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CNWs loaded poly(SA) hydrogels: Effect of high concentration of CNWs on water uptake and mechanical properties

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ABSTRACT

In this work, poly(sodium acrylate) (poly(SA)) hydrogel films, doped with cellulose nano-whiskers (CNWs), are prepared via free radical polymerization of sodium acrylate (SA) in aqueous medium. The CNWs were added into the polymerization feed mixture, in the concentration range of 4.8–24.3 wt% of monomer and the resulting CNWs/poly(SA) hydrogel films were investigated for their water absorbency in the physiological fluid (PF). The addition of CNWs caused a decrease in the equilibrium water uptake. The kinetic water uptake data of all hydrogel samples were best interpreted by the second order kinetic. The water vapor permeation studies were also carried out. The water vapor transmission rate (WVTR) of all the film samples was quite low. The mechanical properties of films such as tensile strength (TS) and percent elongation (PE) varied with the CNWs content. All the film samples showed fair folding endurance (FE), with more than 600 times folding without suffering from any crack.

1. Introduction

The term hydrogel describes three-dimensional network structures obtained from a class of synthetic and/or natural polymers, which can absorb and retain significant amount of water (Hennink & Nostrum, 2012). The presence of hydrophilic groups in hydrogels is responsible for their water absorption capacity (Pal, Banthia, & Majumdar, 2009). Hydrogels find a wide range of applications which include; drug delivery systems (Shin et al., 2013; Spizzirri et al., 2013), super absorbents (Li et al., 2012; Liu et al., 2013), release of agrochemicals (Singh, Sharma, & Gupta, 2008; Ni, Liu, Lu, Xie, & Wang, 2011), scaffolds (Palumbo, Pitarresi, Fiorica, Rigogliuso, & Ghersi, 2013; Tonsomboon & Oyen, 2013)· targeted drug delivery (Tripathi & Mishra, 2012) etc. It is observed that for a variety of applications such as wound dressings, the hydrogel films should have fair mechanical properties so that they can withstand the applied or external shear (Khan, Peh, & Ch'ng, 2000) .This is usually achieved by increasing the quantity of cross-linking agent used to prepare polymer network. This increases the number of cross-links per unit volume within the network and so a compact network is produced (Wenbo & Aiqin, 2010). However, this may reduce the flexibility of the polymeric segments and impart it a brittle nature to the wound dressing film. Under this condition, the hydrogel film may break when exposed to external stress (Grover et al., 2012) .Therefore, a strategy is needed that can enhance mechanical strength without much compromising with the flexibility and water absorbing capacity of the polymer.

Cellulose is a biocompatible and biodegradable biopolymer and is found abundant in nature. It is a linear syndiotactic homopolymer composed of D-anhydro glucopyranose units, which are linked by β-(1 → 4)-glycosidic bonds. It exhibits extensive intra and inter molecular hydrogen bonding interactions due to the presence of a number of —OH groups along its backbone. That is why cellulose is insoluble in most of the solvents including water. Because of its crystalline and biocompatible nature, it has been widely used, as re-enforcing agent in other polymeric materials to enhance mechanical strength .However, the uniform mixing of cellulose into other polymer is essential to obtain a composite material with uniform strength and other physic-chemical properties. Therefore, it is required that cellulose must be mixed uniformly with the other polymer, before transformation into composites. This may best be achieved by disintegration of cellulose particles into nano size, which possess a fair dispersion capacity. Cellulose nano-whiskers (CNWs) are the new class of

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cellulose materials that are characterized by increased crystallinity, high aspect ratio, developed specific surface, improved dispersion ability, biodegradability, and a fair stability against moderate temperatures and proteolytic enzymes. Due to these features, CNWs are frequently used as a high quality reinforcing fillers in polymers and biodegradable materials. There have been several reports describing use of CNWs as drug carrier and implants, etc (Dash and Ragauskas, 2012; Czaja, Young, KaweckI, & Brown, 2007) .The Young's modulus of CNW is as high as 114 GPa while the tensile strength of the crystal structure was estimated in the range of 0.8–10 GPa (McKenna, Michelson, Wehr, Gidley, & Menzies, 2009).

Most recently, we have reported (Bajpai, Pathak, Chand, & Soni, 2013) acid hydrolyzed synthesis of CNWs, their complete characterization and impact of their loading into poly(sodium acrylate) hydrogels at low concentrations. The presence of low content of CNWs enhanced the water uptake of poly(SA) hydrogels. In the present work, the poly(SA) hydrogel films have been loaded with high CNWs content and the water absorption behavior and mechanical properties of these films have been investigated. The purpose of this work is to prepare CNWs/poly(SA) films with fair mechanical properties, with minimum compromise of their flexibility and water absorption behavior.

2. Materials and methods

2.1. Materials

The cellulose pulp, used to prepare CNWs, was obtained from a paper mill (Amlai Paper Mill, Shahdol, M.P., and India) and was used without any further chemical or physical treatments. The monomer sodium acrylate (SA), cross-linker N,N′-methylenebis-acrylamide (MB), initiator potassium persulfate (KPS), and catalyst N,N,N,N′-tetra methyl ethylenediamine (TEMED) were obtained from Hi Media Chemicals, Mumbai, India. Other salts, used to prepare various buffer solutions, were obtained from E. Merck, Mumbai, India and were analytical grade. The double distilled water was used throughout the investigations.

2.2. Method of preparation and characterization of CNWs

In order to obtain cellulose nano-whiskers (CNWs), the controlled acid hydrolysis of de-watered cellulose pulp (DCP) was carried out. The synthesis conditions were as follows: concentration of sulphuric acid = 64 (wt%), hydrolysis temperature = 45 °C, and reaction time = 45 min. The CNWs, so obtained, were characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) analysis (Bajpai et al., 2013).

2.3. Preparation of CNWs/poly(SA) hydrogel films

The CNWs/poly(SA) hydrogel films were prepared by carrying out free radicals initiated aqueous polymerization of monomer sodium acrylate in the presence of well-dispersed CNWs using MB as cross-linker and TEMED as catalyst. In brief, a pre-determined quantity of CNWs was dispersed in 5.0 mL of water and to this dispersion, 21.28 mmol of monomer SA and 195 μmol of cross linker MB were added under constant stirring to ensure complete dissolution and the total volume of the reaction mixture was made up to 10.0 mL .Now, 223 μmol of initiator KPS was added and the whole reaction mixture was again kept under stirring at a normal rate of 200 rpm to ensure complete dissolution. Finally, 60 μL of the catalyst TEMED was added and the whole reaction mixture was transferred into Petri plates, each of diameter 9 cm and kept in an Electric oven (Revotek, India) at 60 °C for a period of 2 h. After the polymerization was over, the hydrogel films were taken out, and allowed to equilibrate in distilled water for a period of 3 days for complete expulsion of un-reacted chemicals from the films. Finally, the films were dried in vacuum chamber at ambient temperature until constant weight and were stored in desiccators in moisture-free environment for further use. In all six such films, containing varying quantities of CNWs were prepared. Their compositions are given in Table 1.

2.4. Water absorption behavior of CNWs/poly(SA) films

The study of water absorption behavior of polymeric films is very important when the films are to be used in biomedical applications such as drug delivery vehicles, wound dressing material etc. The water uptake data is used to estimate capacity of films to absorb wound exudates.

The pre-weighed film sample was placed in 500 mL of physiological fluid at 37 °C and was taken out at different time intervals, wiped superficially with tissue paper to remove extra surface water, weighed accurately in an electronic balance (Denber, Germany), and then transferred again into the swelling medium. The swelling ratio (SR) was determined using the following expression (Bajpai et al., 2013):

$$SR = \frac{M_t - M_0}{M_0} \tag{1}$$

where M_0 and M_t are the initial mass and mass at different time intervals respectively. In order to determine equilibrium swelling ratio (ESR), M_t was replaced by M_e which is the mass of the swollen hydrogel film at equilibrium.

2.5. Water vapor permeation studies

Water vapor transmission of film was measured using ASTM E 96-93 method. The test cups were filled with 20 g of silica gel (desiccant) to produce a 0% relative humidity (RH) below the film. A sample was placed in between the cups and the silicon coated ring cover and held with four screws around the cups circumference. The air gap was at approximately 1.5 cm in between the film surface and desiccant. The water vapor transmission rate (WVTR) of each film was measured at 40% RH and 25 ± 1 °C. After taking initial weight of the test cup, it was placed in glass desiccators containing saturated salt solution to provide 40% RH. The cups were taken out at different time intervals and weighed accurately. Three replicates of each sample were measured. The water vapor transmission rate (WVTR) was calculated as (Chourasia, Bajpai, & Chand, 2010):

$$WVTR = \frac{\Delta W}{\Delta t \cdot A}\ \mathrm{mg\ h^{-1}\ cm^{-2}} \tag{2}$$

where $\Delta W/\Delta t$ is the amount of water gain per unit time of transfer, A = area exposed to water surface in cm^2.

The Permeance is given as

$$\text{Permeance} = \frac{\Delta W}{\Delta t \cdot A \Delta P}\ \mathrm{mg\ h^{-1}\ cm^{-2}\ Pa^{-1}} \tag{3}$$

The Permeability can be calculated using the expression

$$\text{Permeability} = \frac{\Delta W \cdot d}{\Delta t \cdot A \Delta P}\ \mathrm{mg\ h^{-1} cm^{-2}\ Pa^{-1}} \tag{4}$$

Here, ΔP is the water vapor pressure difference across the both sides of the film and d is the thickness of the film.

2.6. Determination of mechanical properties of films

The mechanical properties of the films were determined using Unique Tensile Tester (UTM, Universal Tensile Tester, and Pune, India) according to the standard testing method ASTM D882-97 (Limpisophon, Tanaka, Weng, Abe, & Osako, 2009). The measurements were made at 25 °C under the constant humidity of 50%.

Table 1
Compositions of various CNWs/poly(SA) film samples synthesized.[a]

Sample code	SA (mmol)	MB (μmol)	KPS (μmol)	TEMED (μmol)	CNW (wt%)
CNWs/poly(SA) (0)	21.28	195	223	60	0
CNWs/poly(SA)(4.8)	21.28	195	223	60	4.8
CNWs/poly(SA)(9.7)	21.28	195	223	60	9.7
CNWs/poly(SA)(14.5)	21.28	195	223	60	14.5
CNWs/poly(SA)(19.4)	21.28	195	223	60	19.4
CNW/poly(SA)(24.3)	21.28	195	223	60	24.3

[a] The total volume of the reaction mixture was 10.0 mL.

The samples were cut into strips, each of width 5 mm and length 50 mm. The initial grip separation and mechanical crosshead speed were set at 25 mm and 100 mm per min respectively. The various formulae used are shown as below:

$$\text{Tensile strength}\,(\sigma) = \frac{\text{Force or load}\,(F)}{MA} \tag{5}$$

where F is the maximum load and MA is the minimum cross-sectional area of the film specimen. Results were converted to mega Pascal units (MPa).

$$\begin{aligned}\text{Young Modulus}\,(Y) &= \frac{\text{Tensile strength}}{\text{Tensile strain}}\\ &= \frac{F \times L_0}{MA \times (L_0 - L)}\end{aligned} \tag{6}$$

$$\%\text{Elongation} = \frac{L_0 - L}{L_0} \times 100 \tag{7}$$

L_0 refers to initial length of the film sample and L is the elongation when the film breaks.

In order to ensure comfortable and secured application of film on the wound, the film must be flexible so that it can withstand the external stress. The flexibility of the film was accessed from the determination of the folding endurance (FE) of film. The FE was determined by repeatedly folding a film at the same place until it breaks. The number of times the film could be folded at the same place without breaking is termed as the folding endurance (Kumar, Prabhushankar, & Sathesh babu, 2010).

3. Results and discussion

3.1. Formation of CNWs

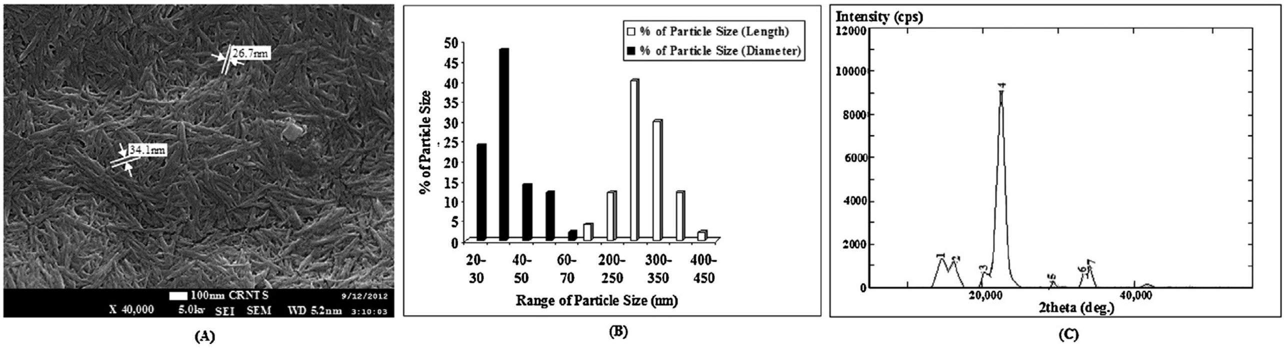
The repeating unit of cellulose is composed of two glucose molecules by bonds etherified (1,4)-β-glycosides. This repeating unit, known as cellobiose, contains six hydroxyl groups that provide hydrogen bonding and intra–inter molecular interactions. Due to these hydrogen bonds, cellulose has a strong tendency to form crystals that become insoluble in water and most organic solvents. The cellulose chains have more ordered structure, with crystallinity depending upon the source from which it has been derived (Khanna, Agrawal, & Ahuja, 1997).

The main process for the isolation of CNWs from cellulose fibers is based on acid hydrolysis. Disordered or Para crystalline regions of cellulose are preferentially hydrolyzed, whereas crystalline regions, that have a higher resistance to acid attack, remain intact (Araujo, Waldoman, & de Paoli, 2008). When cellulose pulp is treated with 64% (w/v) sulphuric acid, the amorphous region is cleaved transversally and finally results in formation of cellulose nano-whiskers (CNWs). It is believed that acid interacts mainly with the amorphous regions of cellulose, as they are the most easily accessible and have the greatest surface area. Therefore, the amorphous regions are the first to be targeted by the strong acid, followed by regions of increased crystallinity. It is noteworthy that during the traditional preparation process of CNWs, the hydrolyzing agent, sulfuric acid introduces charged sulphate ester groups onto the hydroxyl groups, thus stabilizing the CNWs in solution by preventing their agglomeration (Eichhorn et al., 2010).

In our previous work (Bajpai et al., 2013); we reported a detailed investigation of preparation and characterization of cellulose nano-whiskers (CNWs). The FE-SEM image along with the size distribution of CNWs and XRD pattern are shown in Fig. 1.The length, diameter, and aspect ratio (AR) were 258.5 nm, 35.2 nm and 7.3, respectively. The crystallinity index (CI), as revealed by XRD, was 0.925. These CNWs were also used in the present work.

3.2. Effect of CNWs content on equilibrium swelling ratio (ESR)

In order to investigate the effect of CNWs content on the swelling ratios of CNWs/poly(SA) hydrogels, we prepared a number of hydrogel samples, containing different quantities of CNWs, in the range of 0 to 24.3 wt% of monomer SA, and determined their equilibrium swelling ratios in the physiological fluid of pH 7.4. The results, as depicted in Fig. 2(A), reveal that with the increase in the CNWs content from 0 to 2.4 wt%, the ESR also increases from 24.43 to 31.47 g water/g gel. However, with the further increase in the CNWs content up to 24.3 wt%, the ESR shows a decreasing trend and attains a minimum value of 6.97 g water/g gel for the sample with CNWs content of 24.3 wt%. When CNWs content in the hydrogel network is low, the —OH groups, present on the surface of cellulose nano crystals provide additional active sites for binding of incoming water molecules. Therefore, water molecules not only occupy the space available within the three dimensional cross linked hydrogel matrixes, but they also bind to the surface hydroxyls of CNWs. This finally results in enhanced water uptake. However, with the increase in CNWs content in the hydrogel, the number of surface hydroxyls of CNWs increases and they begin to interact with $—COO^-$ and NH_2 groups of poly(SA) network chains through H-bonding and produce additional physical crosslinks. Therefore, apart from covalent crosslinks already produced by crosslinking agent MB, physical crosslinks also exist in the hydrogel matrix. This reduces the space available per unit crosslinks for accommodation of invading water molecules. Hence entrance of water in to hydrogel matrix is discouraged. Therefore, ESR of hydrogels with high CNWs content is low. The above explanation has been illustrated by “Physical cross linking model” in Fig. 2(B). It can be seen that when CNWs content is low, the chances of physical interaction between polar functionalities of CNWs and poly(SA) are very rare. However, with high CNWs content, there may exist physical cross links between surface hydroxyls of CNWs and carboxylate groups of poly(SA) chains. There are chances of H-bonding interaction among surface hydroxyls also. It is also probable that when there is higher CNWs content, the surface hydroxyl groups may take part in polymerization reaction by combining with monomer molecules, thus producing a more entangled and dense network .This may also reduce the water uptake. These results indicate that water absorption capacity of the hydrogel can easily be controlled by varying the CNWs content at fixed concentration of cross-linker MB.

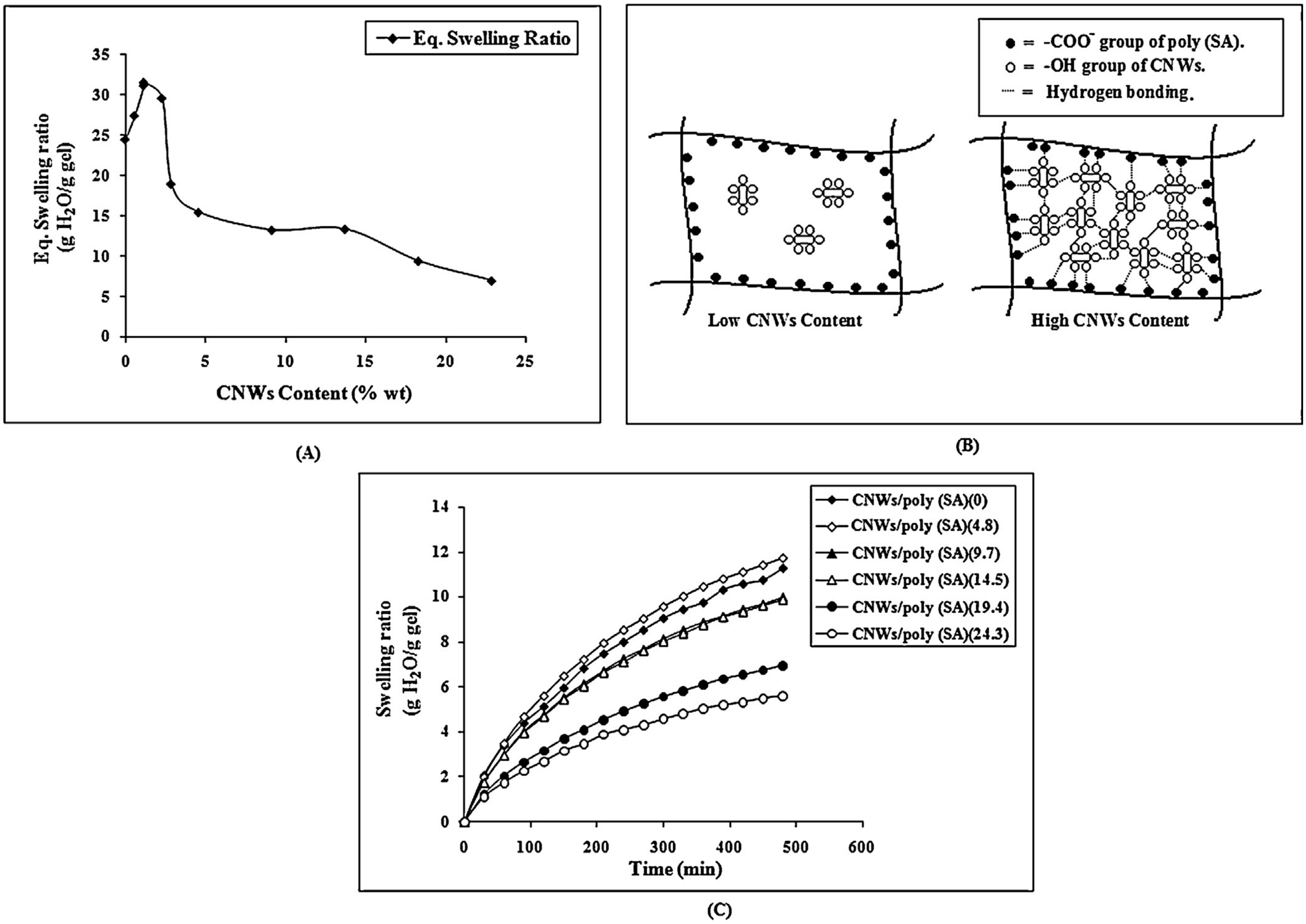


(A) (B) (C)

Fig. 1. (A) FE-SEM, (B) distribution curves, and (C) XRD analysis of CNWs.

3.3. *Dynamic uptake analysis of CNWs/poly(SA) hydrogel films*

We also investigated the dynamic water uptake of CNWs/poly(SA) samples in the physiological pH of 7.4 at 37 °C. The total ESR was attained in 2440 min. The dynamic uptake of various hydrogel film samples is shown in Fig. 2(C). A close look at these profiles reveals some interesting observations. For example, the swelling profiles of samples CNWs/poly(SA) (0) and CNWs/poly(SA) (4.8) run almost parallel to each other and the CNWs/poly(SA) (4.8) sample shows a little higher water uptake as compared to the plain sample CNWs/poly(SA)(0). However, the equilibrium swelling exhibited by these samples is 15.4 and 24.4 g water/g gel respectively. The reason for slightly higher water uptake of CNWs/poly(SA) (4.8) sample may probably be because the surface hydroxyls of CNWs bind to incoming water molecules and enhance water absorbency. Later on, the plain hydrogel absorbs more and more water while CNWs containing sample restricts the chain relaxation of poly(SA) chains due to entanglements of cellulose nano-crystals with poly(SA) chains. In addition, the mutually bound crystalline networks of CNWs discourage absorption of water molecules. Thus, the plain sample finally attains higher water uptake as shown in previous Fig. 2(A). If we observe initial swelling profiles of samples CNWs/poly(SA) (9.7) and CNWs/poly(SA) (14.5), they appear to coincide and their equilibrium water absorption was almost the same, i.e. 13.34 and 13.23 g water/g gel respectively. Finally, the samples



(A) (B) (C)

Fig. 2. (A) ESR, (B) physical crosslink model, and (C) dynamic water uptake.

CNWs/poly(SA) (19.4) and CNWs/poly(SA) (24.3) demonstrate ESR of 9.38 and 6.97 respectively. The overall conclusion is that there is gradual decrease in ESR with increase in CNWs contents, though their kinetic profiles show a little deviation from this final trend.

The swelling of hydrogel in water is supposed to be composed of two molecular processes i.e. penetration of the solvent molecules into the void spaces in the network and subsequent relaxation of the polymeric chains. The fundamental equation, used to describe the water penetration mechanism for initial 60% data, is (Elazzouzi-Hafraoui et al., 2008).

$$F = \frac{M_t}{M_\infty} = kt^n \tag{8}$$

where F (=M_t/M_∞) is the fractional water uptake at time t, M_t and M_∞ are water uptakes at time t and at equilibrium respectively, k is gel characteristic constant and n is the swelling exponent, which indicates Fickian or non-Fickian behavior of the swelling device. The swelling exponent n and constant k are determined using slope and intercept of $\ln F$ versus $\ln t$ plots. The dynamic water uptake data, displayed in Fig. 2(C), was used to get linear plots between $\ln F$ and $\ln t$ and the swelling exponent 'n' and gel constant k were evaluated using slopes and intercepts of linear plots. The values of swelling exponent 'n' and gel characteristic constant 'k' along with their respective regressions (data not shown) are shown in Table 2. The regression values were high thus indicating suitability of power model on dynamic uptake data.

The values of swelling exponent 'n', displayed in the Table 2 are slightly greater than 0.50 for all the samples, thus suggesting that the water uptake mechanism, for all these samples, is almost non-Fickian. This may simply be attributed to the fact that in the swelling medium of physiological fluid, the poly(sodium acrylate) chains are in relaxed state due to repulsive forces among similarly charged —COO$^-$ groups. In addition, presence of sulphate ester groups on the surface of CNWs also causes repulsion between similar charges. Here, it is to be noted that these values are slightly higher than 0.5, which is the upper limit for diffusion controlled water sorption mechanism. It indicates that, out of the two rates, namely rate of water diffusion into polymer matrix and rate of polymeric chain relaxation, the former one is more dominating. It is well known that poly(SA) is an anionic polymer and it exhibits chain relaxation controlled water sorption mechanism due to repulsive forces operating between carboxylate groups. For example, in a study (Karadeg & Saraydin, 2002), poly(acrylamide)/poly(sodium acrylate) hydrogels, prepared with MB as crosslinker showed swelling exponent values in the range of 0.90–1.60 (i.e. non-Fickian to case-II transport) for SA content of 70–100 mg/g of other monomer acrylamide. However, in the present case, the presence of cellulose nano-whiskers in the polymer matrix may restrict chain relaxation process due to their entanglements with poly(sodium acrylate) chains. This may be the reason for the water transport mechanism to be more diffusion controlled rather than chains relaxation controlled. In order to further confirm this, we also plotted M_t/M_∞ values against $t^{1/2}$ to see whether the water absorption was diffusion controlled. The results, as shown in Fig. 3(A), indicate that the plots obtained are linear and pass through the origin with fairly higher regressions in the range of 0.973–0.996. This indicates that sorption of water into the CNWs/Poly(SA) hydrogels is governed mainly by diffusion-controlled mechanism along with a little contribution of chain relaxation process. This probably could be due to the presence of cellulose nanowhiskers, which acts as diffusion barrier during the water penetration into the polymer networks.

The kinetic uptake data was also applied on the first order kinetic equation, developed by Beren and Hopfenberg (Wang, Ding, & Cheng, 2007), according to which the rate of water uptake at any time is proportional to the first power of the amount of water to be absorbed to attain equilibrium i.e.

$$\frac{dM_t}{dt} = k_1(M_\infty - M_t) \tag{9}$$

where k_1 is relaxation rate constant. The integration of Eq. (9) leads to

$$\frac{M_t}{M_\infty} = 1 - A.e^{-k_1 t}$$

The logarithmic form of above equation is,

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = -k_1 t \tag{10}$$

The $\ln(1 - M_t/M_\infty)$ versus t plots was drawn for all the six samples. The plots were not linear and had poor regression values (data not shown).

The second order kinetic model was also applied on the dynamic water uptake data. This model is supposed to be more suitable for long-term swelling measurements. According to this model (Habibi, Lucia, & Rojas, 2010); the swelling rate at any time is directly proportional to the quadratic of the swelling capacity before the attainment of equilibrium state. This can be represented in quantitative form as follows:

$$\frac{dM_t}{dt} = k_2(M_\infty - M_t)2 \tag{11}$$

where M_t is the water uptake at time't' and 'k_2' is the second order rate constant for water absorption process. On integrating above equation within the limits $t=0$ $M_t=0$ and $t=\infty$ $M=M_\infty$, following equation is obtained:

$$\frac{t}{M_t} = \frac{1}{k_2 M_\infty^2} + \frac{t}{M_\infty}$$

or

$$\frac{t}{M_t} = A + Bt \tag{12}$$

where, A and B are two coefficients whose physical meaning is interpreted as follows: At a long retention time $Bt \gg$ A and therefore $B = 1/M_\infty$, that is, B is reciprocal of the maximum water uptake. On the contrast, at a very short time interval $Bt \ll$ A and so,

$$\underset{t \to 0}{Lt}\left(\frac{dM_t}{dt}\right) = \frac{1}{A} \tag{13}$$

Therefore, the intercept A is reciprocal of initial swelling rate. In order to apply this model, the kinetic data were used to draw plots between t/M_t and t as shown in Fig. 3(B). The slopes and intercepts of linear plots were employed to evaluate the rate constant k, equilibrium water uptake M_∞ and initial swelling rate (i.e. $r_{\text{ini}} = 1/A$). All these parameters are shown in Table 2. A close look at the values obtained reveals that all the plots exhibit high regressions thus indicating the suitability of this model. Similar types of results have also been reported by others. For example, dynamic swelling behavior of guar gum/poly(sodium acrylate) super absorbents have also demonstrated second order kinetic model (Langer, Peppas & Macromol, 1983). Similarly, hydrolyzed carboxymethyl cellulose-poly(sodium acrylate-co-acrylamide) hydrogels have also followed second order swelling kinetics (Berens & Hopfenberg, 1978). It should also be noted that the M_∞ values for various samples, as displayed in Table 2, indicate that there is not much agreement between the theoretical and experimental values. In fact, theoretical values are much less than the experimental ones .This may probably be due to the fact that CNWs/Poly(SA) hydrogels are heterogeneous systems, consisting of two chemical entities of almost different nature, one being continuous phase of poly(sodium

Table 2
Swelling parameters for water uptake analysis of various hydrogels and parameters associated with second order kinetic model.

Sample code	Swelling parameters			Second order kinetic parameters				
	N	$K \times 10^3$	R^2	$K_2 \times 10^4$ (g gel/g water min)	$M_{\infty\,(\mathrm{exp})}$ (g water/g gel)	$M_{\infty\,(\mathrm{theor})}$ (g water/g gel)	$r_{\mathrm{ini}} = (1/A)$ (g gel/g water/min)	R^2
CNWs/poly(SA) (0)	0.5909	12.35	0.994	2.231	24.43	17.123	0.0654	0.990
CNWs/poly(SA)(4.8)	0.6302	16.99	0.988	2.236	15.43	17.730	0.0703	0.993
CNWs/poly(SA)(9.7)	0.6238	17.53	0.988	2.733	13.34	14.903	0.0607	0.996
CNWs/poly(SA)(14.5)	0.6259	19.01	0.988	2.733	13.32	14.771	0.0596	0.995
CNWs/poly(SA)(19.4)	0.6302	15.91	0.988	3.517	9.38	10.650	0.0599	0.990
CNW/poly(SA)(24.3)	0.599	22.28	0.993	5.337	6.37	8.183	0.0357	0.991

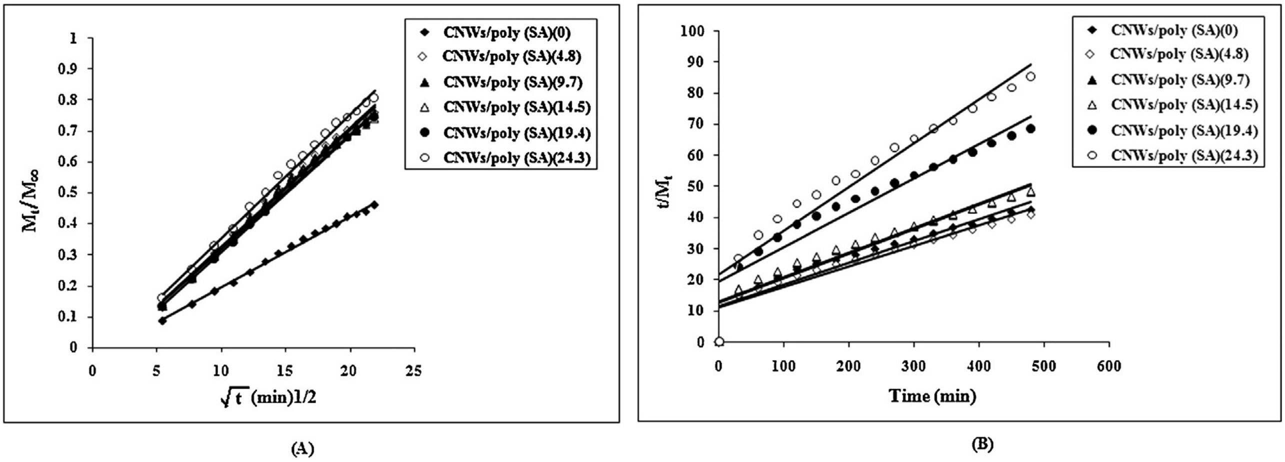


Fig. 3. (A) F v/s $t^{1/2}$ (B) t/M_t v/s t plots for various samples.

acrylate) networks while the other being dispersed cellulose nanowhiskers. Therefore, the theoretical predictions of Schott model may not be fully satisfied in the present polymer system.

3.4. *Water vapor permeation studies*

It has been reported that permeation of water vapor molecules through the film takes place through so many successive steps. First, the vapor molecules condense on the surface and solubilize in to the film (inside the available void spaces). Now these molecules diffuse through the width of the film and reach the other side of the film. Finally, the water vapor molecules leave the surface. Once these steps are complete, the process is repeated and the permeation continues. This is the reason that in most of the permeation studies, initial permeation data (may be for 1–2 h) is non-linear and then linearity persists in the data obtained for following times. The reason is that once transient period is over; there is smooth passage for the incoming water vapor molecules to pass through the hydrated path along the width of the film. The observed linearity allows determination of water vapor transmission rate (WVTR) (Dias et al., 2011). The results of permeation experiments are shown in Fig. 4. A linear relation between amount of vapor permeated (i.e. water gain) and time can be seen thus enabling us to determine WVTR. However, due to the involvement of various steps mentioned above during the initial transmission of moisture through film, the initial data points obtained are scattered. The slopes of the linear plots were used to evaluate different permeation parameters as shown in Table 3. The WVTR of various polymeric films, containing different amounts of cellulose nano-whiskers, are in the narrow range of 0.934–1.699 mg h^{-1} cm^{-2}. It is well known that the wound dressing film must be permeable to the moisture to an extent that neither there should be excessive loss of moisture to result in a dry wound, nor there should be such a low permeability which may cause leakage of exudates (Singh & Pal, 2012). Therefore, WVTR is a significant parameter to keep the wound comfortable and under healing. According to a report (Xu, Ma, Shi, Gao, & Han, 2007), the average WVTR of a normal and injured skin are 0.85 mg h^{-1} cm^{-2} and 1.16–21.40 mg h^{-1} cm^{-2}, respectively. Similarly, it has been suggested that wound dressings having low WVTR, in the range of 7.8–24.1 mg h^{-1} cm^{-2} are suitable for wounds with low exudates (Thomas, 1997). A comparison of these values of WVTR with the vales obtained in the films for the present study indicates that CNWs/poly(SA) hydrogel films have very low vapor transmission rate. The reason for this may be that these films have been prepared with relatively higher concentration of cross linker MB (i.e. 195 μmol) and therefore the presence of highly cross linked three-dimensional networks restricts the permeation of vapor molecules through the cross linked film matrix. In addition, one interesting observation is that the film containing 4.4 wt% of CNWs shows higher permeation rate as compared to the plain film (i.e. without

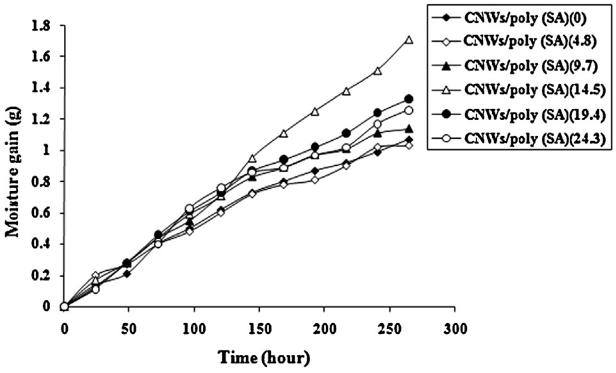


Fig. 4. Dynamic moisture permeation data for various samples.

Table 3
Water vapor permeation parameters for various samples.

Sample code	Water vapor transmission rate (mg h^{-1} cm^{-2})	Permeance (mg h^{-1} cm^{-2} Pa^{-1})	Water vapor permeability (mg h^{-1} cm^{-1} Pa^{-1})
CNWs/poly(SA) (0)	1.189	0.448	0.0305
CNWs/poly(SA)(4.8)	1.699	0.640	0.0288
CNWs/poly(SA)(9.7)	1.104	0.416	0.0262
CNWs/poly(SA)(14.5)	1.444	0.544	0.0343
CNWs/poly(SA)(19.4)	1.019	0.384	0.0211
CNWs/poly(SA)(24.3)	0.934	0.352	0.0236

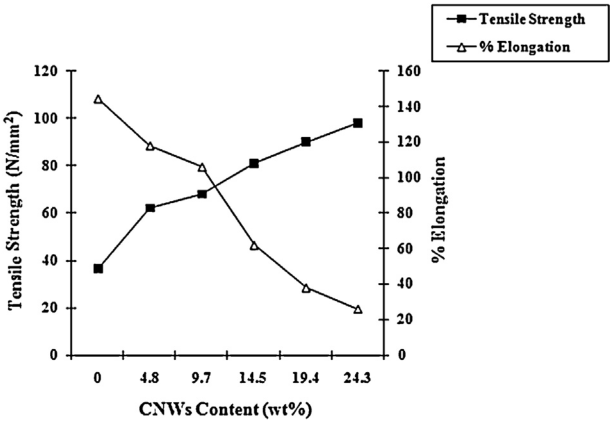


Fig. 5. Effect of CNWs content on TS and % elongation for various samples.

CNWs). This may be attributable to the enhanced water absorption of CNWs/poly(SA) (4.8) hydrogel film as compared to the plain film. However, with the further increase in the CNWs contents in the film, the WVTR shows a slight decreasing trend. This may be due to decrease in the water absorption capacity of the resulting films. In addition, dispersed cellulose nano-whiskers may possibly act as diffusion barrier and lower the transmission of vapor molecules. However, the observed decrease is not so remarkable.

Therefore, it is concluded that the films, in the present study, are having very low WVTR and are not suitable for wounds with high exudates. However, they may be used in the case of wounds with very low exudates. This indicates that the WVTR of these films must be improved or enhanced for their practical use.

3.5. *Mechanical strength of CNWs/poly(SA) films*

The mechanical properties of polymeric films, to be used in wound dressings and other biomedical applications, play significant role in establishing their suitability. The films must be able to withstand the appropriate stress when used on wounds. If some strip like cotton gauge further supports wound dressing film then it can easily withstand the external shear even if its tensile strength (TS) is low. More importantly, the film must have significant flexibility so that it does not break during the process of exudates absorption. The flexibility of a film is usually measured in the terms of percent elongation (PE). Therefore, percent elongation is rather more important property than the tensile strength for wound dressing films. The variations in tensile strength (TS) and percent elongation (PE) of the films with varying CNWs contents are shown in Fig. 5. The results reveal that TS increases with CNWs content while the PE shows a decreasing trend. The observed increase in TS with CNWs contents may simply be attributed to the fact that with increasing CNWs content, the film acquires more crystalline nature and thus show greater strength against applied force. In addition, the enhanced crystallinity renders brittleness to the films and they become less flexible. Moreover, the H-bonding type interactions between surface hydroxyls of CNWs and —COO^- groups from poly(SA) chains also restrict the flexibility of the polymeric chains thus causing a decrease in the PE. The TS and percent elongation for different CNWs loaded films were in the range of 36.54–98.11 × 10^{-2} MPa and 144–26 respectively. It is clear that TS values of these films are quite low while their PE values are quite satisfactory. In a study (Thu, Zulfakar, & Ng, 2012), the alginate based single and bi-layer hydrocolloid films had PE values of 23.78 and 59.05 whereas their TS were 20.82 and 27.22 respectively. Similarly, the wound dressing films, prepared from Haruan and Fusidic acid spray were reported to have TS and PE in the range of 15.09–28.17, and 7.61–39.63, respectively. (Febriyenti, Noor, & Bate, 2010). These films also had high mechanical strength. However, the films prepared in the present work, though have fair percent elongation, but their TS values are quite low. It appears that nature of polymers used for film preparations also plays a crucial role in governing these properties. A composite film, prepared by Agar, gelatin and Turmeric has exhibited very low TS and PE values (Saraswathy, Rohit, Shanmugam, Sozheeswari, & Charanya Ramlingam, 2012). The films were prepared with different compositions of various polymers along with plasticizers. However, the overall TS and PE were obtained in the range of 0.007–0.051 MPa and 13.8–25.5 respectively. Although, in this work no additional plasticizer was used but still the PE values were quite appreciable. It appears that presence of moisture in the hydrophilic network of films serves as plasticizer. In a study (Pawar, Boateng, and Tetteh, 2013) the PE for polyox-carrageenan-diclofenac sodium film was reported to be 1031. Such an abnormally higher percent elongation was because the films were prepared using glycerol as plasticizer.

3.6. *Folding endurance*

Finally, the folding endurance (FE) values for all the films are shown in along with other mechanical properties. Films did not show any cracks even after folding for more than 600 times. These indicates that all the films, containing different quantities of CNWs, pass through the Folding Endurance test and are suitable for wound dressing applications. The observed higher FE values are supported by the fact that all the films possess fair flexibility. This may be due to the fact that the two components of films, namely cellulose nano-whiskers and poly(SA), are hydrophilic and therefore, even at room temperature they possess enough moisture within the film matrices which act as plasticizer (Bourtoom, 2008). Therefore, it is most probable that these water molecules act as plasticizing agent and impart a higher folding endurance to these films. In a recent work (Mohamed, Haider, & Ali, 2011), buccal mucoadhesive films have been prepared with sodium carboxymethyl cellulose and hydroxypropyl cellulose without using glycerol and they showed folding endurance values of 200 plus for all compositions prepared. However, in most of the cases some plasticizing agents such as glycerol are used to impart flexibility to the films.

4. Conclusion

It may be concluded from the above study that cellulose pulp, from a paper industry, can be acid hydrolyzed to yield highly crystalline and thermally stable nano-whiskers. These CNWs, when present in a small quantity in poly(SA) hydrogels, (nearly 0.608–3.041 weight percent of polymer sodium acrylate) cause a slight enhancement in the water absorption behavior of resulting hydrogel films. However, as the CNWs contents exceed the above range the equilibrium water uptake is found to decrease. The CNW/poly(SA) films follow Second order swelling kinetics. The tensile strength (TS) of the films is found to increase due to addition of CNWs while PE and FE show decreasing trends. It is noteworthy that as the next phase of this study, the suitability of these films is to be tested as wound dressings. We propose to load antibacterial drug like gentamicin sulphate or miconazole nitrate into these films and carry out a detailed investigation of their drug releasing behavior, moisture and oxygen permeability and their biocidal action against *Staphylococcus aureus* and *Escherichia coli*. The work is under investigation.

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