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Hybrid films of cellulose nanofibrils, chitosan and nanosilica—Structural, thermal, optical, and mechanical properties

Mostafa Y. Ismail¹, Minna Patanen², Juho Antti Sirviö¹, Miikka Visanko¹, Takuji Ohigashi³, Nobuhiro Kosugi³, Marko Huttula², Henrikki Liimatainen¹

¹Fibre and Particle Engineering, P.O. Box 4300, FI-90014, University of Oulu, Finland

²Nano and Molecular Systems Research Unit, Faculty of Science, P.O. Box 3000, FI-90014, University of Oulu, Finland

³UVSOR Synchrotron Facility, Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

Corresponding Author.

Henrikki Liimatainen

Henrikki.Liimatainen@oulu.fi

Highlights

- We report the structural, chemical, and mechanical properties of hybrid films.

- Synchrotron-based microscopy verified the composition and structure of the film.
- Films show high mechanical properties, thermal stability and UV-absorption ability.

Abstract.

Organic-inorganic hybrid films were fabricated from cellulose nanofibrils (CNF) and nanosilica (5 - 30% wt) embedded in a chitosan (Chi) biopolymer matrix using a slow evaporation method. The self-standing films exhibited high strength and modulus up to 120 ± 5 MPa and 7.5 ± 0.4 GPa, respectively, which are remarkably high values for biopolymer/chitosan hybrids. Scanning electron microscopy showed that the nanosilica is formed of larger aggregates within the lamellar CNF network structure. This observation was further confirmed using synchrotron-based scanning transmission x-ray microscopy (STXM) with the capability to determine the spatial and chemical distribution analysis of the constituents of films. It is interesting that the thermal stability of the hybrid films improved as the nanosilica content increased. Furthermore, the nanosilica effectively filled the pores in the CNF network, thus decreasing the UV transmission and the visible light transmittance of the films.

Keywords: Nanopaper, nanocomposites, spectroscopy, STXM, XPS, chitosan

1. Introduction

Cellulose nanofibrils or nanofibers (CNF) have been a keen focus of researchers during the last decade due to outstanding characteristics such as their good stiffness/strength to weight ratio, availability, and renewable origin (Benítez & Walther, 2017). Hybrid biomaterials and composites fabricated from CNFs are popular due to their relatively high strength, remarkable barrier properties, and ability to embed variable functional constituents (Börjesson, Sahlin, Bernin, & Westman, 2018; Liimatainen et al., 2013; Oksman et al., 2016). CNF composites

typically exhibit a hierarchical structure that can mimic natural composites such as classic nacre-like morphology (Espinosa, Rim, Barthelat, & Buehler, 2009). CNF is embedded in a continuous matrix that forms a porous network wherein inorganic particles can incorporate themselves (Sehaqui, Zhou, Ikkala, & Berglund, 2011), providing novel properties for the hybrid materials. These properties make the material suitable for applications such as barrier coatings, optoelectronic devices, and packaging films (Lavoine, Desloges, Dufresne, & Bras, 2012; Liimatainen et al., 2013).

Chitosan is a linear polysaccharide composed of $\beta(1\rightarrow4)$ -linked D-glucosamine (deacetylated unit) randomly allocated with a N-acetyl-D-glucosamine (acetylated unit) (Ahlafi et al., 2013). Chitosan has antibacterial properties due to the interaction of charges between the polycationic chitosan and the microbial cell walls (Chan, Mao, & Leong, 2001; Park, Marsh, & Rhim, 2002). Moreover, chitosan is promising as a packaging material, not only for its antibacterial properties—which can help to preserve food—but also for its antioxidation ability and lower permeability when filled with natural antioxidants such as green tea extract (Siripatrawan & Noipha, 2012) and olive pomace (de Moraes Crizel et al., 2018).

Silica (SiO_2) is one of the most complex families of materials and plays a role in synthetic products with low production costs (Ruiz, Ferrão, Cardoso, Moncada, & dos Santos, 2016). SiO_2 nanoparticles have been used in many areas, such as catalysis, electrochemistry, coatings, and chromatography (Liu et al., 2011; Loh et al., 2014; Wang et al., 2015). Nanosilica has been found to be effective in filling the pore structure in a cellulose network with low dispersion. Some studies report the formation of nanosilica clusters of 70 nm to 4 μm (Garusinghe et al., 2017), which can play a role in the pore filling in the fiber networks. This, in turn, can affect the mechanical and thermal properties of CNF hybrid structures (Fu et al., 2016; Witoon, Chareonpanich, & Limtrakul, 2009).

In the present study, we incorporated cellulose nanofibers and nanosilica as reinforcements and functional nanofillers in a chitosan matrix, the combination of these constituents can result in a sustainable packaging material with tailored characteristics such as microbial resistance with the help of chitosan, high strength and stiffness and biodegradability with the aid of CNF and nanosilica (Kargarzadeh et al., 2018). In particular, the relationship between the structure and composition of CNF hybrids and their mechanical, optical, and thermal performance were investigated. First, we utilized field emission scanning electron microscopy (FESEM) to understand the morphology of the hybrids. Chemical characterization was carried out using x-ray photoelectron spectroscopy (XPS) and synchrotron-based scanning transmission soft x-ray microscopy (STXM), the latter technique also being capable of showing the spatial distribution of hybrid constituents. The mechanical characteristics of CNF hybrids were determined using a standard tensile test, and thermogravimetric analysis (TGA) was used to analyze the thermal stability of the hybrids. Finally, UV-vis transmission of the films was also investigated.

2. Experimentation

2.1. Materials.

CNFs were prepared from bleached sulfate spruce pulp acquired in the form of dry sheets from Stora Enso, Veitsiluoto, Finland. A mechanical grinding method with a Masuko grinder was used in the CNF fabrication as reported in our previous work (Visanko et al., 2017). In this work the pulp was passed once through a 0 and 50 μm disc clearances, and 10 times through the 100 μm disc clearance.

Chitosan was purchased from Sigma-Aldrich Co. (Germany) and was used without any further refinement. The chitosan possessed a medium molecular weight (190,000-310,000 grams/mole) and had degree of deacetylation of 67.2% (Sirviö, Visanko, & Liimatainen, 2016).

Nanosilica (Sigma-Aldrich Co. (Germany)), was characterized using a transmission electron microscope (TEM) (Figure 1, S1) with a particle size of 5 to 7 nm, a surface area of $359 \pm 25 \text{ m}^2/\text{g}$, and a bulk density of 0.037 g/cm^3 .

2.2. Preparation of CNF-chitosan-nanosilica hybrid films.

A chitosan solution (1 wt%) was prepared by mixing chitosan powder (4 g) with acetic acid (2 wt% in water) to obtain a solution of 400 ml with a pH of 3.75. The CNF suspension (0.96 wt% dry material) and chitosan solution were mixed together (1:1 dry mass ratio) and stirred for 10 minutes with a magnetic stirrer. Then the desired amount of nanosilica (5, 10, 20, 30 wt% of the whole weight) was added gradually while stirring (to decrease agglomeration) for another 5 minutes. The solution was further homogenized with an UltraTurrax (UT) (IKA T25, Germany) mixer for 2 minutes at 1,200 rpm to improve the dispersion of the components. Finally, the solution was cast in a petri dish to form hybrid films with a grammage of 40 g/m^2 . The cast solutions were allowed to dry freely in the conditioning room (with 50% humidity) until self-standing hybrid films were obtained.

In addition, reference films were fabricated from pure CNF, chitosan, and their dual mixture (1:1 wt. ratio). A schematic illustration of the fabrication process and a summary of the prepared films are shown in Figure 1 and Table 1.

Figure 1: A schematic diagram showing the fabrication of CNF-chitosan-nanosilica hybrid films.

Table 1: Summary of prepared hybrid film samples.

Specimen	Composition (%)(CNF/chitosan/nanosilica)	(wt-	Average thickness (μm)	Nomenclature
CNF	100/0/0		31.9 ± 0.7	CNF
Chitosan	0/100/0		42.3 ± 1.6	Chi
CNF + Chitosan	50/50/0		38.2 ± 2.5	CNF-Chi
CNF + Chitosan + 5% Nanosilica	47.5/47.5/5		36.1 ± 1.8	H5%
CNF + Chitosan + 10% Nanosilica	45/45/10		32.4 ± 2.1	H10%
CNF + Chitosan + 20% Nanosilica	40/40/20		26.9 ± 2.2	H20%
CNF + Chitosan + 30% Nanosilica	35/35/30		31.8 ± 2.0	H30%

As indicated by the film thickness values, pure CNF resulted in the densest structure while more bulky structure was obtained with pure chitosan. The combined films had the thicknesses varying between the values of these pure materials when taking account the standard deviations, except the film with 30% of silica.

2.3. Field emission scanning electron microscopy (FESEM).

A FESEM (Zeiss Ultra Plus, Carl Zeiss SMT AG, Germany) was employed to study the morphology of the hybrid and reference films in planar and cross-sectional directions. Films were coated with Pd and a 3-5 kV acceleration voltage was used.

2.4. X-ray photoelectron spectroscopy (XPS).

Thermo Fisher Scientific ESCALAB 250Xi (UK) with a monochromatized Al K α -ray source (specifications described in our previous work [Laitinen et al., 2017]) with a total photoelectron energy resolution of 0.4 eV was used to chemically analyze the films. Data analysis was performed using Avantage Software (UK). Atomic concentration ratios were calculated from the peak areas. The C 1s, O 1s, and N 1s peaks were decomposed and fitted with the software's 70:30 Gaussian–Lorentzian product function.

2.5. Scanning transmission soft X-ray microscopy (STXM).

The structural details of the hybrid films were investigated on the BL4U undulator beamline at the synchrotron facility in Okazaki, Japan, using a 0.75 GeV UVSOR-III storage ring with a 300 mA current in top-up mode (Ohigashi et al., 2013). The samples were cut into thin specimens (~70 nm thick) and then subjected to monochromatic soft x-rays to measure the photoabsorption at the C 1s and Si 2p edges. The count rate was around 10^7 photons/s and the samples were constantly checked to ensure that no radiation damage occurred. Counting periods (dwell times) of 2-5 ms per pixel were used for imaging. The spatial resolution of the microscope is 30-55 nm and spatial step size varied from 1.6 μ m in coarse scans to 50 nm in high resolution scans. The energy scans were performed with a varying step size of 0.4-0.5 eV above- resonance region, 0.25 eV below- absorption edge, and 0.1 eV in the resonance region. STXM imaging was performed in a 'stack' manner at different photon energies.

All STXM data was analyzed using aXis2000 program as described in other studies (I. Koprinarov, Hitchcock, Li, Heng, & Stöver, 2001; I. N. Koprinarov, Hitchcock, McCrory, &

Childs, 2002). Image stacks and reference absorption spectra were converted to optical density (OD) using a spectrum recorded in a hollow area (where no sample existed). Each sample required approximately 2 hours of testing under helium atmosphere (20 mbar).

2.6. Mechanical properties.

An analysis of the mechanical properties of the films was performed with a universal tensile testing machine (Zwick/ Roell, Germany) equipped with a load cell of max 2.5 kN as described in the supplementary data.

2.7. Thermogravimetric analysis.

TGA measurements were carried out under nitrogen flow with Netzsch STA 449 F3 thermal analyzer apparatus (Germany) as reported in the supplementary data.

2.8. UV transmittance.

The transmittance of the hybrid films, the nanosilica filled and the pure reference films was measured at wavelengths of 200–800 nm using a UV–vis spectrophotometer (Shimadzu, Japan). In order to ensure the perpendicular arrangement of the film in correspondence with the incoming beam, the films were located between two quartz glass slides, then set up in a cuvette stand.

The transmittance (ratio of transmitted $[I]$ and incoming $[I_0]$ flux) depends on the absorption coefficient μ and the path length of the light x , as shown by the Beer-Lambert law

$$\frac{I}{I_0} = e^{-\mu x}, \quad (1)$$

This was used to convert the measured transmittance values to transmittance of equal thickness for easier comparison.

3. Results and Discussion

3.1. The structural characteristics of hybrids.

The obtained CNF-chitosan-nanosilica hybrid films were flexible and optically opaque with a thickness varying from 26 to 50 μm (Figure 1). Figure 2 shows the morphology of the

fabricated CNF-chitosan-nanosilica hybrids in planar and cross-sectional directions. The FESEM showed that the nanosilica particles tend to agglomerate in the hybrid structure. These aggregates were surrounded by the chitosan matrix and reinforced with a layered CNF network. The area of nanosilica aggregates ranged from 1.19 to 3.4 μm^2 as calculated from the FESEM images using Fiji[®] image analysis tool. The nanosilica surface containing hybrids was rougher and non-homogenous compared to the samples without the nanosilica filler. The nanosilica seemed to effectively seal the voids of a porous nanofiber network and was shown to be merged with the structure despite the aggregation.

Figure 2. FESEM images of a) CNF, b) CNF-Chi, and c) H30% surfaces and cross sectional areas of d) CNF, e) CNF-Chi, f) H30%, and g) H30% with a higher magnification to demonstrate the nanosilica aggregates.

3.2. Spectroscopy Investigation.

3.2.1. STXM.

As a complementary imaging method to FESEM, the STXM technique was used to analyze the hybrids. STXM is a nondestructive method that can detect the chemical and spatial distribution of constituents in a specimen. STXM has not been widely applied to nanocellulosic materials (Karunakaran et al., 2015). For reference, soft x-ray absorption spectra at the C K-edge of pure cellulose nanofibers, chitosan, and embedding resin were recorded (supplementary data [S1 Fig 2]). The hybrids were “sandwiched” between resin blocks for ultramicrotome sectioning and the reference spectrum of resin was collected to ensure that the thin sample region between the resin blocks was not affected by the embedding material.

Figure 3 (left) presents the optical density STXM images of 5% (Fig. 3d and e) and 10% (Fig. 3a and b) hybrid films and their average absorption spectra (Fig 3f and c, respectively). Figure 3a and d represent the sums of all the single energy image stacks below the C K-edge (shadowed range in spectra in Figures 3c and f), whereas Figures 3b and e show images obtained in the C K-edge resonant region. Figure 3a clearly shows a strongly absorbing white band below the C K-edge. When the energy is in the C K-edge resonance region, as shown in Figure 3b, thin (width <150 nm) lines are clearly highlighted. This indicates that the clearly visible band below the resonance threshold is the SiO₂ region, and the thinner stripes showing at the C K-edge resonance are possibly bundles of nanocellulose fibers that are aligned with the direction of cutting or wrinkles (that occurred during preparation) in the CNF-chitosan film. Similarly, the hybrid film containing 5% of nanosilica shows white spots below the resonance threshold (Figure 3d) and white lines at the C K-edge resonance energies (Figure 3e). Complementary to the FESEM images, STXM verifies the chemical composition of the agglomerates as silica in the hybrid.

Figure 3: (Left) Optical density images of 10% hybrid film imaged at a) below the threshold and b) above the C 1s absorption edge, and c) in the average absorption spectrum. 5% hybrid film d) below and e) above the C 1s absorption edge, and f) average absorption spectrum of the 5% hybrid. In spectra c) and f), the shadowed energy regions indicate energy levels below and on the resonance. threshold (Right) RGB maps of 10% film at g) C K-edge with h) corresponding spectra of indicated regions, i) at Si L2,3-edge, and j) spectra of indicated regions. Scale bar 1 μm .

Figure 3 (above) shows an example of how the spectral information of STXM imaging can be used to further differentiate the silica-rich regions of the hybrid film. The RGB maps were constructed using the “stack fit” function of the aXis2000 software, by extracting the absorption spectra of the C K-edge (Figures 3g and h) and Si L_{2,3}-edge (Figures 3i and j). The weights of the respective component spectra give a specific RGB mixed color to each pixel. The green areas with a cellulose-type spectrum show similar lines to those seen in Figure 3e. The region indicated in blue is selected from the uniform part of the hybrid and its spectrum is close to both the chitosan and cellulose spectra. The red region indicates SiO₂ at the Si L_{2,3}-edge (D. Li et al., 1994). We should note that the cross-section of carbon valence electrons is still significant in the Si L_{2,3}-edge region, although it is rapidly decreasing as a function of photon energy; therefore, even in the Si L_{2,3}-edge region, the assumed cellulose-rich regions in green show a rather strong absorption of carbon valence.

3.2.2. XPS.

The surface composition of the hybrids and reference materials was studied by means of XPS. The spectra are presented in supplementary data (S1 Figure 3) and the binding energies and mole fractions of the main chemical species are reported in Table 2. The C 1s photoelectron

spectrum of all the samples showed three major peaks at 284.8 eV, 286.4 eV, and 288.0 eV. Johansson et al. (Johansson & Campbell, 2004a) performed a detailed XPS study of cellulosic natural fiber materials and our reference spectrum of CNF agrees in general with their reported spectra. Both cellulose and chitosan have all their carbon atoms bound to one or two oxygen atoms, or to a nitrogen atom (for chitosan) so, ideally, the C-(C, H) peak should not be present. As the samples were produced and kept in ambient air and not sputtered before the XPS, this peak represents the adventitious carbon contamination of the surface. When this contamination peak was not taken into account for calculating the atomic percentages, we obtained stoichiometric ratios between C, O, and N: for cellulose, 53% of C and 46% of O (stoichiometric percentages of 54.5% and 45.5%); for chitosan 53% of C, 38% of O, and 8% of N (stoichiometric percentages of 55.6%, 36.1%, and 8.3%, respectively when taking into account the deacetylation degree of 67%). This indicates that the contamination was hydrocarbon surface contamination and did not, for example, originate from the remaining extractives of cellulose (Gray, 1978; Johansson, Tammelin, Campbell, Setälä, & Österberg, 2011). Carbon bound to a single oxygen or nitrogen atom C-(O, N) gives a peak at 286.4 ± 0.1 eV, and carbons bound to two oxygen atoms or a nitrogen and an oxygen atom O-C-O/N-C=O contribute to a peak around 288.0 ± 0.1 eV (Gray, 1978; Johansson & Campbell, 2004b; Matijević, 2008; Rouxhet & Genet, 2011). In general, the C 1s XPS was not affected by the addition of silica, except for the H30% sample, which showed significantly more surface contamination than other hybrids and was excluded from further XPS analysis. The ratio between C-(O, N) and O-C-O/N-C=O was 79% to 21% in CNF-Chi reference film, very close to the expected ratio of 81% to 19%. This ratio did not vary more than 3% for the hybrids with added silica. The N 1s spectrum shows a peak at 399.5 ± 0.1 eV in (Chi, CNF-Chi and H5%), attributed to non-protonated amine or amide (Maachou, Genet, Aliouche, Dupont-Gillain, & Rouxhet, 2013). The broad tail towards higher binding energies was fitted with one peak at

around 401.3 ± 0.3 eV. This was previously determined to be protonated amine (Maachou et al., 2013). In the O 1s spectrum of the same samples, the major peak at 532.8 ± 0.1 eV was due to the oxygen in the polysaccharide backbone of cellulose and chitosan. The O 1s peak is slightly asymmetric in the samples with chitosan as a matrix, and a second small peak was fitted at around 531.2 ± 0.1 eV, which was attributed to C=O in acetylated amine (Maachou et al., 2013). The oxygen signal of SiO₂ is expected to appear at 532.8 eV (Bancroft et al., 2009), overlapping with the main oxygen signal, and thus the addition of SiO₂ cannot be observed from the O 1s spectrum only. The nanosilica-filled hybrids showed the Si 2p_{3/2} peak at 103.2 ± 0.1 eV with a linewidth of approximately 1.3 eV, in line with the values reported for bulk SiO₂ (Bancroft et al., 2009). A small peak at 101.5 ± 0.3 eV with a very low atomic percentage (0.1-0.3%), the intensity of which did not depend on the percentage of nanosilica, was also observed for the all the nanosilica-filled specimens. This peak can be attributed either to another silicon oxidation state (Si²⁺) or to contamination on the surface of the hybrid film; for example, by organic silicon. (Ghita et al., 2011; Himpsel, McFeely, Taleb-Ibrahimi, Yarmoff, & Hollinger, 1988)

Table 2: XPS analysis of the main components in the hybrids and reference materials. Atomic concentration is the fraction of an atom in given chemical environments which gives rise to a well-identified peak in XPS. The percentage is given with respect to other elements except hydrogen. Error bars for the energies are ± 0.1 eV.

	C 1s			O 1s	N 1s	Si 2p _{3/2}
	Component			Component	Component	Component
	C-C	C-(O,N)	O-C-O / N-C=O	O-C	N-C	SiO ₂
CNF						
Binding Energy (eV)	284.8	286.5	287.9	532.8	400.0	
Atomic concentration (%)	25.2	31.0	7.1	33.8	0.4	
Chi						
Binding Energy (eV)	284.8	286.4	288.0	532.8	399.4	
Atomic concentration (%)	22.0	31.8	9.8	26.8	5.9	
CNF-Chi						

Binding Energy (eV)	284.8	286.4	288.0	532.8	399.5	
Atomic concentration (%)	26.6	30.3	8.1	26.7	3.3	
H5%						
Binding Energy (eV)	284.8	286.4	288.0	532.8	399.5	103.2
Atomic concentration (%)	25.8	29.9	7.9	27.8	3.3	0.5
H10%						
Binding Energy (eV)	284.8	286.4	287.9	532.8	399.5	103.2
Atomic concentration (%)	19.0	31.8	9.4	26.9	3.5	1.4
H20%						
Binding Energy (eV)	284.8	286.4	287.9	532.7	399.5	103.2
Atomic concentration (%)	14.9	32.5	8.8	34.0	3.7	2.8

The atomic percentages of Si determined by XPS are much lower than the ratios of raw materials used to prepare the films, namely 0.6, 1.7, 3.2, and 5.4% for H5%, H10%, H20%, and H30%, respectively (surface carbon contamination excluded). This can be understood by taking into account that XPS is an extremely surface sensitive technique and that the inelastic mean free path in SiO₂ is three times smaller than that of the glucose (Tanuma, Powell, & Penn, 1994). Therefore, the information is obtained from only the topmost part of the agglomerates. It is also possible that slight sedimentation of nanosilica occurs during the preparation lowering the amount of silica on the surface. Similar type of non-uniform behavior was observed for cellulose nano crystals in rubber matrix by Flauzino Neto et al., 2016.

3.3. Mechanical properties of hybrids.

Compared to pure biopolymer-based materials, the addition of cellulose nanofibers can result in an increase in magnitude of up to three-times in the modulus of elasticity and of up to 5 times in the tensile strength due to the strong hydrogen bond in the CNF networks(Favier,

Chanzy, & Cavaille, 1995; Tingaut, Zimmermann, & Lopez-Suevos, 2010; Tingaut, Zimmermann, & Sèbe, 2012). Pure CNF nanopaper has high strength and modulus up to about 200 MPa and 10 GPa (M. Henriksson, Henriksson, Berglund, & Lindström, 2007; Marielle Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008)

Pure chitosan films showed the lowest tensile strength and modulus but a high strain value (Table 3), indicating the high elasticity of chitosan polymer. The addition of the CNFs increased the strength by about 40% compared to the pure chitosan. Stiffness also increased almost twofold as indicated by Young's modulus (E_t) values from 4 GPa to 8 GPa. The pure CNF reference film showed the highest tensile strength and Young's modulus values of 130 MPa and 9 GPa, respectively, due to its high specific strength, homogeneity, and self-assembly of the nanofibrils (W. Wang et al., 2015). However, pure CNF film possessed low strain.

The strength of the hybrids increased when a small amount of nanosilica (5%) was added. This was presumably due to the decrease of the matrix's deformability (Ruan, Zhang, Rong, & Friedrich, 2004). However, the stiffness did not change. When higher nanosilica quantities were used, the strength and stiffness of the hybrids decreased (as seen in the H10% and H20% samples) and as seen in similar structures (Liimatainen et al., 2013), probably due to the agglomeration of the nanosilica and inhomogeneity caused to the CNF network as supported by the FESEM and STXM images. The agglomeration phenomenon was probably due to the decrease of the distance between the nanosilica particles, increasing the aggregation factors (Van der Waals attraction) and reducing the dispersion factors (electrostatic or steric repulsion), which in turn resulted in an irreversible agglomeration (Tadano et al., 2014) and led to the decrease of the strength and modulus. In addition, at the pH of our mixture (pH ~4), large mesopores may form in the silica particles, which can act as voids and decrease the strength of the hybrids (Witoon et al., 2009).

The strain of the nanosilica-loaded films was constant across the different hybrid samples. Overall, the observed strength and modulus of the hybrids were high for hybrid film (H.P.S et al., 2016). Additionally, our films showed comparable strength and modulus with other nanosilica reinforced polymer composites (Conradi, 2013). A summary of the mechanical properties of the hybrids is shown in Table 3

Table 3: Young's Modulus (E_t), ultimate tensile strength (σ_M) and strain (ϵ_M) of the hybrid and reference films.

Sample	E_t (GPa)	σ_M (Mpa)	ϵ_M (%)
CNF	9.0 ± 0.4	130.5 ± 11.7	6.5 ± 0.9
Chi	4.0 ± 0.3	72.0 ± 5.9	20.8 ± 5.7
CNF-Chi	7.4 ± 0.4	114.1 ± 6.5	7.4 ± 1.7
H5%	7.5 ± 0.4	119.8 ± 5.6	7.5 ± 0.4
H10%	6.7 ± 0.6	93.0 ± 3.8	5.9 ± 0.7
H20%	4.7 ± 1.0	82.0 ± 8.9	7.5 ± 1.3
H30%	6.0 ± 0.3	96.4 ± 10.5	6.4 ± 1.6

Figure 4: Tensile stress-strain curves of CNF-chitosan-nanosilica hybrid films. The curves presented are the average curves of all six curves of each sample.

3.4. Thermogravimetric analysis.

The TGA was measured, in addition, DTG; the first derivative curve of the TGA was calculated for all the films including the reference films. The onset temperature (where the material starts to degrade as indicated by the change in the slope of the curves, as shown in the zoomed in area in Figure 5 b) of all the films and the rate of the thermal degradation of the films are shown in Figure 5. The onset temperature increased when the CNF was added to the pure Chi film. Additionally, the H30% appeared to be more thermally stable than the other samples due to the large nanosilica content. Chitosan showed a continuous thermal degradation without any plateau level.

The DTG curves of all the films showed a first degradation step ($T_{5\%}$) at around 100 °C, corresponding to the removal of low molecular volatile substances (i.e. bound water) (Chen et al., 2011). The second peak ($T_{50\%}$) was attributed to the degradation of the major components of the hybrids of the macromolecule. $T_{50\%}$ degradation of the chitosan occurred at a lower temperature (~ 200 °C) compared to all the other films due to its molecular structure and acetylation degree (Celebi & Kurt, 2015; de Britto & Campana-Filho, 2007). Pure films (Chi, CNF) showed one degradation peak ($T_{50\%}$), indicating the thermal degradation of a single component of the film.

The increase in the amount of the nanosilica caused a decrease in terms of the weight loss rate of the hybrids from 7%/min (for Chi) to 4%/min (for H30%) as shown in Figure 5. This can be explained by the presence of a thermally stable inorganic filler such as nanosilica, which can decrease the overall degradation rate. Our hybrids showed good thermal endurance compared to that of the epoxy resin–nanosilica composites (Jumahat, Zamani, Soutis, & Roseley, 2014).

Figure 5: (a) DTG and (b) TGA curves of hybrid and reference films.

3.5 Optical transmittance.

An average film thickness of 30 μm was taken to calculate optical transmittance using Beer-Lambert's law as shown in (Figure 6). At the start of the visible light range (~ 380 nm), chitosan showed the highest clarity due to its 76% transmittance ability. In addition, at the end of the visible range (800 nm), chitosan showed a 90% transmittance ability. Compared to chitosan, CNF-Chi had a 10% and 15% lower transmittance at both the beginning and end of the visible range; hence the opaque appearance of the CNF-Chi film, additionally, the CNF's light absorption can be affected by its fiber size, density and surface properties (P. Li, Sirviö, Haapala, Khakalo, & Liimatainen, 2019). Adding low wt% nanosilica filler affects the visible light in an incremental way. However, the higher the SiO_2 wt%, the lower the transmission at a higher wavelength due to agglomeration as supported by the STXM images showing the bands of nanosilica across the film. Transmittance in the visible light range decreased by 5-10% in the 20 and 30 wt% filled hybrids.

The amount of nanosilica changes the curve reduction in the UV region (>340 nm) (Xiong, Wu, Zhou, & You, 2002). In addition, the nanosilica's optical properties can differ due to the presence of OH groups in the structure, impurities, and voids (Siegel, 1974). Nanosilica's interaction with UV light is not yet fully understood due to its small size. However, it is mainly

dependent on the production of the parameters of the nanosilica and on the pH of the medium they are contained in (Kitamura, Pilon, & Jonasz, 2007).

Figure 6: Transmittance spectra of reference, nanopaper, and nanosilica filled specimens.

4. Conclusions

Multi-technique characterization of hybrid chitosan, cellulose nanofibrils, and nanosilica films was performed in terms of both their structural and mechanical properties. XPS analysis was performed on the hybrids and it indicated that the silica was underrepresented in the vicinity of the information depth of XPS, which can be understood by its tendency to form agglomerates and a smaller inelastic mean free path in SiO_2 compared to cellulose and chitosan. Sub-micron spatial resolution SEM and STXM imaging were used to confirm the “brick-and-mortar” morphologic structure with agglomerates filling the voids in the structure. STXM analysis verifies the composition of the agglomerates to be SiO_2 . STXM-based chemical analysis demonstrated spatially resolved x-ray absorption and provided chemical information for the morphology of the organic and inorganic components.

It was shown that the chitosan film’s properties were improved when CNF was incorporated in the structure. The Chi-CNF films showed strong mechanical properties. To promote better mechanical and thermal properties and selective UV transmission, different wt% of nanosilica were added. In terms of mechanical properties, the 5 wt% nanosilica improved the ultimate

tensile strength and modulus (119.8 ± 5.6 and 7.5 ± 0.4), but greater nanosilica wt% decreased the mechanical properties of the structure due to agglomeration. In terms of thermal stability, the more nanosilica that was added, the more thermally stable the films became, showing the greatest thermal stability with 30 wt% filler. The nanosilica changed the light absorption in the UV region, making the films more responsive to UV light and therefore appropriate for improved packaging material.

Author Information

Notes.

The authors declare that there are no competing financial interests.

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