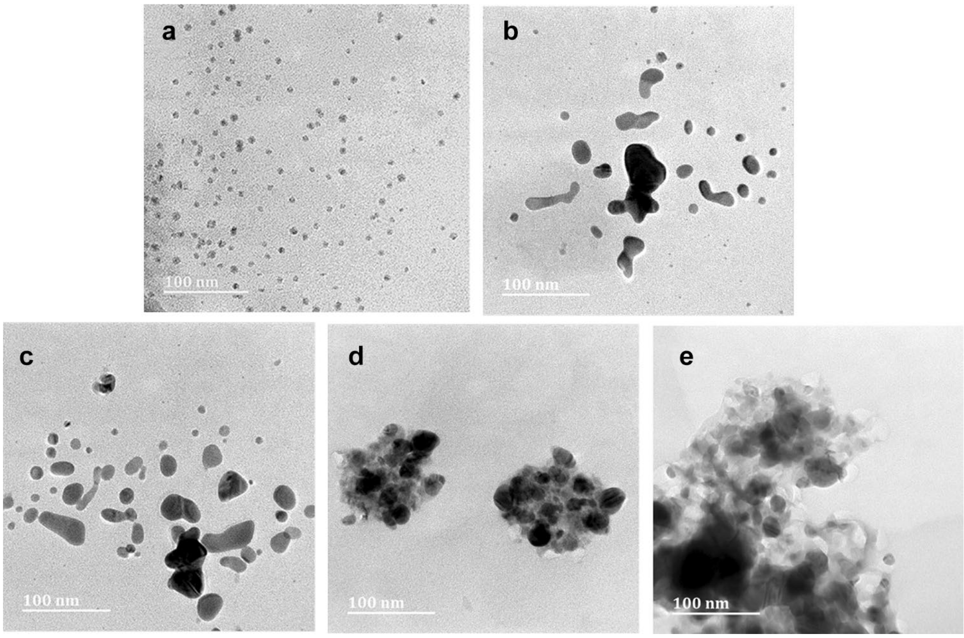


Fig. 2 TEM images of CNPs reinforced cornstarch bioplastic films with **a** 0.5 wt.%, **b** 1 wt.%, **c** 1.5 wt.%, **d** 2 wt.% and **e** 2.5 wt.% of cellulose nanoparticles

CNPs are well embedded in the polymer matrix with improved compatibility.

The TEM image of cornstarch filled with cellulose nanoparticles (CS_CNP) shown in Fig. 2 was compared to that of hybrid cellulose nanoparticle/nanoclay (CS_CNP/NC) filled cornstarch bioplastic material (Fig. 3). Although the morphology of 1.5 wt. % CNPs in Fig. 2a looks like that of 1.5/0.1_CNPs/NC in Fig. 3a, but not in its entirety. The percentage of nanoclay (0.1) in Fig. 3a is very minute (almost not visible), hence making it to be less effective. Notwithstanding, the addition of nanoclay at 0.1 wt. % was still active enough to modify the bioplastic film, causing an interfacial modification to the bioplastic film. The arrows in Fig. 3a show the effect of clay modification to CNPs filled the bioplastic film. When the CNPs and NC were combined as filler in the biopolymer, a proper mixture and proper blend of filler with biopolymer was created without a gap. This suggests good interfacial adhesion between the filler and the biopolymer. Hence, the critical effect was associated with filler/biopolymer interaction. The improvement of the bioplastic with the addition of nanoclay determined by the mechanical properties and the DMA properties of the bioplastic films confirms the effect of nanoclay addition. The TEM images were used to analyze the interfacial properties in bioplastic material. The continuous bright image is the matrix region and the irregular dark discontinuous image is the CNPs phase while the continuous dark image is the clay phase. It was well noted that uniform dispersion of CNPs and NC were observed in biofilm matrix. At lower NC level (up to 0.3 wt.%) nanolayers of clays were randomly dispersed in the polymer, leading to the formation of exfoliated structure. Whereas at 0.5 wt.% NC content, an intercalated nanocomposite structure was obtained.

The TEM result shows that inclusion of nanoclay improved the bioplastic interface adhesion. The reason behind this is because the density of nanoclay is higher than that of the CNPs, which makes the nanoclay dispersed easily in the polymer. However, agglomeration start to set in as more clay is being added (> 0.3 wt.%), leading to excessive agglomeration of CNPs/NC within the starch bioplastic material.

FTIR analysis

The FTIR spectrum of biofilm series was measured. Variation in the %transmittance can be observed with cellulose-nanoparticles/nanoclay addition in the bioplastic material (Fig. 4). The peaks with lower %transmittance value were attributed to weak adhesion between polymer and the

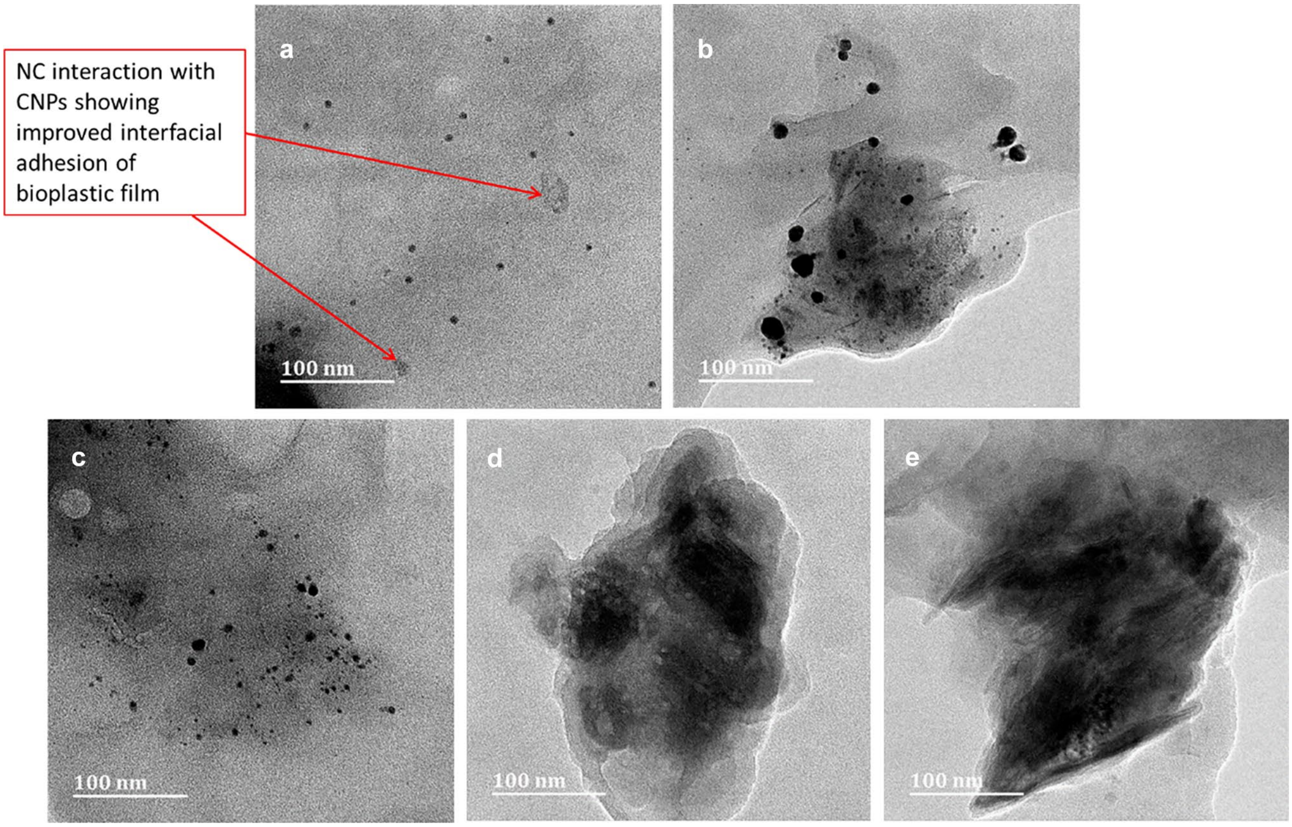


Fig. 3 TEM images of 1.5_CNPs/NC reinforced cornstarch bioplastic films with **a** 0.1 wt.%, **b** 0.2 wt.%, **c** 0.3 wt.%, **d** 0.4 wt.% and **e** 0.5 wt.% of nanoclay

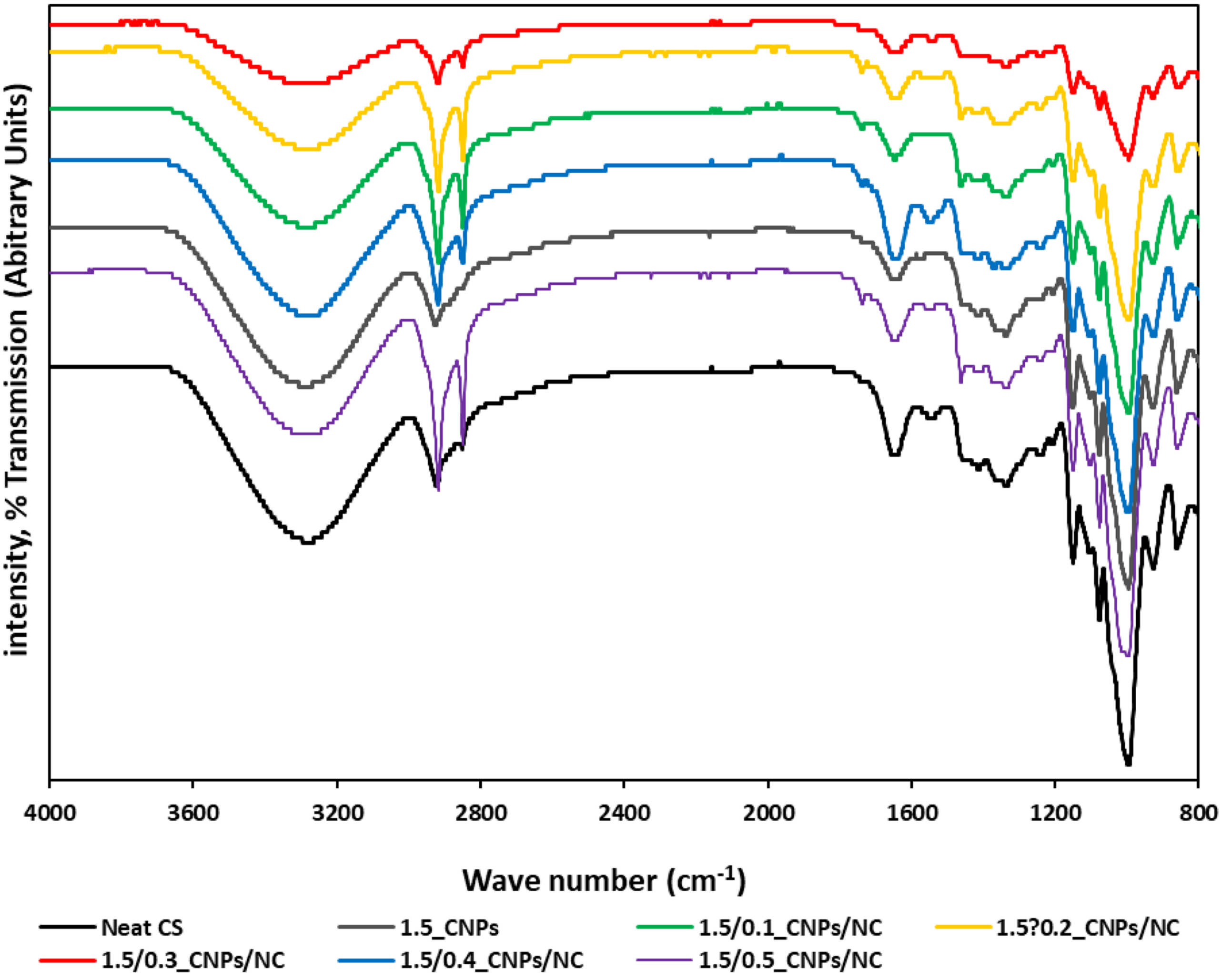


Fig. 4 FTIR spectra of neat CS, 1.5_CNPs bioplastic film and 1.5_CNPs/NC bioplastic film with varying weight fraction of (0.1 – 0.5 wt.%) nanoclay

cellulose filler at 1.5_CNPs, and that of hybrid 1.5/0.1_CNPs/NC, 1.5/0.4_CNPs/NC and 1.5/0.5_CNPs/NC filler content respectively, which possibly might decrease the mechanical properties, whereas %transmittance peaks with high %transmittance value can be corelated to strong adhesion between the polymer and this was predominant in fillers at 1.5/0.3_CNPs/NC, leading to increase in the mechanical properties. Similar result are also reported elsewhere [35, 36].

Changes in the %transmittance peak values were observed in the bioplastic films when neat CS bioplastic and CS_CNPs/NC bioplastic films were compared. There were minor predominant peaks in the %transmittance value at the addition of 0.3 wt.% nanoclay. Within the five peaks selected, 23%, 11%, 13%, 15% and 50% respectively were observed in CS_CNPs/NC with 0.3 wt.% nanoclay addition around 3275 cm^{-1}, 2916 cm^{-1}, 1630 cm^{-1}, 1331 cm^{-1} and 995 cm^{-1} wave numbers, when compared to neat CS bioplastic film %transmittance peak with 3208 cm^{-1}, 2924 cm^{-1}, 1630 cm^{-1}, 1331 cm^{-1} and 999 cm^{-1} wave numbers. This various characteristic of starch bioplastic functional group reveals that neat bioplastic film with 3208 cm^{-1} falls within OH group stretching vibration, 2924 cm^{-1} falls within CH stretching, 1630 cm^{-1} falls within the bending mode of absorbed water, 1331 cm^{-1} falls within C-H ester band due to partial acetylation of hydroxyl group in both polysaccharides, while 999 cm^{-1} falls with C-O stretching. This same observation was observed in CS_CNPs/NC bioplastic film. However, it was observed that the band intensity at the various peaks for neat CS bioplastic film is greater when compared to the band intensity in the CNPs/NC filled starch bioplastic films. Hence, it is well noted that when intensity increases, the band length decreases; and when the band length decreases, the strength increases. Similar study related to the functional group of starch were studied elsewhere [37–39]. It is worth noting that a better interaction between the starch and fillers was observed in all CNPs/NC filled biopolymers, with better improvement in 1.5/0.2_CNPs/NC and 1.5/0.0.3_CNPs/NC bioplastic films respectively. Hence, leading to an increase in the mechanical properties of the bioplastic materials. It can therefore be concluded that the crosslinking of starch with CNPs/NC brought a change to the FTIR spectra.

Tensile properties

The tensile properties of neat cornstarch (CS) bioplastic, cellulose nanoparticles reinforced cornstarch (CS_CNPs) bioplastic as well as cellulose nanoparticles/nanoclay reinforced cornstarch (CS_CNPs/NC) bioplastic were compared. At the initial, various CS_CNPs bioplastic were fabricated with CNPs weight ratio (0.5 – 2.5 wt.%) to corn starch powder. Experimental result showed that increasing the cellulose nanoparticles (CNPs) weight fraction progressively improved the tensile strength of the bioplastic from 1.761 MPa to 2.263 MPa, reaching a maximum of 1.5 wt. % CNPs and drops at more CNPs filler addition (Fig. 5). The resulting maximum reinforced CS_CNPs bioplastic (1.5wt% CNPs) was selected and further hybridized with various nanoclay weight ratio (0.1 – 0.5 wt. %) of cornstarch to form hybrid CS_CNPs/NC bioplastic materials.

The stress–strain curve of the hybrid CS_CNPs/NC bioplastic film is as shown in Fig. 6. Variation in elongation to failure were observed in the hybrid CS_CNPs/NC with the addition of nanoclay. Neat CS bioplastic was observed to display 0.162 mm/mm in strain to failure. While CS_CNPs/NC with 0.1 and 0.5 clay loading display the longest strain to failure, with a value of 0.220 mm and 0.235 mm/mm respectively.

From the experimental results, the highest tensile strength of 4.885 MPa was observed in the CS_CNPs/NC bioplastic, with an increase of 115% when compared to CS_CNPs bioplastic. Although, there was a reduction in strain to failure by -25%, but the modules of the CS_CNPs/NC increased from 19.338 GPa to 142.945 GPa, amounting to 639% increase when compared to neat CS bioplastic material. It was further observed that the reinforcement properties in the CS_CNPs/NC bioplastic material start to reduce at more clay loading.

The addition of small amount of nanoclay contributed to improvement in the elongation, while increase in nanoclay addition at higher percentage act as stress concentrator. The dispersion of the CNPs/NC in the starch polymer and the crosslinking of the CNPs/NC with the starch may be ascribed to the better interfacial adhesion between the starch and the reinforcing agent, which must have encouraged the elongation to occur at such rate. The comparison of strength among the neat CS bioplastic, CS_CNPs bioplastic as well as CS_CNPs/NC were as shown in Fig. 7.

The crosslinking of the starch with the CNPs/NC reveals a better plastic region before the break. At the initial, increase in elongation was observed at lower clay addition. However, as more concentration of the nanoclay was added, the effective stress transfer between starch and the CNPs/NC became difficult due to the existence of these stress concentrating sites which in turn results in the reduction of the elongation

Fig. 5 Tensile strength varying CS bioplastic films with varying weight percentage of (0.5 – 2.5 wt.%) CNPs fillers

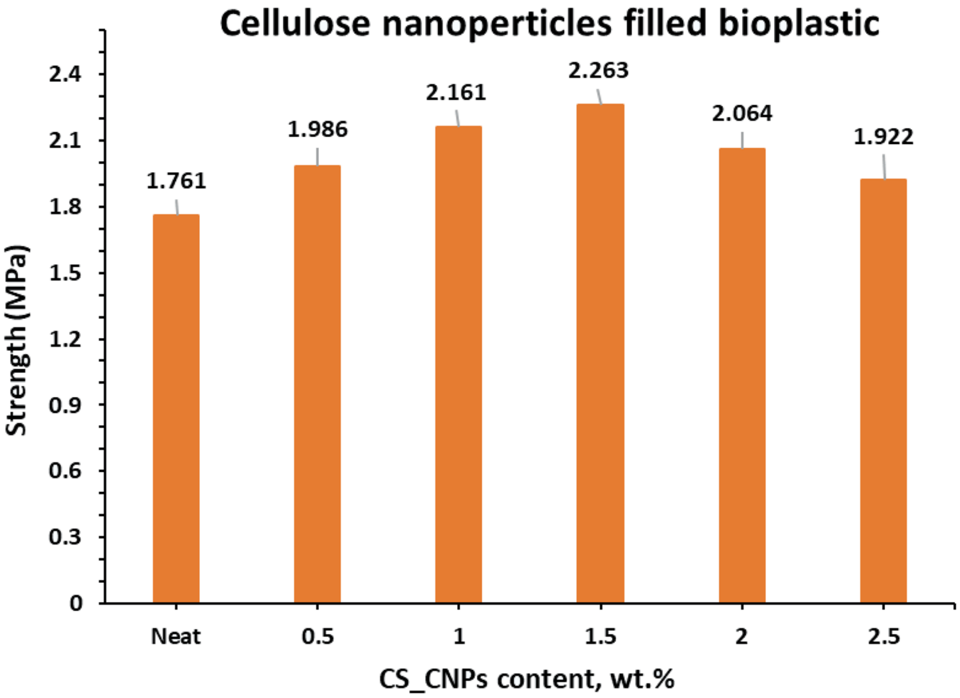
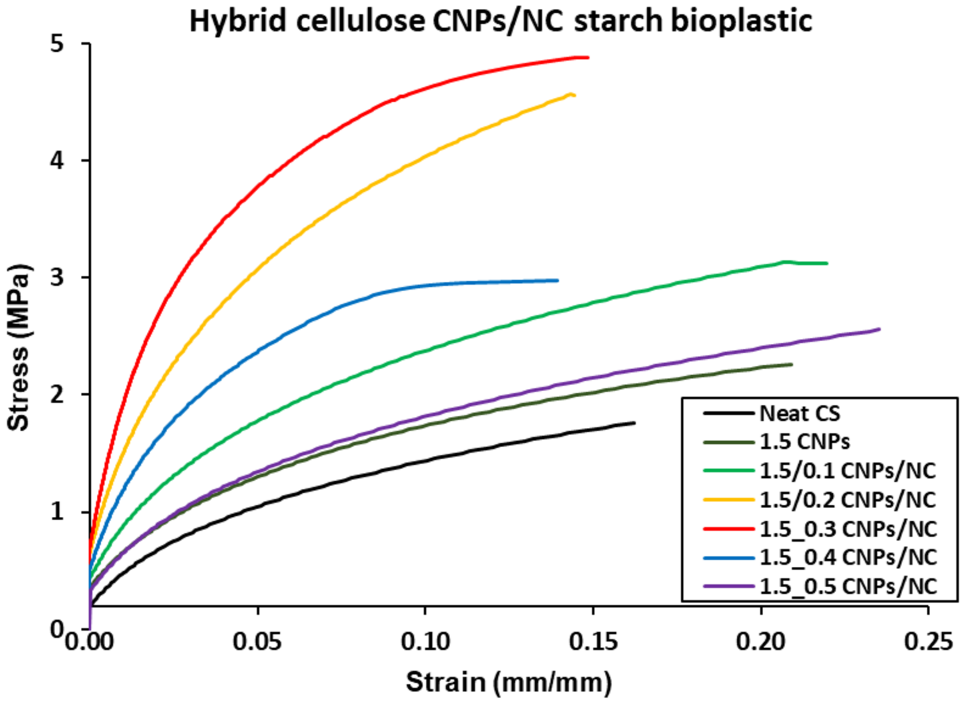


Fig. 6 Stress vs strain curve of CS bioplastic, 1.5_CNPs bioplastic film and 1.5_CNPs/NC bioplastic film with varying weight fraction of (0.1 – 0.5 wt.%) of nanoclay



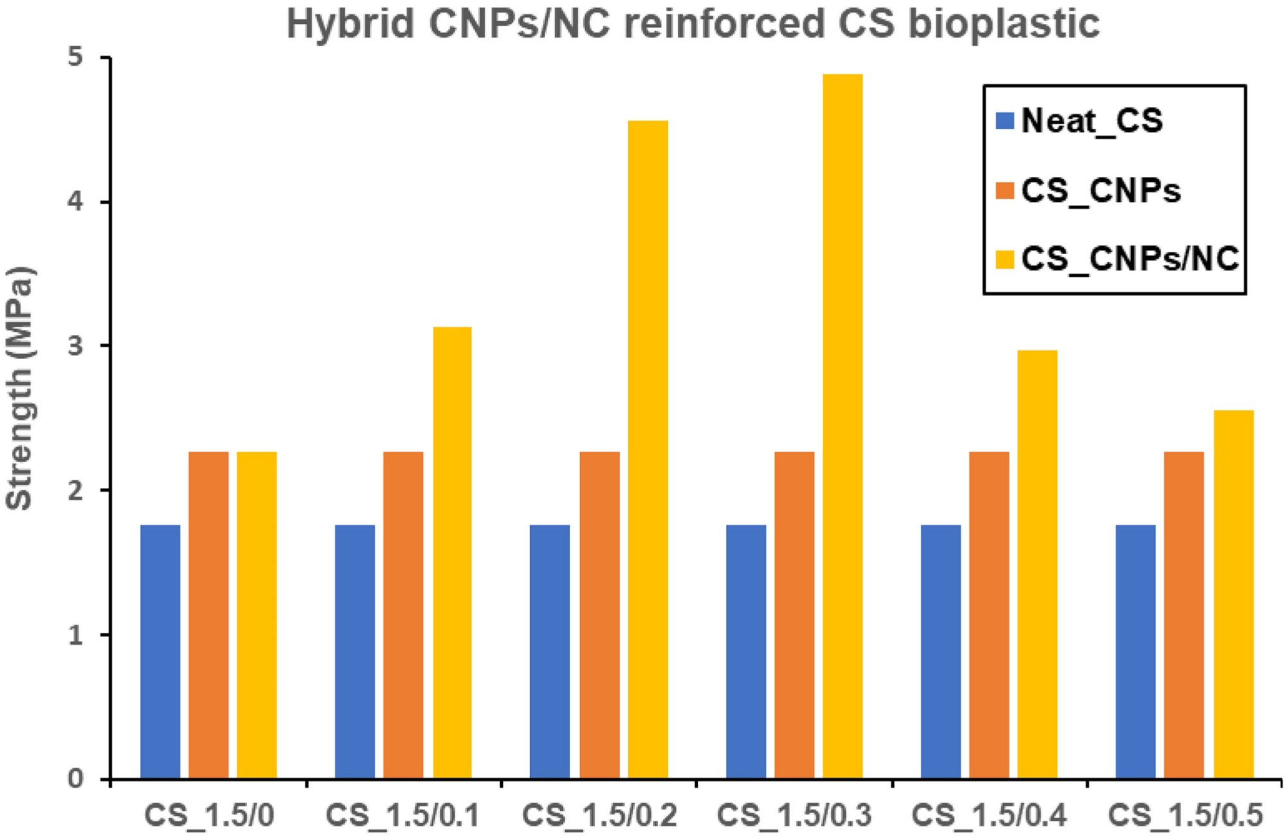


Fig. 7 Tensile strength comparison of CS bioplastic, CS_CNPs bioplastic and CS_CNPs/NC bioplastic materials with varying weight fraction of (0.1 – 0.5 wt.%) of nanoclay

properties of polymer nanocomposites. Hence later pick up at higher clay loading due to agglomeration of nanoclay in the bioplastic material.

To understand the percentage rate at which the varying cellulose nanoparticles/nanoclay (CNPs/NC) infused cornstarch (CS) increases; the increment rate for each various CS_CNPs/NC compared with the neat CS are displayed in Table 1.

It was observed that all modulus values of the CS_CNPs/NC bioplastic were higher than neat CS bioplastic materials, with the CS_CNPs/NC at 0.3 wt.% resulting in about 639% modulus value more that neat CS bioplastic film This can be attributed to better enhancement property of the nanoclay with proper interfacial properties of the bioplastic film. It was well noted that a proper dispersion of nanoclay was thereby administered in the starch polymer.

Dynamic mechanical analysis

The cellulose nanoparticles/nanoclay content within the starch polymer was studied by dynamic mechanical analysis. Curves for the storage modulus, loss modulus and tan delta were obtained for neat CS, CS_CNPs and the CS_CNPs/NC bioplastic films series as shown in Fig. 8a–c respectively. Tan delta glass transition temperatures *(T_g)*, storage modulus at 40 °C and storage modulus at 160 °C are listed in Table 2. The Glass transition temperature of starch polymer bioplastic material shifted from 128 °C to 142 °C with the addition of 0.3 wt. % nanoclay in the bioplastic material. The nanoclay in the starch polymer led to the increment of glass transition temperature. The increase in the T_g of the hybrid cellulose/clay bioplastic film compared to the neat starch bioplastic film is primarily attributed to the restriction in segmental motion of polymer because of good adhesion, leading to better interfacial properties of the CS_CNPs/NC bioplastic material. In Fig. 8c, the loss modulus peak temperature reduces as nanoclay fillers were added to the biopolymer as seen on the image. The loss modulus peak temperature values reduction was observed more in 1.5/0.2_CNPs/NC and 1.5/.0.3_CNPs/NC bioplastic films respectively. This shows nanoclay improvement of the bioplastic film.

The effect of the nanoclay addition at 0.3 wt.% nanoclay addition can be supported by the storage modulus values around the glassy phase with the highest value of 451.2 MPa at 40 °C. The reinforcement effect continues throughout 0.3 wt.% nanoclay filled bioplastic film reaching a value of 215.8 MPa at the rubbery phase around 160 °C. This shows that the interfacial property of the bioplastic was improved with the addition of little amount of nanoclay. The amount of polymer chains confined at the clay infusion was determined and quantified using the results obtained from the storage modulus of the DMA. CS_CNPs/NC bioplastic films with 0.1 wt. % to 0.3 wt. % nanoclay addition exhibited higher volume fraction when compared to neat starch polymer. Hence, reduction in the storage modulus occurs at higher clay loading. Furthermore, there was reduction in the glass transition temperature *(T_g)* at 0.4 wt. % and 0.5 wt. % clay loading when compared to the neat starch polymer bioplastic material.

The effectiveness of reinforcing agent during matrix relaxation process was studied by Joy et al. [40]. The stiffness parameter and confinement region at the fiber-matrix interface was analyzed using stiffness parameter (*βf*) as expressed following Eq. (2) below:

$$(\text{Stiffness parameter})\ \beta_f = \frac{\left(\frac{G_g}{G_r}\right)composite}{\left(\frac{G_g}{G_r}\right)matrix} \tag{2}$$

where, G_g and G_r are the storage modulus (*E'*) in the glassy region before (T_g) and rubbery region after (T_g) respectively.

The effective reinforcement of the filler during relaxation stage within the glassy region and the rubbery region were indicated by the stiffness parameter (β_f). The β_f value for neat CS bioplastic and CS_CNPs/NC bioplastic are recorded in Table 3. With an indication of the nanoclay in the starch polymer, the effective reinforcement of the CNPs/NC reinforced bioplastic film was quite effective when compared to the neat bioplastic film.

The lower the value of β_f, the higher the effectiveness of the filler in reinforcing the matrix. Although, the low β_f value start to occur 0.2 wt. % clay loading. This was found to be 0.81. Hence, addition of only 0.3 wt. % nanoclay

Table 1 Increase in stress–strain and modulus values of CS bioplastic, CS_CNPs bioplastic and CS_CNPs/NC bioplastic materials with varying weight fraction (0.1 – 0.5 wt.%) of nanoclay

Bioplastic Films	Stress (MPa)	Increase (%)	Strain (mm/mm)	Increase (%)	Modulus GPA	Modulus (%)
Neat_CS	1.761	-	0.162	-	17.258	-
1.5_CNPs	2.263	29	0.209	29	19.338	12
1.5/0.1_CNPs/NC	3.129	38	0.220	5	34.452	78
1.5/0.2_CNPs/NC	4.456	97	0.145	-31	87.381	351
1.5/0.3_CNPs/NC	4.885	115	0.148	-29	142.945	639
1.5/0.4_CNPs/NC	2.973	27	0.139	-33	66.131	241
1.5/0.5_CNPs/NC	2.556	13	0.235	12	22.859	18

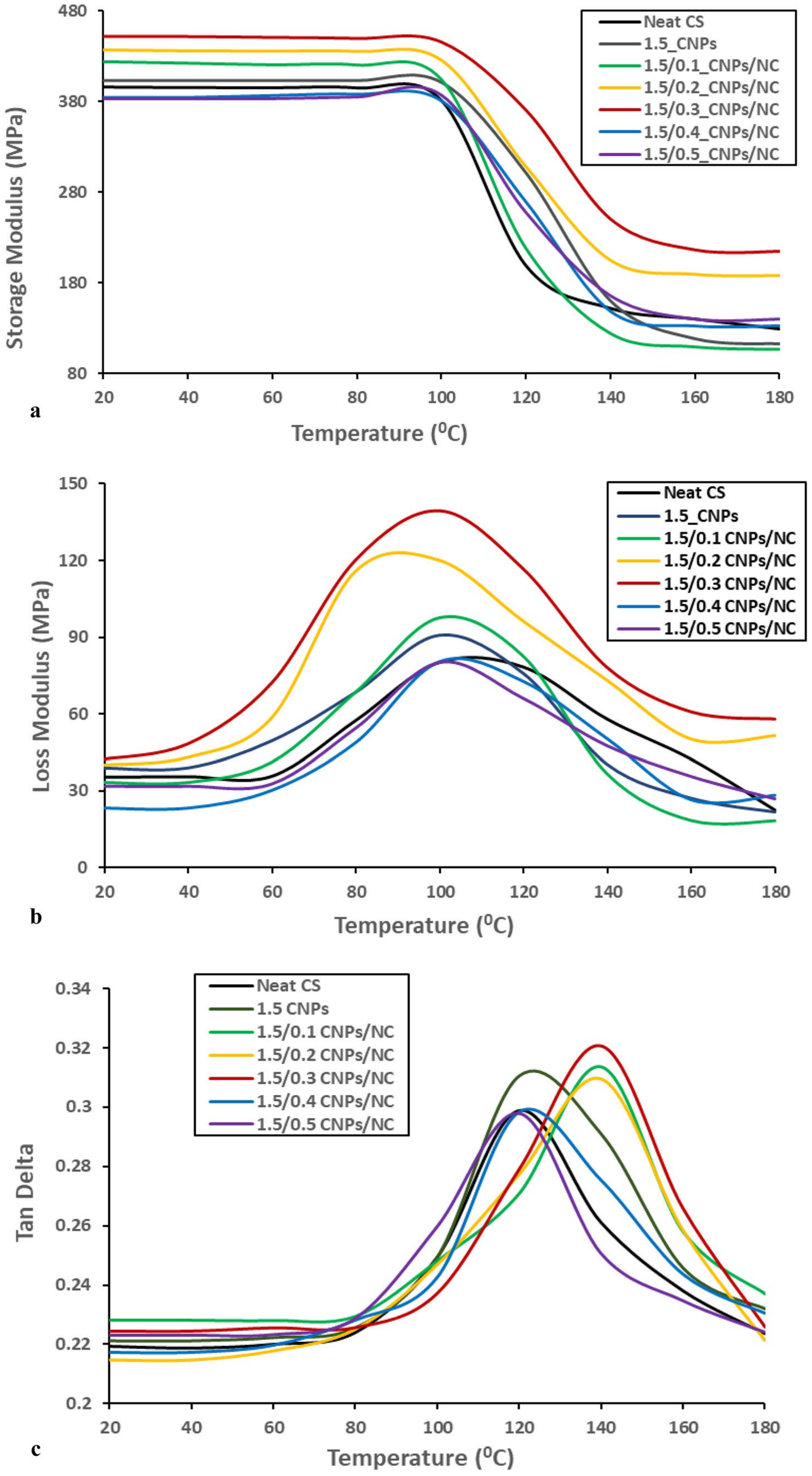


Fig. 8 **a** Storage modulus of neat CS and CS_CNPs/NC bioplastic materials with varying weight fraction of (0.1 – 0.5 wt.%) nanoclay. **b** Loss modulus of neat CS and CS_CNPs/NC bioplastic materials with varying weight fraction of (0.1 – 0.5 wt.%) nanoclay. **c** Tan delta of neat CS and CS_CNPs/NC bioplastic materials with varying weight fraction of (0.1 – 0.5 wt.%) nanoclay

Table 2 Glass transition temperature (T_g) of neat CS and CS_CNPs/NC bioplastic materials

Bioplastic Films	Tan Delta T_g (°C)	Storage modulus at 40 °C (MPa)	Storage modulus at 160 °C (MPa)	Loss modulus (°C)
Neat_CS	128	395.8	139.7	106
1.5_CNPs	130	403.2	118.3	102
1.5/0.1_CNPs/NC	138	422.6	108.9	102
1.5/0.2_CNPs/NC	140	435.8	189.6	94
1.5/0.3_CNPs/NC	142	451.2	215.8	98
1.5/0.4_CNPs/NC	126	384.5	132.2	102
1.5/0.5_CNPs/NC	124	383.3	139.7	102

had a very good reinforcing effect on the starch polymer system with β_f found to be 0.70. This was an indication of good nanoclay infused starch polymer bioplastic material. Nevertheless, the effectiveness of nanoclay infusion starch polymer is quite effective during relaxation process.

During relaxation process around T_g, the confinement region between polymer and fiber interface plays a crucial role in determining the effectiveness of reinforcement. The volume fraction of this confinement region C, can be measured by the Eq. (3).

$$(\text{Confinement region})\; C = 1 - \frac{W}{W_0} \tag{3}$$

where C is the volume fraction of the confined region of composite, W and W_0 are depended upon Tan δ peak value (Π) of composite and matrix respectively, which can be obtained from the Eq. (4).

$$(\text{Tan } \delta \text{ peak value})\; \mathrm{W} = \frac{\Pi \mathrm{Tan}\delta}{\Pi \mathrm{Tan}\delta + 1} \tag{4}$$

Table 3 Stiffness of the starch bioplastic determined from the storage modulus (*E'*) near the glassy region and the rubbery region

Polymer Films	Glassy region *E'* (MPa)	Rubbery region *E'* (MPa)	G_g^1/G_r^1	β_f
Neat_CS	396	152	2.46	-
1.5_CNPs	403	160	2.52	0.97
1.5/0.1_CNPs/NC	423	124	3.41	1.31
1.5/0.2_CNPs/NC	435	205	2.12	0.81
1.5/0.3_CNPs/NC	451	249	1.81	**0.70**
1.5/0.4_CNPs/NC	385	132.2	2.92	1.12
1.5/0.5_CNPs/NC	383	166	2.31	0.89

Lower value of the stiffness parameter (β_f) is an indication of higher effectiveness of the filler in the biocomposite film

The C value at 0.3 wt. % nanoclay improved bioplastic material are recorded in Table 4, was found to be 1.03, which is the highest for all hybrid starch bioplastic material. This suggests that clay filled starch polymer bioplastic material effectively contributed to the polymer relaxation process and stiffness parameter. However, it can be observed that the storage modulus of neat starch bioplastic material is lower than that of hybrid CS_CNPs/NC at 0.1 wt. % to 0.3 wt. % clay loading, but higher than 0.4 wt. % and 0.5 wt. % clay filled bioplastic as seen on Fig. 8a, among all the bioplastic series in glassy phase.

Water uptake properties

Water absorption is an important factor in polymer biocomposite film. One of the main disadvantages of starch is its hydrophilic behaviour [41]. The present of hydroxyl in starch makes it a polar substance that attract and absorb water easily. Although the present of glycerol as a plasticizer reduces the absorption rate. From the results of water absorption bioplastic films (Fig. 9), the water absorption rate was high in neat CS bioplastic after 24 h. Hence, the neat bioplastic starts to dissolve at a certain period. All the CS_CNPs/NC bioplastic materials also tends to absorb water at the same period of 24 h; however, the absorption rate starts to reduce without getting dissolved like the neat bioplastic. CNPs have a greater diffusion coefficient because absorption of water could continue, and swelling can increase through the diffusion transport of water via the starch bioplastic material.

However, the water absorption rate was reduced at the addition of nanoclay. This nanoclay slow down the effect of water absorption rate. It can be concluded that water interaction with the bioplastic material changes the CS bioplastic drastically since the starch bioplastic contains no reinforcing

Table 4 Confined region of composite determined from the tan delta peak values of starch bioplastic materials

Polymer Film	Tan δ	Tan δ + 1	Ratio	C
Neat	0.3104	1.3104	0.2369	-
1.5_CNPs	0.2989	1.2989	0.2301	0.97
1.5/0.1_CNPs/NC	0.3126	1.3126	0.2382	1.01
1.5/0.2_CNPs/NC	0.3094	1.3094	0.2363	1.00
1.5/0.3_CNPs/NC	0.3208	1.3208	0.2429	**1.03**
1.5/0.4_CNPs/NC	0.2985	1.2985	0.2299	0.97
1.5/0.5_CNPs/NC	0.2979	1.2979	0.2295	0.97

Higher confinement region (C) is an indication of better nanoclay improved biocomposite film

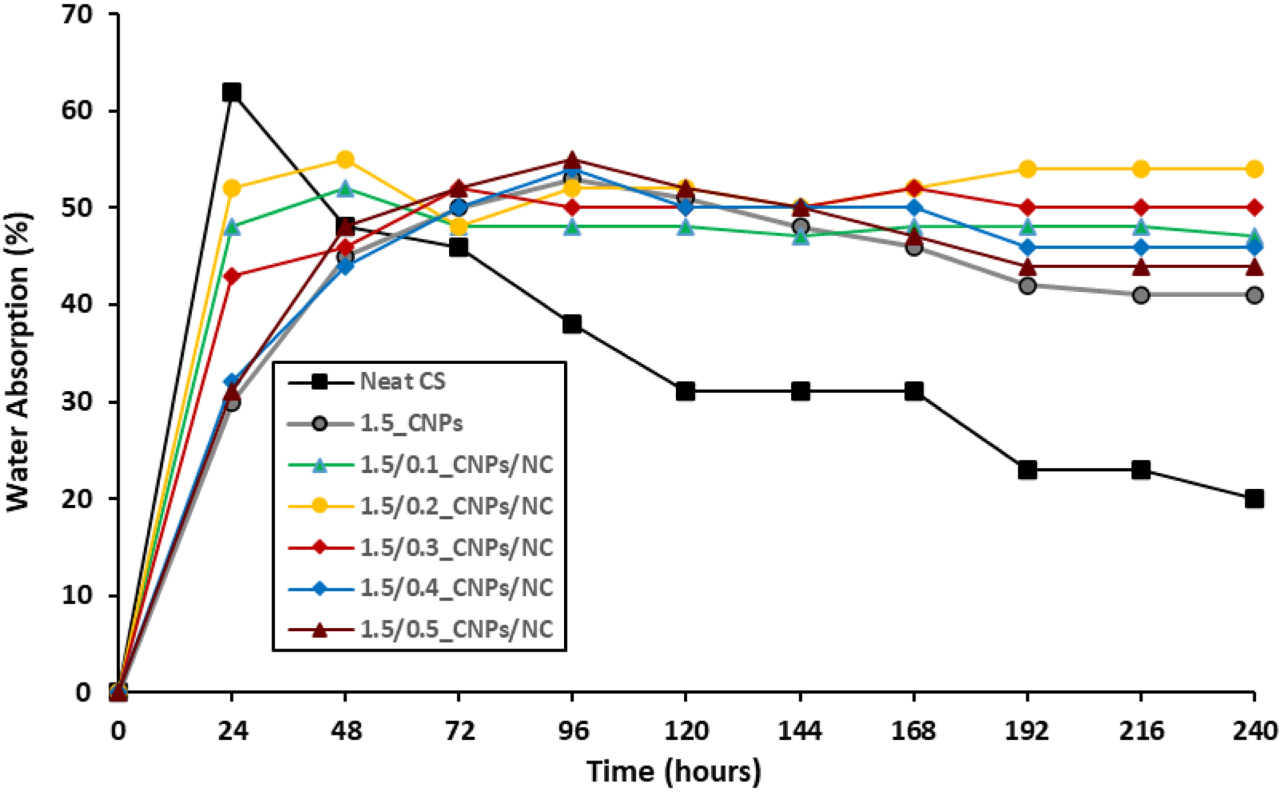


Fig. 9 Water uptake rate of neat CS and CS_CNPs/NC bioplastic materials with varying weight fraction of (0.1 – 0.5 wt.%) nanoclay

agents. This weakens the interaction among the starch molecules and make the molecular motion flexible. It also causes partial or completely degradation of the CS bioplastic due to the bioplastic being embedded in the water. The incorporation of nanoclay in the CNPs filled bioplastic film normalizes the water uptake. This was because of the glycerol gelatinization reaction in the starch bioplastic, which causes interconnecting bonds of CNPs/NC and the CS starch polymer matrix. It can be clearly noticed from (Fig. 9) that the absorption rate starts to increase and was later normalizing as more nanoclay are being added. However, there is consistency in the absorption rate at some point, which is attributed to the fact that the presence of nanoclay reduces the hydrophilicity of the bioplastic material.

Conclusion

In this work, interfacial properties of nanoclay (NC) on cellulose nanoparticles (CNPs) filled corn starch (CS) bioplastic material was studied. Various CNPs concentration (0.5 – 2.5 wt.%) were dispersed in cornstarch biopolymer matrix to form bioplastic films. Cornstarch bioplastic filled with 1.5 wt.% of CNPs showed optimum improvement in thermal and mechanical properties. Tensile result showed that increasing the CNPs weight fraction progressively increase the tensile strength of the bioplastic from 1.761 MPa to 2.263 MPa at an increase of 1.5 wt. % CNPs filler. Furthermore, nanoclay (NC) of varying weight percentage (0.1 – 0.5 wt. %) were added to the optimum improved 1.5 wt.% CNPs filled cornstarch bioplastic material. Further addition of nanoclay up to 0.3 wt. %, increase the tensile strength to 4.885 MPa. The hybrid 1.5/0.3_CNPs/NC filled bioplastic tensile strength and modulus was increase by 115% and 639% respectively when compared to 1.5_CNPs filled bioplastic material. The morphological analysis reveals that bioplastic with little addition of 0.3 wt. % nanoclay improved the bioplastic material by breaking up of cellulose filler agglomerations in the mixing ratio of the cellulose reinforced starch bioplastic material. The TEM image shows that individual cellulose-fiber was randomly dispersed in the starch polymer just like the micrographs of whisker shaped particles without any aggregation. By introducing NC in the CNPs reinforced bioplastic material, the properties of the bioplastic material were improved. FTIR result shows increase in the intensity of the %Transmittance up to 0.3 wt. % clay loading, this causes a good bonding of the CS_CNPs/NC bioplastic material, leading to increase in the mechanical and thermal properties of the bioplastic material. Within the five peaks selected, 23%, 11%, 13%, 15% and 50% respectively were observed in CS_CNPs/NC with 0.3 wt.% nanoclay addition around 3275 cm^{-1}, 2916 cm^{-1}, 1630 cm^{-1}, 1331 cm^{-1} and 995 cm^{-1} wave numbers, when compared to neat CS bioplastic film %transmittance peak with 3208 cm^{-1}, 2924 cm^{-1}, 1630 cm^{-1}, 1331 cm^{-1} and 999 cm^{-1} wave numbers. DMA result shows that the T_g of CS_CNPs/NC polymer bioplastic increased by 14 °C from 128 °C to 142 °C with the addition of 0.3 wt. % nanoclay. The stiffness parameter (β_f) of the bioplastic showed that during relaxation stage, the modified bioplastic material was quite effective when compared to the neat bioplastic film. Both the stiffness parameter (β_f) and confinement region (C) of the bioplastic during relaxation stage were 0.70 and 1.03 respectively for hybrid fillers at 1.5/0.3_CNPs/NC. Water uptake result revealed that NC and CNPs addition protects the biofilm against dissolution and water uptake. The incorporation of nanoclay in the CNPs filled bioplastic film normalizes the water uptake. There is consistency in the absorption rate at some point, which is attributed to the fact that the presence of nanoclay reduces the hydrophilicity of the bioplastic material.

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Declarations

Conflicts of interest The authors declare that the authors have no conflict of interest as all authors are affiliated to the same institution as academic staff and students.

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