



Review

A review on chitosan-cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their applications



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ABSTRACT

Chitin is one of the most abundant natural polymers in world and it is used for the production of chitosan by deacetylation. Chitosan is antibacterial in nature, non-toxic, and biodegradable thus it can be used for the production of biodegradable film which is a green alternative to commercially available synthetic counterparts. However, their poor mechanical and thermal properties restricted its wide spread applications. Chitosan is highly compatible with other biopolymers thus its blending with cellulose and/or incorporation of nanofiber isolated from cellulose namely cellulose nanofiber and cellulose nanowhiskers are generally useful. Cellulosic fibers in nano scale are attractive reinforcement in chitosan to produce environmental friendly composite films with improved physical properties. Thus chitosan based composites have wide applicability and potential in the field of biomedical, packaging and water treatment. This review summarises properties and preparation procedure of chitosan-cellulose blends and nano size cellulose reinforcement in chitosan bionanocomposites for different applications.

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Contents

1. Introduction	217
2. Chronological events and applications of chitosan	217
3. Types and advantages of nanocellulosic fibers	217
3.1. Types of nanocellulose fibers	217
3.2. Advantages of nanocellulosic fibers	219
4. Chitosan reinforced nanocellulose biocomposites	219
4.1. Chitosan-cellulose nanofiber (CNF) nanocomposites	219
4.1.1. Properties of chitosan-cellulose nanofiber nanocomposites	219
4.1.2. Preparation process of chitosan-cellulose nanofiber nanocomposites	219
4.2. Chitosan-cellulose nanowhisker (CNW) nanocomposites	219
4.2.1. Properties of chitosan-cellulose nanowhisker nanocomposites	219
4.2.2. Preparation process of chitosan-cellulose nanowhisker nanocomposites	220
4.3. Chitosan-cellulose nanowhisker polyelectrolytes	221
4.3.1. Properties of chitosan-cellulose nanowhisker polyelectrolytes	221
4.3.2. Preparation process of chitosan-cellulose nanowhisker polyelectrolytes	222
4.4. Multi-components chitosan-nanocellulose nanocomposites	222
4.4.1. Properties of multi-components chitosan-nanocellulose nanocomposites	222

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4.4.2. Preparation process of multi-components chitosan-nanocellulose nanocomposites	222
5. Chitosan-cellulose blends	222
5.1. Properties of chitosan-cellulose blends	222
5.2. Preparation process of chitosan-cellulose blends	223
5.3. Potential, challenges and applications of chitosan-cellulose blend	224
6. Conclusions	224
Acknowledgement	225
References	225

1. Introduction

In recent years extensive efforts have been taken for the development of sustainable composite materials for various industrial purposes due to its renewability, biodegradability, low cost, non-petroleum based source and low carbon dioxide release (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). In this regard, polysaccharide particularly cellulose and chitin are very important because they are the two most abundant natural polymers.

Chitin is a typical constituent of the cell walls of fungi, the exoskeletons of insects, crustaceans and radulae of mollusks. Chitin is a linear polysaccharide comprised of β -1,4-*N*-acetylglucosamine. It is insoluble in common solvents because of its high crystalline structure and hydrogen bonding between carbonyl, hydroxyl and acetamide groups. Chitosan is obtained by *N*-deacetylation of chitin and it is composed of glucosamine and *N*-acetylglucosamine units (Yen, Yang, & Mau, 2009). Chitosan has been extensively studied for various applications because of its biocompatibility, biodegradability, mucoadhesiveness, and derivability from abundant and inexpensive biomass (Szymanska & Winnicka, 2015). It also possesses antimicrobial activity, wound healing properties and hemostatic activity which make chitosan based composites very useful in the field of biomedical. Moreover, it has also been used in agriculture as a fertilizer, in food as stabilizer and thickener, and in water treatment as ion exchanger (Yen, Yang, & Mau, 2008). Beside that chitosan is readily processed into nanofibers, sponges, nanoparticles, gel, beads, scaffolds, membranes and stand-alone films (Jayakumar, Menon, Manzoor, Nair, & Tamura, 2010). Chitosan films have poor mechanical properties which limit its applications. Functional properties of chitosan based composites can be improved by reinforcement of nano size cellulose (Fernandes, Freire, Silvestre, Pascoal Neto, & Gandini, 2011).

Cellulose is a linear homopolymer of β -D, 1,4, glucose unit linked by glycosidic bond. It is comprised of microfibrils having nano size diameter and surrounded by lignin and hemicellulose (Habibi, Lucia, & Rojas, 2010). Nano-cellulose is a term referring to either cellulose nanowhiskers (CNW) or cellulose nanofibers (CNF). Both types of nano-cellulose are used in various applications due to their low density, low cost, abundance, renewability, high mechanical properties, large surface area and aspect ratio, notable flexibility, specific barrier properties and low thermal expansion (Liu, Chen, Yue, Chen, & Wu, 2011). Nano-cellulose is extensively researched for decades due to their unique optical, rheological and mechanical properties. Nano sized cellulose could impart higher stiffness to the nanocomposites even at low concentration when incorporated in polymer matrices due to their large aspect ratio and ability to form interconnected network structures through hydrogen bonding. Their aforementioned characteristics and reinforcing ability makes them an ideal reinforcement agent in polymer composites. Modulus and bending strength of cellulose nanofibrils is 150 GPa (Helbert, Cavaille, & Dufresne, 1996; Šturcová, Davies, & Eichorn, 2005) and 10 GPa (Helbert et al., 1996), respectively, thus its incorporation in chitosan matrix can improve mechanical properties of chitosan based nanocomposite materials. This review effectively summarises the preparation procedure, properties and

applications of chitosan based cellulose blends and nano-cellulose composites, furthermore, their future potentials and challenges is also discussed.

2. Chronological events and applications of chitosan

As per available literature, when the amount of *N*-glucosamine units is higher than 50% it is called as chitosan and when the units of *N*-acetyl-glucosamine is more than 50% it is called chitin (Croisier & Jérôme, 2013). Chitin is highly insoluble with low chemical reactivity, however, chitosan possess some unique characteristics that make it more applicable as compared to chitin, including its availability in different physical forms, solubility in alkaline, acidic and neutral solutions etc (Tsigos, Martinou, Kafetzopoulos, & Bouriotis, 2000).

The use of chitosan has become increasingly popular due to growing concerns regarding the impacts of petroleum-based polymers on our environment. Recent developments in the field of chitosan lead towards its utilization in wide range of applications. Table 1 displays the chronological event of research on chitosan and its subsequent applications in various fields.

3. Types and advantages of nanocellulosic fibers

In total 36 single cellulose molecules joined together to form elementary fibrils having diameter of 5 nm, assembly of these elementary fibrils produce microfibrillated cellulose (MFC) with diameter of 20–50 nm and finally MFC packed together to create cellulose fibers (Lavoine, Desloges, Dufresne, & Bras, 2012).

3.1. Types of nanocellulose fibers

Generally there are two types of nanocellulose isolated from plant fiber; cellulose nanowhisker (CNW) and cellulose nanofibers (CNF). The main process to obtain CNW is acid hydrolysis using sulphuric acid, hydrochloric acid, etc. It is a rigid and short nanocrystal with rod-like structure (Fig. 1a). The cleavage of glycosidic bond, removal of amorphous regions and the persistence of intact crystalline domains occur during acid hydrolysis (Abdul Khalil et al., 2014, 2012). The difference between hydrolysis kinetics of crystalline and amorphous regions of cellulose leads to exclusion of amorphous parts during CNW production process (Habibi et al., 2010). CNW surface can be modified through reactive hydroxyl groups. Young's modulus of CNW ranges from 130 GPa (Sakurada & Nukushina, 1962) to 250 GPa (Zimmermann, Pohler, & Geiger, 2004). These values are close to the modulus of perfect crystals from native cellulose because CNW contain only a small number of defects (Siqueira, Bras, & Dufresne, 2010).

On the other hand, CNF is a flexible and has entangled network structure (Fig. 1b) which is isolated by mechanical methods such as high pressure homogenization, grinding, ultrasonication, etc. Usually in mechanical methods, some chemical or mechanical pre-treatments are performed in order to reduce energy consumption and to prevent the clogging of instrumental nozzle by breaking fibers in smaller fractions. Alkaline-acid, enzyme and TEMPO

Table 1
Chronological events of chitosan study and its related applications.

Year	Progress	Applications	References
1983	Proposed a new method for <i>N</i> -deacetylation of chitosan	Polymer	Domard & Rinaudo (1983)
1988	Identified the tissue organization stages regulated by chitosan	Tissue repair	Muzzarelli et al. (1988)
1999	Summarized some of the important developments related to food applications of chitin, chitosan and their derivatives	Food	Shahidi, Arachchi, and Jeon (1999)
2000	Processing, properties, and applications of chitosan as controlled drug release.	Controlled drug release	Gupta & Kumar (2000)
2001	The potential use of chitosan and its derivatives for the delivery of macromolecular drugs and vaccine	Mucosal drug and vaccine delivery	Van der Lubben, Verhoef, Borchard, and Junginger (2001)
2003	Increase the viscosity of food and act as a thickening agent	Food	Agulló, Rodríguez, Ramos, and Albertengo (2003)
2004	Biosensors for in situ measurements of environmental pollutants	Enzyme immobilizations	Krajewska, (2004)
2004	Recovery of toxic and/or valuable metal anions	Ultrafiltration and sorption	Chassary, Vincent, and Guibal (2004)
2005	Hydrogenation, oxidation, and fine chemical synthesis reactions	Heterogeneous catalysts	Guibal, (2005)
2008	Adsorption of dye from aqueous solutions in waste water treatment	Adsorption science	Crini & Badot (2008)
2009	Chitin fibers have comparable properties to those of collagen and lactide fibers	Biomedical applications of chitosan fiber	Pillai, Paul, and Sharma (2009)
2009	Hg(II) removal in waste water treatment	Removal of mercury from contaminated water	Miretzky & Cirelli (2009)
2010	Adsorption of selected heavy metals from aqueous media	Adsorption of Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Zinc	Wu, Tseng, and Juang (2010), Wan, Kan, Rogel, & Dalida (2010), Cao, Tan, Che, and Xin (2010)
2010	Cancer diagnosis, drug delivery, tissue, Engineering and wound dressing based on chitosan nanomaterials	Biomedical applications of chitin and chitosan based nanomaterials	Jayakumar et al. (2010)
2011	Bio-imaging, drug delivery, green chemistry, gene therapy, tissue engineering, wound healing	Biomedical applications	Dash, Chiellini, Ottenbrite, and Chiellini (2011), Anitha et al. (2011), Zhang, Tao, Li, and Wei (2011)
2012	Decontamination of organic pollutants	Biomedical and bio-mimetic optical nanomaterials	Lin, Huang, and Dufresne (2012)
2013	Chitosan and modified chitosan can chelate toxic pollutant like heavy metals and dyes	Bio-sensor and water treatment	Shukla, Mishra, Arotiba, and Mamba (2013)
2013	Chitosan has antibacterial and antifungal properties which qualify it for food protection	Edible films and coatings	Elsabee & Abdou (2013)
2013	Potential application in pharmaceutical sector	Kidney function modulator	Gavhane, Gurav, and Yadav (2013)
2014	Drug delivery of different therapeutic agents	Drug delivery based on self-assembled chitosan nanomaterials	Yang et al. (2014)
2014	Supported catalysts, antimicrobial supports, sensors etc	Metal ion biosorption	Guibal, Vincent, and Navarro (2014)
2015	In vitro and in vivo analyses should be conducted to assess the risk of using chitosan	Oxalate kidney stone formation	Fernandes Queiroz, Melo, Sabry, Sasaki, and Rocha (2015)

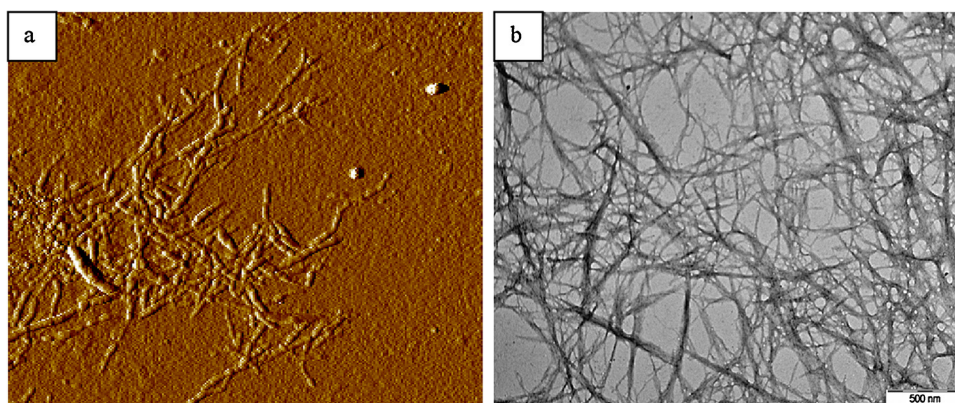


Fig. 1. (a) Atomic force microscopy image of kenaf bast CNW with diameter of 15 nm obtained from hydrolysis by 60% H_2SO_4 , 45 °C, 1 h, (b) transmission electron microscopy image of kenaf bast CNF with diameter of 10 nm obtained by high pressure homogenization at 50 MPa pressure.

(2,2,6,6-tetramethylpiperidine-1-oxyl) oxidization are main chemical pre-treatments, whereas, refining and cryocrushing are most commonly used mechanical pre-treatment for CNF isolation (Abdul Khalil et al., 2014; Abdul Khalil, Bhat, & Ireana Yusra, 2012). CNF have high strength with large surface area that increases its interac-

tion with secondary materials at nano level which might introduce a new functionality in the hybrid material (Stenstad, Andresen, Tanem, & Stenius, 2008). Atomic force microscopy (AFM) was used to evaluate the elastic modulus of single cellulosic nanofibrils and it was observed with values of 145.2 ± 31.3 GPa and 150.7 ± 28.8 GPa

for CNF prepared by TEMPO-oxidation and acid hydrolysis, respectively (Iwamoto, Kai, Isogai, & Iwata, 2009). Modulus of tunicate CNW was 143 GPa and thus it can be concluded that modulus of CNW is close to the perfect crystal (Eichhorn, 2011). Crystalline domains of CNF and CNW resulted in its high modulus and it leads to an increase in mechanical properties of nanocellulose incorporated composites.

3.2. Advantages of nanocellulosic fibers

Both types of nanocellulose have notable characteristics that could be of interest to produce new materials, specifically reinforced polymer nanocomposites. Strong inter-particle bonds prevent molecule from penetrating into CNW structure (Nair, Zhu, Deng, & Ragauskas, 2014), however, partially crystalline structure of CNF (amorphous and crystalline regions) leads to gas diffusion through the voids in its structure (Aulin, Gallstedt, & Lindstrom, 2010). Thus their incorporation might induce low gas permeability in composites. Nanocellulose did not affect the transparency of polymeric nanocomposites unless significant nanofiber agglomeration occurs (Shimazaki et al., 2007). This phenomenon is attributed to the diameter of CNF which is less than 50 nm as well as the small difference between refractive index of polymer and CNF (Shimazaki et al., 2007). Furthermore, Fernandes et al. (2010) observed that the addition of 5% nanofibrillated cellulose (NFC) had no effect on the transmittance of chitosan films, however, with the addition of 10% or higher NFC a reduction in transmittance was observed. In another study, it was reported that polymers other than cellulose when reinforced with CNF or CNW exhibit optical transparency (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009). Furthermore, Koga et al. (2013) reported that the transparent and conductive film of carbon nanotube (CNT)-TEMPO oxidized CNF (TOCN) produced by casting method has enough electrical conductivity to turn on a LED light.

CNW forms chiral nematic phase in water which is attributed to the twisted morphology of CNW and this twist morphology is the result of interaction between chiral surfaces as well as intrinsic chirality of cellulose (Khandelwal & Windle, 2014). Thermal conductivity of polymeric nanocomposite when reinforced with CNF is $>1 \text{ W m}^{-1} \text{ K}^{-1}$ which is 3–5 times greater than conventional resins (Shimazaki et al., 2007). Nanofibers in the form of microfibril bundles are comprised of crystalline cellulose chains and therefore photon scattering is very small in CNF compare to the amorphous resin. CNF can be a pathway for photons in the composite and increase its thermal conductivity (Shimazaki et al., 2007). From available literature it can be concluded that nanocellulose incorporation might lead towards an increase in thermal conductivity, optical transparency, gas barrier properties and Young's modulus.

4. Chitosan reinforced nanocellulose biocomposites

4.1. Chitosan-cellulose nanofiber (CNF) nanocomposites

4.1.1. Properties of chitosan-cellulose nanofiber nanocomposites

Fernandes et al. (2010) proposed that mechanical properties of chitosan (low molecular weight (LCH), high molecular weight (HCH), water soluble chitosan (WCH)) film reinforced with CNF was higher than non-reinforced chitosan films. Moreover, the addition of CNF increased flexibility and thermal stability of chitosan-CNF films compare to native chitosan films. Aforementioned characteristics of chitosan-CNF film makes them useful for various applications such as electronic devices, medical and antibacterial packaging.

In another study, Azeredo et al. (2010) investigated the optimization of CNF content (0–20%) and glycerol concentration

(0–30%) as plasticizer on mechanical, thermal and barrier properties of chitosan-CNF nanocomposite films (% is g/100 g in film on dry basis). They found that the optimum conditions were 15% CNF and 18% glycerol to obtained good dispersion of CNF in resultant film with improved mechanical and barrier properties (Fig. 2). Incorporation of CNF resulted in an increase in surface root mean square roughness of the chitosan films from 1.6 to 8.3 nm. In another work, Wu, Farnood, O'Kelly, and Chen (2014) found that 32% loading of CNF in chitosan films produced by solution casting method caused 12 and 30 times improvement in the tensile strength and Young's modulus, respectively. They observed that enhancement of mechanical properties was remarkable in wet condition than dry one and this biocompatible, transparent and biodegradable nanocomposites has potential for wound dressing applications.

Increasing use of nanoparticles in various applications raises concern about the contamination of water by these nanomaterials. One way to overcome this problem is the removal of nanoparticles from the contaminated water using chitosan-nanocellulose mixture. For instance, chitosan coated with sugarcane bagasse based CNF illustrated 80–90% extraction efficiency for gold and silver nanoparticles as well as 13.1, 17.9 and 17.4 mg/g adsorption efficiency for polyvinylpyrrolidone capped silver nanoparticles, citrate and polyvinylpyrrolidone capped gold nanoparticles, respectively (Mahanta, Leong, & Valiyaveetil, 2012). It can be concluded on the basis of available literature that CNF incorporation resulted in improved functional, mechanical and barrier properties of chitosan composites which resulted in its wider applicability.

4.1.2. Preparation process of chitosan-cellulose nanofiber nanocomposites

Several pre-treatments usually perform before the isolation of CNF. These pretreatments may have effects on the properties of resultant CNF and therefore on the characteristics of nanocomposites reinforced with CNF as well. For example, Hassan, Hassan, and Oksman (2011) showed that alkali or xylanase enzyme treated CNF-reinforced chitosan films have greater wet and dry tensile strength than untreated CNF-reinforced chitosan film. Furthermore, treated CNFs reinforced chitosan nanocomposites had higher storage modulus and glass transition temperature than untreated CNF reinforced nanocomposites. Azeredo et al. (2010) optimize CNF and glycerol concentration in chitosan film by using central composite design and the film was produced by casting technique which is one of the most frequently used method for production of biopolymers based films. Similar methodology was used by Fernandes et al. (2010) and Wu et al. (2014) for the development of chitosan films reinforced with nanocellulose. However, Mahanta et al. (2012) coated nanofibers with chitosan to introduce additional functional groups on the surface for removal of nanomaterials from the environment. Overall, there are various methods available in literature for the preparation of chitosan based CNF composites as food packaging films, membrane for water treatment etc.

4.2. Chitosan-cellulose nanowhisker (CNW) nanocomposites

4.2.1. Properties of chitosan-cellulose nanowhisker nanocomposites

It has been illustrated that CNW as a reinforcement in nanocomposite improves mechanical (Khan et al., 2012), barrier and thermal properties (Ten, Turtle, Bahr, Jiang, & Wolcott, 2010). On the other hand pure chitosan films usually suffer from low mechanical (Rao, Kanatt, Chawla, & Sharma, 2010) and barrier properties (Ojagh, Rezaei, Razavi, & Hosseini, 2010). Production of chitosan based films with varying concentration of CNW was the subject of research by Khan et al. (2012). The results exhibited that 5 wt% CNW loading is optimum which resulted in 26% improvement in tensile strength and 27% reduction in water vapour permeability.

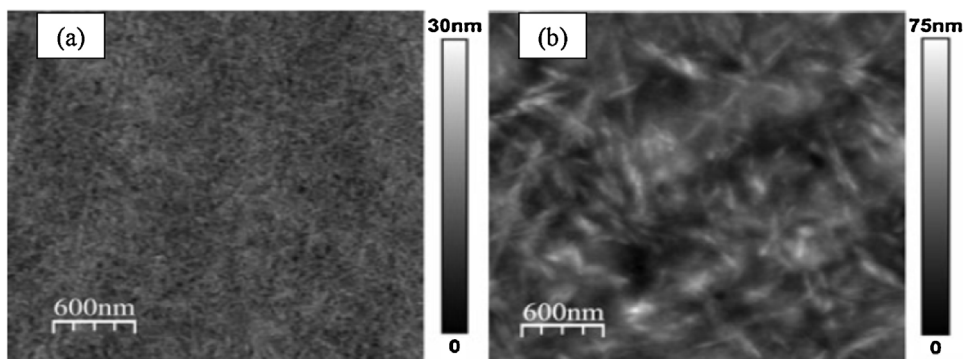


Fig. 2. AFM topography images of chitosan films with (a) 15% CNF and 18% glycerol, (b) 18% glycerol only.

(Source: [Azaredo et al., 2010](#))

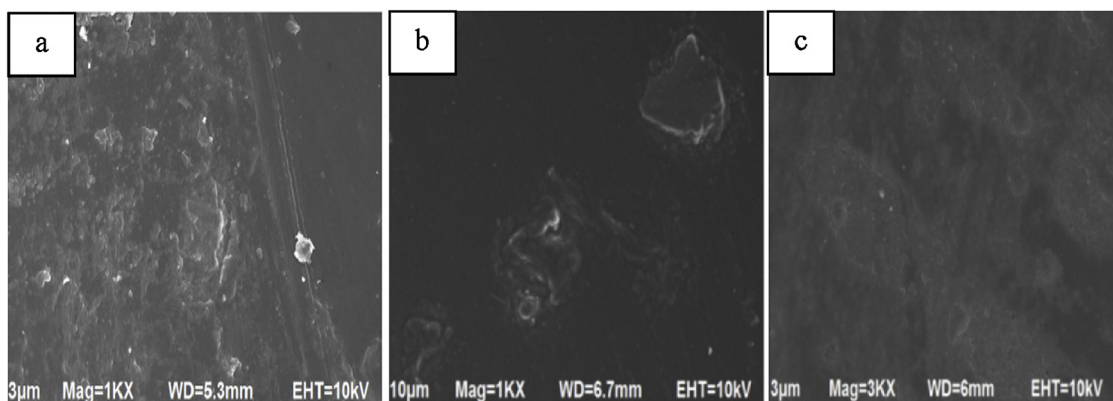


Fig. 3. Field emission scanning electron microscopy (FESEM) images of chitosan–CNW–GLY nanocomposites at (a) 1.15% chitosan, 90% GLY, (b) 1% chitosan, 1% CNW, 30% GLY, (c) 1.15% chitosan, 2% CNW, 90% GLY.

(Source: [Dehnad, Mirzaei et al., 2014](#))

However, thermal properties of films did not affected by varying CNW content. [Li, Zhou, and Zhang \(2009\)](#) reported that by increasing CNW concentration from 0 to 20 wt% dry tensile strength of chitosan nanocomposite films raised from 85 to 120 MPa while wet tensile strength increased from 9.9 to 17.3 MPa. They also observed that incorporation of CNW enhanced water resistance and thermal stability of chitosan films. Since different percentages of CNW have been applied in various works it seems necessary to obtain the optimum range in order to get the best properties for chitosan–CNW nanocomposites. Optimization of high molecular weight chitosan powder (600–800 kDa), CNW particles (diameter 20–50 nm) as well as content of acetic acid and glycerol (GLY) to obtain the best homogeneity and enhanced nanocomposites characteristics for packaging applications was conducted by [Dehnad, Emam-Djomeh, Mirzaei, Jafari, and Dadashi \(2014\)](#). Optimized film was composed of 1% chitosan (%w/0.6v), 0.18% (%w/w chitosan) CNW and 30% (%v/w chitosan) GLY which resulted in tensile strength of 245 MPa, Young's modulus of 4430 MPa, elongation at break of 47% and water vapor permeability of 0.23×10^{-11} (g/m s Pa). [Fig. 3](#) displays the surface morphology of nanocomposites at different component loadings. White colour impurities ([Fig. 3a](#)), efficient dispersion of nanofillers in matrix ([Fig. 3b](#)) and homogeneous distribution of CNW in chitosan matrix ([Fig. 3c](#)) were observed.

In another work authors found that chitosan–CNW based composites showed excellent inhibitory effects against both gram-positive and gram-negative bacteria and had higher T_g and T_m values compare to most of the synthetic films ([Dehnad, Mirzaei Emam-Djomeh, Jafari, & Dadashi 2014](#)). Lactic acid bacterial population was reduced by 3.1 log cycle when nanocomposite was applied on the ground meat and stored at 25 °C for 6 days. It can

be concluded that CNW incorporation in chitosan lead to improved mechanical and barrier properties with antimicrobial activity in packaging films which resulted in longer shelf life of packed food products.

4.2.2. Preparation process of chitosan–cellulose nanowhisker nanocomposites

Preparation technique of chitosan–CNW films is crucial because it affects the dispersion of CNW in chitosan and hence controls the interaction between these two constituents. From this point of view, different processes have been employed for the production of nanocomposites films. [Karim, Mathew, Grahn, Mouzon, and Oksman \(2014\)](#) prepared bio-nanocomposite membranes by freeze drying followed by compacting process. In this method, chitosan was bound to CNW in nanoporous membrane structure and cross-linked with glutaraldehyde vapours for further stabilization. The obtained membranes was designed for water purification and it successfully removed 98% of Victoria Blue 2B, 84% of Methyl Violet 2B and 70% of Rhodamine 6G dyes after 24 h ([Fig. 4](#)). Electrostatic interaction between positively charged dyes and negatively charged CNW cause the removal of dyes.

Another method for preparation of chitosan–CNW based composites is layer by layer procedure. [De Mesquita, Donnici, and Pereira \(2010\)](#) prepared chitosan–CNW multilayers using layer by layer assembly of highly de-acetylated chitosan (cationic phase) and CNW (anionic phase). They proposed that hydrogen bond and electrostatic interactions between ammonium groups of chitosan and sulphate groups of CNW led to the growth of multilayered films. These multilayered films showed maximum load transfer between chitosan and CNW due to homogenous distribution of

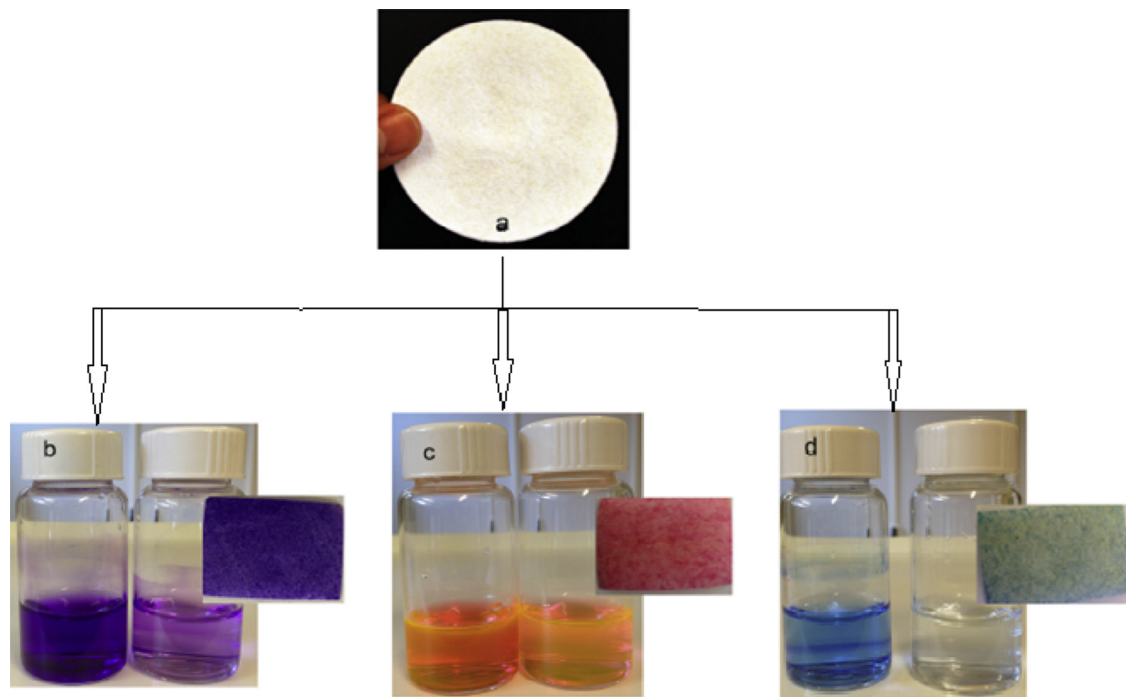


Fig. 4. A schematic representation of removal efficiency of cross-linked composite membrane (a) Photograph of the membrane, water before and after adsorption test for (b) Methyl Violet, (c) Rhodamine 6G, (d) Victoria Blue and the membranes with respective adsorbed dyes. (Source: Karim et al., 2014)

CNW on each chitosan layers without agglomeration. In another study, author demonstrated that covalent linkage between reactive end groups of methyl adipoyl chloride of CNW and amino groups of chitosan in aqueous medium resulted in nanocomposites with enhanced mechanical properties and low hydrophilicity (De Mesquita, Donnici, Teixeira, & Pereira, 2012).

In another work, Karim, Grahn, Oksman, and Mathew (2013) prepared chitosan-CNW nanocomposite membranes by solution mixing and then freeze-drying process with their ratio ranges from 1:1 to 1:3. Dehnad, Emam-Djomeh et al. (2014) prepared chitosan/CNW composites using Response Surface Method with Box–Behnken design having three independent variables and the desirability of 75% in terms of superior mechanical and barrier properties. Recently, Khan et al. (2014) studied the effect of microfluidization of nanocomposite suspension on mechanical properties of nanocomposite films. Their independent variables were number of cycle and pressure of microfluidization as well as CNW content. A CNW content of 8–9 wt%, microfluidization pressure of 6500–8000 psi and 5–6 numbers of cycle were reported as the optimized condition to achieve best mechanical properties. Obtained optimized condition resulted in 10–15 times decrease in agglomerate size. Li et al. (2009) described optical transparency (T_r) of film is an important measure to judge the miscibility of composite materials. In this work, optical properties of CNW reinforced chitosan films were evaluated by measuring their transmittance in the range between 200 and 1000 nm. Observed high T_r suggested good adhesion between CNW and chitosan matrix in the composite films. However, T_r of films decreased with increase in CNW content suggesting the occurrence of microphase separation due to aggregation of fillers within matrix.

Electrospinning is very simple method to produce nanofiber mat from one or more than one polymer (called hybrid or composite nanofiber mat). In hybrid form, first a solution of two or more components should be prepared and then electrospinning of solution perform. Chitosan-CNW nanocomposite mat can also be produced by this technique. In this regard, Naseri, Mathew,

Girandon, Fröhlich, and Oksman (2014) investigated the influence of surface charge of CNW on properties of nanocomposites using chitosan-polyethylene oxide matrix for wound dressing. They demonstrated that CNW obtained from HCl hydrolysis shows better spinning solution properties (conductivity, zeta potential, viscosity and dispersion) as well as better homogeneity, crosslinking and spinnability than nanocomposites prepared from H_2SO_4 hydrolyzed CNW. Their results exhibited that HCl hydrolyzed CNW reinforced mat crosslinked by genipin lead towards reduction of porosity and increase of tensile strength (from 30 to 58 MPa) and Young's modulus (from 1.5 to 3.1 MPa), better CNW incorporation with matrix, increase water vapour permeability, enhance CO_2 and O_2 transmission rate. Published literature suggest that there are various methods available for the preparation of chitosan based CNW composites as wound dressing materials, packaging films, membrane for water purification etc.

4.3. Chitosan-cellulose nanowhisker polyelectrolytes

4.3.1. Properties of chitosan-cellulose nanowhisker polyelectrolytes

Polyelectrolytes are polymers that have positive or negative charge (at neutral pH) and usually are soluble in water due to the electrostatic interactions between charged monomer and water (Lankalapalli and Kolapalli, 2009). Blending of two oppositely charged polyelectrolytes result in the formation of networks by electrostatic (ionic) interaction called polyelectrolytes complex (PEC) (Han, Zhou, Yin, Yang, & Nie, 2010). A wide variety of parameters affect PECs formation and stability such as concentration and mixing ratio of polyelectrolytes, position and nature of ionic groups, pH, degree of ionization, temperature, charge density, molecular weight, etc (Hamman, 2010). Chitosan and CNW can be mixed together in order to produce PEC. The effect of mixing sequences, CNW concentrations and cellulose/chitosan ratio on the charge, shape and size of polyelectrolyte-macroion complexes (PMCs) was the subject of research by Wang & Roman (2011).

Obtained positively charged and nearly spherical shape of PMC particles at amino/sulfate group ratio of above 1 whereas PMC particles with negative charge and non-spherical shape was observed at amino/sulfate group ratio of below 1. Additionally, the size of PMC particles was in the range of hundred nm to several μm . In another study, dynamic mechanical tests of polyelectrolyte films composed of chitosan, glycerol, CNW indicated two major relaxations for all examined films which attributed to glycerol rich and chitosan rich phases, respectively (Pereda, Dufresne, Aranguren, & Marcovich, 2014). Chitosan and CNW based PEC have excellent functional properties with wide applicability due to interaction between opposite charge chitosan (cationic phase) and CNW (anionic phase).

4.3.2. Preparation process of chitosan-cellulose nanowhisker polyelectrolytes

Wang & Roman (2011) employed turbidimetric titration for the preparation of PMCs and suggested its potential application in drug delivery. In another work, Pereda, Dufresne, Aranguren, and Marcovich (2014) applied emulsion casting method to produce polyelectrolyte films using chitosan, olive oil, glycerol and CNW for food packaging. They reported that CNW and olive oil decrease water vapour permeability and improve tensile strength and by increasing CNW content opacity, water solubility and contact angle reduces. Wang, Qian, and Roman, (2011) prepared chitosan-cellulose nanocrystal PMCs by using potentiometric titration and turbidimetric titration. Further the effects of pH and salt concentration on the formation and properties of PMCs were investigated. De Mesquita et al. (2010) prepared PECs from layer-by-layer technique using highly deacetylated chitosan and eucalyptus wood CNWs. Electrostatic interactions and hydrogen bonding between ammonium groups of chitosan and negatively charged sulphate groups on whisker surface were responsible for the growth of multilayered films. Thus it can be concluded that titration is one of the most frequently used methods for production of chitosan/CNW based PECs.

4.4. Multi-components chitosan-nanocellulose nanocomposites

4.4.1. Properties of multi-components chitosan-nanocellulose nanocomposites

New materials with promising characteristics can be produced by the incorporation of two or more polymers. These new types of blend materials illustrate notable properties that cannot be obtained by individual polymers. However, in the recent years very few researches have been dedicated for the preparation of blend material by combining more than two polymers. Polyvinyl alcohol (PVA) is one of the most frequently used polymers in combination with chitosan and nanocellulose. It has excellent physical and optical properties, great flexibility and tensile strength, film forming properties that can be useful in packaging, textile sizing agents, adhesiveness, coating ability, etc (Tang & Alavi, 2011). The existence of hydroxyl and amino groups in chitosan may lead to formation of hydrogen bond and specific intermolecular interactions with PVA in chitosan-PVA blend and therefore enhance chemical and mechanical properties as well as create three dimensional network for dye (Zhu et al., 2012) and heavy metal absorption (Li, Li, & Ye, 2011). For instance, novel magnetic hydrogel beads, comprise of carboxylated CNF, chitosan-PVA blend and amine functionalized magnetite nanoparticles, were produced by Zhou, Fu, Zhang, Zhan, and Levit (2014) for the elimination of Pb(II) ions from aqueous solutions. Higher adsorption capacity of novel hydrogels was because of carboxylated groups on the surface of CNF. Addition of more than one types of nanofillers into chitosan-PVA blends possibly resulted in the development of novel high performance materials. The influence of CNW and zinc oxide-silver (ZnO-Ag) nanoparticles on various properties of chitosan-PVA based nanocomposites was

studied by Azizi, Ahmad, Hussein, Ibrahim, and Namvar (2014). The XRD analysis showed homogenous dispersion of CNW and ZnO-Ag nanoparticles in matrix and the crystallinity of resultant matrix increases with nanofiller content. Furthermore, developed nanocomposites demonstrated an increase in tensile strength from 0.055 to 0.205 GPa and Young's modulus from 0.395 to 1.20 GPa as compared to neat chitosan-PVA films. They also reported excellent antimicrobial characteristics, good ultraviolet-shielding and good visibility for CNW-ZnO-Ag nanoparticles reinforced chitosan-PVA nanocomposites. In another study, Trigueiro, Silva, Pereira, and Lavall (2014) observed that by increasing the number of bilayers (chitosan-multi wall carbon nanotubes (CNTs) film and CNW-multi wall CNT film) from 5 to 20 the electrochemical properties reduced in two orders of magnitude due to increase in the amount of multi wall CNT as conductive material. The thin films obtained with up to 20 bilayers showed more than 90% transmittance in visible range and it can be used as transparent electrode. Thus it can be concluded that beside addition of nanocellulose in chitosan matrix incorporation of other polymers and nanoparticles results in enhanced mechanical, barrier and antimicrobial properties of chitosan/nanocellulose based multi component composites.

4.4.2. Preparation process of multi-components chitosan-nanocellulose nanocomposites

Instantaneous gelation technique was used by Zhou et al. (2014) for the preparation of novel magnetic hydrogel beads consisting of carboxylated CNFs and PVA blended chitosan. In this method aqueous acetic acid solubilise chitosan was mixed with aqueous PVA solution along with magnetite (1.0 g) and carboxylated CNFs. Obtained mixture was dropped through a syringe needle into a NaOH bath and spherical hydrogel beads were formed instantaneously.

CNTs are allotropes of carbon with a cylindrical nanostructure (Wang et al., 2009). CNT has excellent magnetic, mechanical and electrical properties and this lead to various studies on CNT incorporated hybrid materials (Sahoo, Rana, Cho, Li, & Chan, 2010). CNT has potential to form composites with various polymer especially chitosan. However, the challenging issue in blending of CNT with polymer is related to its agglomeration due to nanosize diameter, high aspect ratio, large surface area, Van der Waals force and electrostatic interactions (Ma, Siddiqui, Marom & Kim, 2010). In order to tackle the dispersion problem of CNT, Trigueiro et al. (2014) prepared highly stable multi wall CNT dispersion using CNW suspension and chitosan solution. They applied layer by layer self-assembly method to produce multilayer hybrid thin films from chitosan-multi wall CNT film and CNW-multi wall CNT film. They observed that multi wall CNT homogeneously dispersed on each layer and the surface of films was relatively smooth with the root-mean-squared roughness of 5.8 ± 0.4 nm. Few literatures are available on the dispersion of CNT in biopolymer based composites. Thus extensive research required to further facilitate the dispersion of CNT in chitosan/nanocellulose composites with enhanced physical properties.

5. Chitosan-cellulose blends

5.1. Properties of chitosan-cellulose blends

Cellulose have been extensively used in combination with chitosan to produce new blend materials with antibacterial activity (Wu et al., 2004), metal ions adsorption (Liu et al., 2012), odour treatment properties (Twu, Huang, Chang, & Wang, 2003), improved water absorption capacity and mechanical characteristics (Liu et al., 2011), good antistatic and moisture absorption properties (Xu et al., 2010), high porosity and interconnected



Fig. 5. Image of regenerated (a) chitosan gel, (b) chitosan-cellulose membrane, (c) chitosan-cellulose-multi wall CNT membrane, (d) chitosan-cellulose fibers, (e) chitosan-cellulose-multi wall CNT fibers.

(Source: Xiao et al., 2013)

porous structures (Lv, Wang, Zhu, & Zhang, 2014), self-healing characteristics (Duan, Han, Liu, Jiang, & Li, 2016), etc. In order to attain comprehensive improvement in electrical, physical, mechanical and thermal characteristics of chitosan-cellulose blend materials tertiary component usually incorporate with it. Xiao et al. (2013) studied the influence of various multi walled carbon nanotubes (MWCNT) loadings on the properties of chitosan-cellulose hybrid fiber and membrane (Fig. 5). As they proposed 4 wt% loading of MWCNT resulted in best performance of hybrid membrane and fiber in terms of electrical conductivity, mechanical and thermal properties. They utilized 1-H-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride ionic liquids to disperse MWCNT as well as to dissolve cellulose and chitosan. Brown colour of chitosan-cellulose membrane turned in to black by incorporation of multi wall CNT and thus illustrated the uniform mixing of all the components (Fig. 5).

Various mechanical properties of chitosan-cellulose blends have been reported by Shih, Shieh, & Twu (2009). SEM and tensile strength test revealed that the surface of blend films tended to become smoother and strength of films was enhanced with increase in chitosan content in blend films. However, at higher concentration of chitosan films again became coarse. This was due to the change in proportion which led to phase separation between chitosan and cellulose and caused the significant reduction tensile strength. Developed blend films had non-diffusible antibacterial properties as observed from antibacterial assessment and halo zone test results. Duan et al. (2016) reported that the cellulose and chitosan can bind by intermolecular inclusion interaction. In this work, they studied the self-healing properties of the blend and found that the healed gel can recover 72.77% of its original compressive strength due to the host-guest interactions. In other work, Stefanescu, Daly, and Negulescu, (2012) has successfully prepared blend membranes from chitosan and cellulose using trifluoroacetic acid as a solvent. They suggested that cellulose/chitosan blends were considerably immiscible because mechanical and dynamic mechanical thermal properties of cellulose/chitosan blends were virtually dominated by cellulose. Furthermore, based on water vapour transpiration rate and antimicrobial capability against *Escherichia coli* and *Staphylococcus aureus* they concluded that chi-

tosan/cellulose membranes can be used for wound dressing since it has the potential to prevent wound from excessive dehydration and infection.

Liu et al. (2013) reported that the addition of cellulose into chitosan resulted in denser and mechanically stronger hydrogel beads. Chitosan-cellulose beads had high adsorption capacities for Cu, however, adsorption was pH-dependent (with maximum adsorption at a neutral pH) and crosslinked beads had slightly lower adsorption capacity. Twu et al. (2003) demonstrated that chitosan/cellulose beads had high specific area and functionalities thus they are useful in deodorants for adsorbing abhorrent gases. The sorption efficiency significantly modified when chitosan was incorporated in cellulose beads. Increase in concentration of chitosan resulted in better interactions between chitosan and trimethylamine (fishy odour) hence sorption activity enhances. In future deodorizing properties of chitosan/cellulose blends against other obnoxious gases can be investigated in order to commercially utilize the sorption capacity of various blends in odour treatments.

5.2. Preparation process of chitosan-cellulose blends

Chitosan and cellulose should be dissolved prior to preparation of blends. Commonly used methods for blend preparation are electrospinning (Du & Hsieh, 2009), casting (Stefanescu et al., 2012) and sol-gel transition (Liu et al., 2012). However, cellulose and chitosan is not readily dissolved in common solvents because of presence of strong hydrogen bond in their molecular chains. Nevertheless, researchers have proposed wide varieties of solvent or solvent systems for preparation of chitosan-cellulose blends. These two components can be dissolved either in the same solvent/solvent systems or in different solvents. Wu et al. (2004) applied aqueous acetic acid and co-solvent of tetrafluoroacetic acid while Shih et al. (2009) prepared chitosan-cellulose blend by *N*-methylmorpholine-*N*-oxide (NMMO). Besides that, NaOH/thiourea solvent was utilized by Almeida, Frollini, Castellan, & Coma (2010) for the production of biofilm from chitosan and cellulose. In another work, cyclodextrin-chitosan and ferrocene cellulose were dissolved in *N,N*-dimethylformamide (DMF) and lithium chloride (LiCl) to synthesize chitosan-cellulose gel (Duan et al., 2016). They proposed

Table 2
Some of the potential applications of chitosan–cellulose blends.

Potential applications	References
Coronary artery bypass graft	Azevedo, Raghavan, Raghavan, and Kumar (2013)
Adsorbent for removal of heavy metal ions	Li & Bai (2005), Liu et al. (2012)
Textile	Xu et al. (2010)
Biocomposite films	Stefanescu et al. (2012)
Food packaging	Bao et al. (2015)
Wound dressing	Tran, Duri, and Harkins (2013), Harkins, Duri, Kloth, and Tran (2014)
Medical material	Yu et al. (2013)
Wound healing (good antibacterial effect)	Abou-Zeid et al. (2011)
Drug delivery	Feng, Zhang, and Zhu (2013)
Biomedical applications	Wu et al. (2004)
Adsorbent for the removal of acidic reagents, metals, amino acids, proteins, and other compounds	Rogovina, Akopova, Vikhoreva, and Gorbacheva (2001)
Odour treatment	Twu et al. (2003)
Self-healing	Duan et al. (2016)

that cellulose and chitosan bind together through intermolecular inclusion interaction in obtained gel.

Furthermore, in order to overcome the difficulty of dissolution of cellulose and chitosan in common solvents researchers have been employed two ways. One way is the application of their derivatives. Du and Hsieh (2009) established an easy method to form chitosan/cellulose nanofibers by electrospinning of dibutyl chitin and cellulose acetate and finally regeneration of hybrid nanofibers using alkaline hydrolysis. They found that solvent system of acetone/acetic acid with ratio of 1:1 is optimum for the production of cellulose–chitosan nanofiber with diameter of 30–350 nm without any phase separation. In addition, they reported that the optimal conditions for regeneration of chitosan–cellulose nanofibers were hydrolysis with 5 N NaOH for 3 h at 100 °C. There are various other established methods in which dissolution step is not required. For instance, Xu et al. (2010) applied viscose process for spinning the blend of cellulose xanthate and O-hydroxyethyl chitosan xanthate to manufacture hybrid fibers. Alonso et al. (2009) cross-linked chitosan to UV-irradiated cellulose using sodium phosphate (NaH_2PO_4) as catalyst and citric acid as the cross-linker in order to confer antimicrobial activity to cellulose. Lim & Hudson (2004) fabricated antimicrobial textile finish using a cold pad-batch procedure applied on cotton fabrics by reactive chitosan derivative and an alkaline catalyst. Thus it can be concluded that extensive research led to the development of various solvents, solvent systems and derivatives of polymer for the preparation of blends with novel characteristics.

5.3. Potential, challenges and applications of chitosan–cellulose blend

Over the last few decades, a great deal of attention has been focused on the use of chitosan in biomedical and pharmaceutical fields. However, it is difficult to find any available products based on chitosan in the market. This is due to the involvement of several challenges when working with chitosan such as its strong hygroscopic nature and the fact that it is extracted from various sources. Properties of chitosan extracted from different sources differ significantly in terms of its molecular weight and molecular weight distribution, degree of deacetylation and purity level. In addition, chitosan is prone to environmental factors and processing conditions (such as heating or freezing) which can impose stress on its structure and cause polymer degradation.

Several strategies have been proposed by the researchers to improve the stability of chitosan and chitosan based materials by preventing degradation of polymer chain (Szymanska & Winnicka, 2015). Stability of chitosan blend depends on specific interactions which may include hydrogen, ionic bonds, or dipole interference and final properties strongly depend on the miscibility of the com-

ponents. Miscibility, structure and properties are critical factors in studies concerning polymer blends. Miscibility is one of the key factors affecting the structure and properties of a polymer blend which are important in applications. Chitosan can be modified by blending it with other polymeric materials such as cellulose because it has modifiable functional groups thus the stability of blends enhances. Some of the potential applications of chitosan–cellulose blends are tabulated in Table 2. Biopolymer based blends have new and enhanced properties that can be commercially utilized (Ramya, Sudha, & Mahalakshmi, 2012). Overall it can be concluded that stability of chitosan based materials can be improved by blending it with other compatible biopolymer especially cellulose. Challenges still exist in the discovery of suitable methods to produce chitosan–cellulose blends with homogeneous dispersion. Furthermore, the use of micro or nano cellulose to improve the properties of chitosan–cellulose blends is still unexplored. In future, research on blends should be focused on their potential use in biomedical, packaging, coatings and water treatment.

6. Conclusions

There is growing concern regarding the use of petroleum based composites due to their non-biodegradability and non-renewability. Biopolymer based composites and blends can suitably address the challenges raised by their synthetic counterparts. Cellulose and chitosan are two most abundant natural polymers with promising characteristics as composite materials. However, biopolymer based materials have relatively poor mechanical, thermal and barrier properties. Addition of two or more polymers, nanomaterials can significantly increase the properties of composites. In this regards, chitosan based cellulose/nanocellulose materials are extensively explored.

Incorporation of nanocellulose (CNW or CNF) in chitosan matrices resulted in improved function properties of obtained materials which has wide applicability in field of food packaging, biomedical, water treatment etc. There are various methods available in literature according to the application for the development of nanocomposites like solvent casting method is frequently used for the preparation of packaging films, coating of nanofiber with chitosan for water treatment. Furthermore, chitosan (cationic) and CNW (anionic) can be mixed together to fabricate polyelectrolyte complexes using titration. Besides such two phase (chitosan and cellulose) based composites researcher also successfully developed multi phase containing materials with better functional properties. For example polyvinyl alcohol in combination with chitosan and nanocellulose resulted in composite material with high affinity towards heavy metal absorption.

Furthermore, blends of chitosan and cellulose resulted in material with antibacterial activity, metal ions adsorption, odour

treatment properties etc. Commonly used methods for blending are electrospinning, casting and sol–gel transition. Despite, extensive research in the field of chitosan based cellulose/nanocellulose composites their commercial applicability is still limited this might be due to their uneconomical production procedure and poor properties as compared to synthetic counter parts. Future studies should be focused on their economical production with synthetic materials like properties.

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