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Thermal responsive hydrogels based on semi interpenetrating network of poly(NIPAm) and cellulose nanowhiskers

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ABSTRACT

A hybrid hydrogel nanocomposite was developed based on semi interpenetrating network that was formed as a result of concurrent free radical polymerization of N-isopropylacrylamide (NIPAm) and methylenebis acrylamide (MBA) crosslinker along with cellulose nanowhiskers (CNWs). CNWs were synthesized through sulfuric acid hydrolysis and used in preparation of semi interpenetrating network (IPN). CNWs have considered as reinforcement materials for poly(NIPAm) because CNWs were distributed as strengthening entities in Poly(NIPAm). N-isopropylacrylamide was polymerized in presence of methylenebis acrylamide crosslinking agent using K2S2O8 as initiator at 700 C for 1 h. The resulting hydrogel's structure, morphology, thermal sensitive property and swelling behavior were investigated. It was found that introducing CNWs into Poly(NIPAm) causes a huge increase in the value of equilibrium swelling ratio (ESR) as compared with the pure PNIPAm. The ESR ranges from 21.6 g/g to 5 g/g as the swelling temperature changes from 310 °C to 340 °C; hence, the hydrogel exhibits a good responsive temperature at about 320 °C.

1. Introduction

Smart materials are those materials which have one or more properties can be response to changes produced by external stimuli. Smart hydrogels are very sensitive to environmental stimulus, which manifested by a sharp phase transition; a feature which is important for their application particularly in pharmaceutical field. It is well known that hydrogel are defined as water swollen three-dimensional cross-linked networks of hydrophilic polymers (Koschella, Hartlieb, & Heinze, 2011). Hydrogel can be formed by physical (Hoare & Kohane, 2008) or chemical crosslinks (Hennink & van Nostrum, 2002) of homopolymers or copolymers. There are several research works dealt with hydrogel, therefore, the hydrogel have a wide range of applications, such as sustained-release drug delivery systems (Ischakov, Adler-Abramovich, Buzhansky, Shekhter, & Gazit, 2013), contact lenses (Yesilirmak & Altinors, 2013), biosensors (Wang, Papadimitrakopoulos, & Burgess, 2013), etc.

There are a lot of different kinds of polymeric materials are being investigated for their application in the fields of biomedicine and biotechnology. Dextran (Wang et al., 2013a), hyaluronic acid (Fakhari & Berkland, 2013), alginate (Pereira et al., 2013), chitosan (Anisha et al., 2013), cellulose (Cherian et al., 2011), polyacrylamide (Mandal, Kapoor, & Kundu, 2009), poly(*N*-isopropyl acrylamide) (Matricardi, Di Meo, Coviello, Hennink, & Alhaique, 2013; Nistor, Chiriac, Vasile, Verestiuc, & Nita, 2011), and their derivatives are examples of the most commonly used polymers to prepare interpenetrating network. Among these smart materials, poly(*N*-isopropyl acrylamide) (PNIPAm) was widely studied and used in temperature-responsive polymers because it is easily prepared and useful for such applications (Liu, Zhu, Wu, Wang, & Han, 2013). In particular, it exhibits phase transition temperature (LCST) at about 32–33 °C close to human body temperature (O'Shea, Qiao, & Franks, 2011), (Cha, He, & Ni, 2012). This behavior of PNIPAm makes it a very attractive candidate for making stimuli-responsive hydrogels. However, PNIPAm has the fatal defects of weak strength (Yi et al., 2011). Therefore, significant efforts have been directed toward enhancing strength and improving response of the hydrogel.

Recently, cellulose and its derivatives have been widely used in preparation of hydrogels (Hashem, Sharaf, Abd El-Hady, & Hebeish, 2013). Basically, various sources such as natural fibers (Fortunati et al., 2013; Lavoine, Desloges, Dufresne, & Bras, 2012) and sea animals (Anglès & Dufresne, 2000) can be used in preparation of nanometer-sized single crystals of cellulose, commonly referred to as whiskers, nanowhiskers. Cellulose nanowhiskers (CNWs) are regions growing under controlled conditions of acid hydrolysis. Meanwhile, acid hydrolysis dissolves amorphous regions and allows individual high-purity crystals to form. (Azizi Samir, Alloin, & Dufresne, 2005; Dash, Li, & Ragauskas, 2012). Sulfuric acid is most

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typically used as it produces a negative surface charge on the particles, leading to more stable suspensions (Hubbe, Rojas, Lucia, & Sain, 2008).

Zoppe et al. investigated the colloidal stability and thermo responsive behavior of poly(N-isopropyl acrylamide) brushes grafted from cellulose nanocrystals (Zoppe, Osterberg, Venditti, Laine, & Rojas, 2011). Carboxylated nanocellulose has been used as a matrix material for the preparation of *N*-isopropyl acrylamide-based thermal/pH sensitive hydrogels (Cha et al., 2012). The results indicate that the water holding capacities of the hydrogels increased significantly with the addition of carboxylated nanocellulose. We undertake the present work with a view to synthesize and characterize (a) cellulose nanowhiskers and (b) novel hybrid s which are temperature-sensitive. This hydrogel is developed based on semi interpenetrating network formed through concurrent free radical polymerization of NIPAm and crosslinking MBA along with cellulose nanowhiskers. Factors affecting formation of the hybrids are studied. The onset of changes in the structure of the hydrogels by such factors are also examined. Furthermore, the ultrafine microstructure features of the hybrids and their impact on the swelling properties of the hybrid s are highlighted.

2. Experimental

2.1. Materials

Cotton sliver, Giza 86 was kindly supplied by Cotton Research Institute, Giza. Sodium hydroxide, Sodium perborate, sulfuric acid (95–98%), *N*-isopropyl acrylamide (NIPAm, purchased from Aldrich Chemical Co.), *N*,*N*′-methylenebisacrylamide (MBA) and potassium persulfate ($K_2S_2O_8$) were all of laboratory grade chemicals.

2.2. Preparation of cellulose nanowhiskers

Cellulose nanowhiskers were prepared by subjecting the cotton slivers to three successive treatments, namely, alkali treatment, perborate treatment, and sulfuric acid treatment. While the first two treatments address the purification of the cotton fibers, the third treatment is concerned with conversion of the purified fibers to cellulose nanowhiskers. The experiments techniques adopted were as follows.

2.2.1. Alkali treatment

Cotton sliver was boiled in an aqueous solution containing 2.5 g/l sodium hydroxide and 2.0 g/l nonionic wetting agent, under reflux for 60 min using a material to liquor ratio 1:20. The cotton sliver was then washed three times with boiling water, twice with cold water and finally air dried. This alkali treatment removes all the impurities excepts the natural coloring matters which is removed by subsequent treatment with sodium perborate as described under.

2.2.2. Perborate treatment

The alkali treated cotton sliver was further purified by boiling in an aqueous solution containing 2.5 g/l sodium perborate, 0.5 g/l urea and 2.0 g/l nonionic wetting agent, under reflux for 60 min using a material to liquor ratio 1:20. The sliver was then washed three times with boiling water, twice with cold water and finally air dried.

2.2.3. Sulfuric acid treatment

The as purified cotton slivers were cut into small pieces prior to hydrolysis treatment with sulfuric acid. The hydrolysis was carried out by introducing the small pieces of the cotton into 60% (w/w) sulfuric acid (10 ml/g cotton) to form suspension. This suspension was held at 60 °C under strong mechanical stirring for 60 min to allow for hydrolysis. Immediately, following hydrolysis, the suspension was diluted five-fold with cold distilled water to stop the reaction. The suspension was then transferred into centrifuge bottles and centrifuged at 12,000 rpm for 10 min and decanted to separate the crystals. The solid aggregates in the suspension were disrupted by sonication. The residual materials were then washed with distilled water and the mixture was centrifuged again to remove traces of sulfate groups. Dialysis against distilled water was performed to remove free acid in the dispersion using dialysis tubing (MWCO 12,000–14,000). This was verified by neutrality of the dialysis effluent. The resultant CNWs suspension was frozen. After freezing, samples were freeze-dried (−60 °C, 0.1 mbar, under such pressure cellulose nanostructure will not be affected) as powders.

2.3. Preparation of CNWs based hydrogels nanocomposites

The CNWs based hydrogels nanocomposites were prepared by concurrent crosslinking and free radical polymerization of NIPAm in CNWs suspension. A typical procedure for co-polymerization is described as follows: the monomer *N*-isopropyl acrylamide and the crosslinking agent *N*,*N*′-methylenebisacrylamide (MBA) were first dissolved in little amount of distilled water before addition to CNWs suspension, followed by vigorous stirring of the mixture to produce uniform suspension. The total concentration of both NIPAm and CNWs used in hydrogel preparation is 10% (w/v). The mixtures of CNWs, NIPAm and crosslinker were heated reaching the temperature of 70 °C. After that, the initiator potassium persulfate (KPS) was dissolved and added drop wise into the mixture, and then polymerized for 1 h. The as-resulted hydrogel after polymerization for 1 h was purified by immersing into excessive distilled water followed by washing several times. The purified PNIPAm/CNWs hydrogel was dried under mild condition and subsequently frozen for further drying using freeze-drier (−60 °C, 0.1 mbar).

Preparation of PNIPAm/CNWs was conducted under a variety of conditions including CNWs: NIPAm ratio, crosslinker concentration, initiator concentration and temperature responsive for swelling behavior of the hybrid s as detailed in the next section

2.4. Characterization

Characterization of the nanohydrogel hybrid composites was performed using the state-of-art facilities as given under.

2.4.1. Transmission Electron Microscope (TEM)

The morphology of cellulose nanowhiskers (CNWs) was characterized using Transmission Electron Microscopy (TEM) (JEOL 1200, JEOL USA, Inc.) with an accelerating voltage of 80 kV. The 0.1 wt% nano-crystal suspensions were dropped onto copper grids coated with a carbon support film (Wang et al., 2012).

2.4.2. X-ray diffraction (XRD) analysis

The XRD patterns of dried CNWs were obtained using a D500 diffractometer (SIEMENS) operated at 30 kV and 15 mA, utilizing a Cu-Kα radiation source ($k = 0.154$). The scans were controlled by the Diffrac-AC software program. The crystallinity index of cotton slivers (native cellulose) and CNWs were calculated according to Eq. (1).

$$I_c(\%) = \frac{I_{(Crys+am)} - I_{(am)}}{I_{(Crys+am)}} \times 100 \quad (1)$$

where $I(crys + am)$ represents the peak intensity (count persecond) around 22.8° for the crystalline and amorphous part. I(am) is the peak intensity around 18° and represents the amorphous part of the cellulose (Hossain et al., 2012).

2.4.3. Fourier-transformed infrared spectroscopy (FT-IR)

FT-IR spectra were recorded using a S-100 FT-IR spectrometer (Perkin Elmer) and scanned from 4000 to 400 cm^{-1} in ATR mode and using KBr as supporting material. Characterization of samples using FT-IR technique was carried out to follow the change in the functionality of CNW as a result of being crosslinked with poly *N*-isopropyl acrylamide (PNIPAm) (Cha et al., 2012).

2.4.4. Thermogravimetric analysis (TGA)

The thermal properties of PNIPAm/CNWs hydrogel, PNIPAm and CNWs were measured using thermogravimetric analysis (TGA) STD Q600. In preparation of samples for TGA, the hydrogels were ground to powder form. Decomposition profiles of TGA were recorded at a heating rate of 10.0 °C/min. between room temperature and 600.0 °C in nitrogen (Gupta, Ghute, & Badiger, 2011; Zhang et al., 2009).

2.4.5. Swelling behavior of hydrogel

The classical gravimetric method was used to measure the equilibrium swelling ratio (ESR) of the hydrogels. The hydrogel samples were equilibrated in water at a predetermined temperature 20 °C. The freeze-dried hydrogel sample (about 0.2 g) was soaked in an excessive amount of distilled water to reach the swelling equilibrium. The swollen hydrogels were filtered using a 100-mesh sieve and drained for 20 min to remove free water before weighing the mass of the swollen hydrogels. The equilibrium water absorption was calculated using Eq. (2):

$$ESR = \frac{W_1 - W_o}{W_o} \quad (2)$$

In Eq. (2), ESR is the equilibrium water absorption, defined as grams of water per gram of sample; W_o and W_1 are the weights of sample before and after swelling, respectively (Cha et al., 2012; Ekici, 2011).

2.4.6. Scanning electron microscopy (SEM)

The morphologies of porous structure of PNIPAm/CNWs hydrogel were examined by SEM. To prepare the sample, the swollen hydrogel sample was first equilibrated in distilled water at room temperature, then quickly frozen and freeze-dried in a Crest Freeze Drier under vacuum at −60 °C. After that, the freeze-dried hydrogel sample was fractured carefully, gold-coated and then subjected to the SEM analysis using a scanning electron microscope (JSM-6400, JEOL, Japan) (Wang, Ni, Jahan, Liu, & Schafer, 2011).

3. Results and discussion

Poly(*N*-isopropyl acrylamide) – cellulose nanowhiskers semi interpenetrating polymeric networks (IPN) hydrogels were synthesized by free radical polymerization of NIPAm monomer in presence of MBA crosslinking agent using KPS as initiator. The sulfate anion radical and/or the hydroxyl free radical (produced from the thermal decomposition of KPS and reactions among the KPS decomposition products) abstract hydrogen from the hydroxyl groups of the polysaccharide substrate to form corresponding alkoxy radicals on the substrates (Ekici, 2011; Pourjavadi, Barzegar, & Mahdavinia, 2006). Free radicals formed on NIPAm and crosslinker (MBA) are due to the role of initiator radical, which breaks the double bonds of monomer and crosslinker molecules. Regarding to these free radicals, the semi interpenetrating network hydrogel could be formed through formation of crosslinking points (Ekici, 2011).

3.1. Preparation of cellulose nanowhiskers and their homogenous suspensions

The most promising route for preparation of well-stabilized nanocellulose suspension is acid treatment. Cellulose microfibrils are composed of highly ordered “crystalline” regions and less ordered “amorphous” regions (Barazzouk & Daneault, 2011). Acid hydrolysis extracts the crystalline particles from different cellulosic source materials, thereafter, the cellulose rod-like in shape is obtained called nanocrystals or nanowhiskers (Lu & Hsieh, 2010). In native cellulose, the amorphous regions are more accessible to acid molecules and susceptible to the hydrolytic actions than the crystalline region. With sulfuric acid, the amorphous regions are digested very fast. Under the conditions employed, i.e., 60 min at 60 °C, most of the amorphous regions were removed leaving cellulose nanowhiskers in the reaction solution (Dadkhah Tehrani & Neysi, 2013; Lu & Hsieh, 2010). Also, sulfate groups induced negative charges on cellulose nanowhiskers surface cause anionic stabilization via repulsion forces, which prevent the agglomeration (Beck, 2011).

In the present work, native cotton was purified then subjected to sulfuric acid hydrolysis in order to obtain cellulose nanowhiskers (CNWs) as detailed in Section 2. The weight of the obtained freeze-dried CNWs was about 57% of the initial weight of cotton.

Fig. 1A represents TEM micrograph of cellulose nanowhiskers, while, Fig. 1B and C illustrate the size distribution of cellulose nanowhiskers in diameter and length, respectively. From these figures, it is clear that CNWs could be produced, successfully, by sulfuric acid hydrolysis from cotton fibers at 60% (W/W) sulfuric acid. CNWs are well-stabilized polydispersed nanoparticles with size diameter ranging from 6 to 40 nm and length in range of 80–450 nm. It is certain, however, that the majority of whiskers size are ranging from 10 to 25 nm with a length range of 80–200 nm.

Fig. 1D illustrates the powder X-ray diffractograms obtained from cotton slivers (native cellulose) and CNWs. The principal peaks from XRD patterns (Fig. 1D) are at 2θ values 14°, 16°, 22°, and 35°. These four peaks correlate, respectively, with [1 0 1], $[1\,0\,1]^{-}$, [2 0 0] and [4 0 0] crystal lattice planes which were assigned to typical cellulose I crystalline structure (Hossain et al., 2012). These data confirm that the CNWs are mainly cellulose I and are not converted to cellulose II during sulfuric acid hydrolysis as well as CNWs species were identical to their neat, untreated cellulose sources. With respect to XRD patterns measurements, the crystallinity index give the following values 80.3%, 90% for cotton slivers and CNWs, respectively. CNWs becoming more crystalline than the original cellulose, which due to the preference acidic attack in the amorphous regions in cellulose, which increases the level of the crystalline domains yielding to CNWs.

3.2. Preparation of CNWs based hydrogels nanocomposites

A mixed polymer network was obtained through radical copolymerization of NIPAm and CNWs in presence of MBA as crosslinker and KPS as initiator at 70 °C for 1 h as postulated in Scheme 1. The so-obtained hydrogels were transferred to purify by washing several times with distilled water and then dried under mild condition and subsequently frozen for further drying using freeze-drier (−60 °C, 10 Pa). A small piece of freeze dried sample (about 0.2 g) has been soaked in distilled water to study the swelling ratio behavior of the hydrogel.

3.2.1. Fourier-transformed infrared spectroscopy (FT-IR)

The FTIR spectra of CNWs, PNIPAm and PNIPAm/CNWs hydrogel are shown in Fig. 2. FTIR was used to verify the structure of the so-prepared PNIPAm/CNWs semi IPN hydrogels while the PNIPAm/CNWs spectrum compared with spectrum of NIPAm and

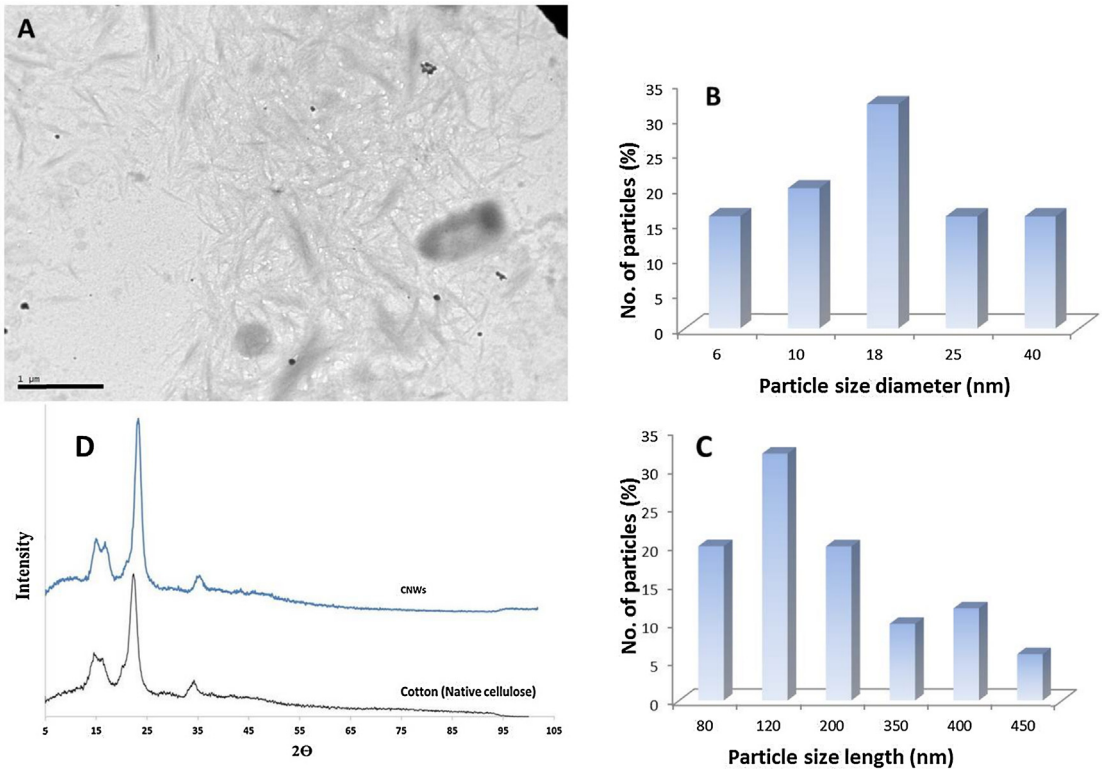
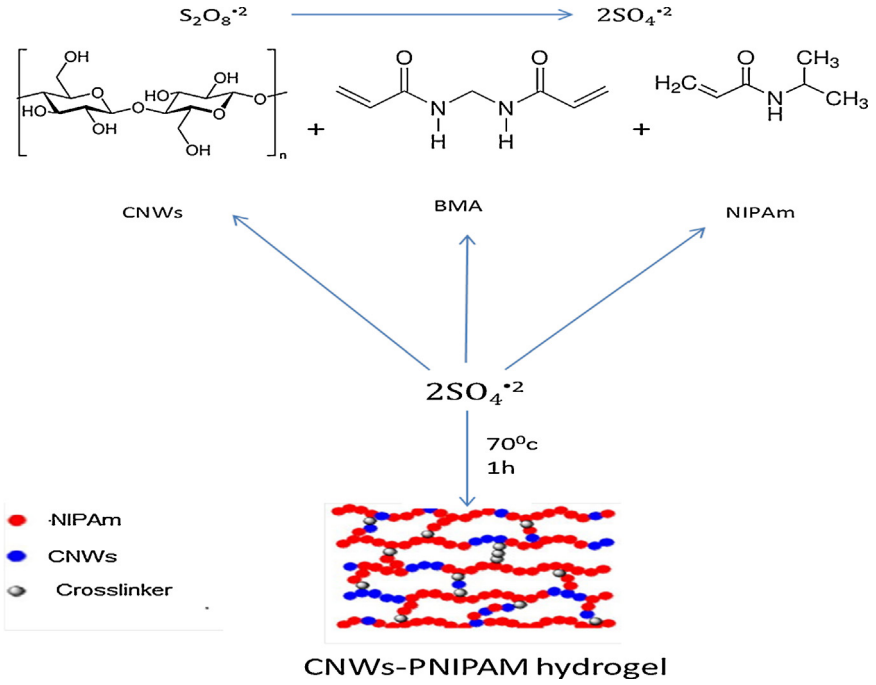


Fig. 1. (A) TEM micrograph of cellulose nanowhiskers; (B and C) histograms showing the distribution of particle size diameter and the distribution of particle size length of cellulose nanowhiskers, respectively, prepared using 60% sulfuric acid at 60 °C for 60 min; and (D) XRD patterns of cotton slivers (native cellulose) and cellulose nanowhiskers (CNWs).

spectrum of CNWs, a characteristic peak observed for NIPAm spectra at 3300 cm^{-1} which could be due to the NH— asymmetric stretching (NH—), changed into a strong, high intensity and broad peak around 3440 cm^{-1} after forming semi IPN PNIPAm/CNWs hydrogel. The broadening of this band is due to the existence of intramolecular hydrogen bonding between —C=O groups and —NH groups of NIPAm and —OH groups of cellulose units. The most obvious characteristic of the spectra which distinguished it from the spectra of the CNWs is the presence of absorption bands at 1549 cm^{-1} and 1632 cm^{-1}, which indicate the presence of amide group of the PNIPAm, also, the three medium strong peaks between 1000 cm^{-1} and 650 cm^{-1}, which were ascribed to CH= vibration



Scheme 1. shows the mechanism of the preparation of CNWs-PNIPAm semi IPN hydrogel in the presence of crosslinker (MBA) and initiator KPS for 1 h at 70 °C.

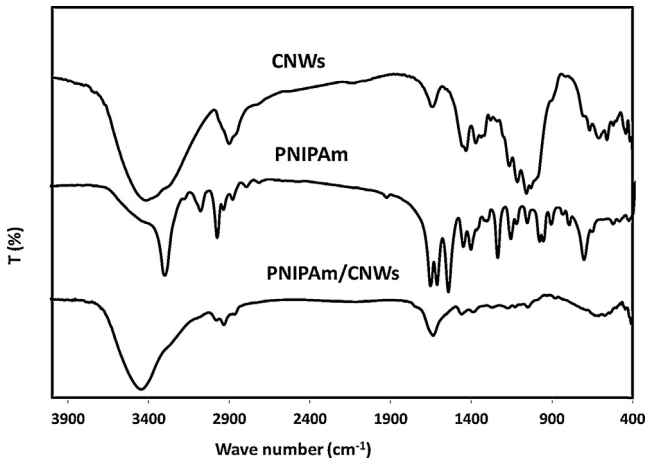


Fig. 2. FTIR of CNWs, PNIPAm and CNWs-PNIPAm semi IPN hydrogel.

of NIPAm disappeared after polymerization confirming that PNIPAm is chemically crosslinked with CNWs backbone as described in Scheme 1. Therefore, it can be concluded that the CNWs/PNIPAm hydrogel has the characteristic features of both CNWs and NIPAm groups. This data confirm the existence of PNIPAm/CNWs semi IPN hydrogel formed by polymerization/crosslinking of NIPAm monomers and CNWs.

3.2.2. Thermo gravimetric analysis (TGA)

The thermal degradation behavior of the hydrogels was studied in the range 25–500 °C under a nitrogen atmosphere. The thermogravimetry curves obtained with PNIPAm and PNIPAm/CNWs hydrogel are presented in Fig. 3. Also, Table 1 shows the relationships between the weight loss % of CNWs, PNIPAm and PNIPAm/CNWs hydrogel at the temperature of pyrolysis concluded from TGA analysis. The first phase of the weight loss (25–150 °C) indicates evaporation of water and shows that both hydrogels are hygroscopic. For PNIPAm, two decomposition phases are observed, one at below 200 °C and the other at about 373 °C, with maximum decomposition rate at 407 °C. For CNWs, the vast majority of the weight loss occurred at higher than 250 °C, with the maximum decomposition rate at 340 °C. The maximum decomposition rate of PNIPAm/CNWs hydrogel occurred at 410 °C. The last degradation temperature of the hydrogels was due to random chain scission of PNIPAm.

A close examination of Fig. 3 (Table 1) would reveal that, weight loss % and residual content are ordered as follows: CNWs > PNIPAm/CNWs hydrogel > PNIPAm. So, the PNIPAm/CNWs hydrogel is more thermally stable than PNIPAm cross-linked hydrogel, most probably due to the presence of CNWs, which conferred more ordered structure on PNIPAm/CNWs semi IPN hydrogel, with respect to crystallinity of CNWs.

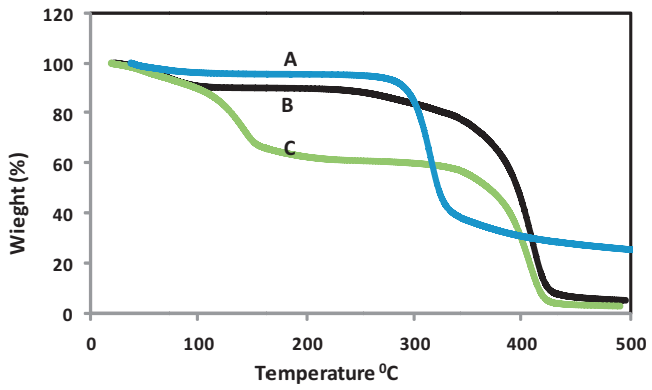


Fig. 3. TGA curves of (A) CNWs; (B) CNWs-PNIPAm hydrogel; and (C) PNIPAm.

3.2.3. Swelling behavior of hydrogels

3.2.3.1. Effect of incorporation of CNWs into hydrogel structures. Fig. 4A shows the influence of incorporation of CNWs into hydrogel structures on the equilibrium swelling ratio (ESR) for which the monomer composition was varied as follows: 0:100, 10:90, 25:75, 50:50 and 100:0 with respect to CNWs%: NIPAm%. Obviously, incorporation of CNWs into PNIPAm by 10% (10:90) and 25% (25:75) causes enhancement in the ESR of the hydrogel. The value of this ESR is higher than that of the control PNIPAm hydrogel (0:100), which could be attributed to increased porosity of the microstructures as a result of the tendency of CNWs to act as crosslinker, meanwhile CNWs induce hydrophilicity thereby rendering the hydrogel water absorbing. However, increasing CNWs content in hydrogel composition than 10% leads to significant decrease in ESR. This result could be related to the interaction of CNWs with the polymer PNIPAm and the role of CNWs as fillers that most probably occupy the void spaces within the polymer network and, in so doing, brings about a more compact gel and hinder the swelling process.

3.2.3.2. Effect of crosslinker concentration on ESR of the hydrogel. Fig. 4B shows the effect of crosslinker (MBA) concentration on ESR of CNWs based hydrogels nanocomposites. As described above in Fig. 4A, the ideal ratio of CNWs% incorporated in the polymer PNIPAm is 10:90. This ratio is applied along with different concentrations of the crosslinker *N,N′*-methylenebisacrylamide (MBA) at constant initiator (KPS) concentration. The concentrations of the crosslinker used were 1.0%, 1.5%, 3.0% and 4.5% (based on weight of NIPAm monomer).

Fig. 4B discloses that the ESR of the formed hydrogels displays a very fast increase upon increasing the crosslinker concentration from 1% to 3%. Above 3% crosslinker concentration, the ESR of the formed hydrogel decreases by increasing the crosslinker concentration up to 6%. It is logical that the role of crosslinker is to pursue network formation via crosslinking which bridges two sites on different polymer chains. Hence, excessive crosslinks brought about at higher concentration of the crosslinker would shorten the distance between the crosslinking sites and, as a consequence, shrinking would occur and the micro-porous size becomes smaller leading to reduced water capacity of the so-prepared hydrogels. The highest ESR value of the hydrogel is achieved when the crosslinker MBA is used at about 3% (based on weight of NIPAm monomer).

3.2.3.3. Effect of initiator concentration on ESR of hydrogel. Fig. 4C shows the ESR of cellulose nanowhiskers (CNWs) – hydrogels nanocomposites as a function of the initiator (KPS) concentration used in the synthesis of the hydrogel. Initiator concentrations used (based on weight of NIPAm monomer) were 1%, 1.5%, 3%, 4.5% and 6%. The CNWs-nanocomposite hydrogel was synthesized using CNWs%:NIPAm% at a ratio of 10:90 along with 3% of the crosslinker MBA.

Results of Fig. 4C depict that the ESR of the hydrogels under investigation exhibits their high values within a very narrow range of initiator concentration. The favorable effect of the initiator starts at initiator concentration of 1% then reaches the highest ESR value at initiator concentration of 1.5%. Further increase in the initiator concentration is accompanied by decreasing ESR values. Such variations seem to be induced and controlled by the initiator concentration. It is understandable that it is so difficult for monomer NIPAm to polymerize completely with insufficient initiator concentration as well as to polymerize quickly and steadily with excessive initiator concentration, so that, the ESR of the hydrogel becomes

Table 1
Weight loss % of CNWs, PNIPAm and CNWs-PNIPAm hydrogel at the temperature of pyrolysis concluded from TGA analysis.

Sample	Evaporation		Main decomposition						Residual content	
	Wt. %	Temp	Decomposition temp.		Remaining weight %		Weight loss %	Rate per temp.	Wt.%	Temp.
			T_0	T_∞	W_0	W_∞				
CNWs	5.96	100	310.33	358.85	91.4	55.5	35.9	1.35	28.6	594
PNIPAm	10.3	100	106.5	407.5	91.14	20.32	70.82	4.25	2.76	486
CNWs-PNIPAm	9.23	100	376.42	410.28	79.47	28.89	50.58	0.67	5.1	490

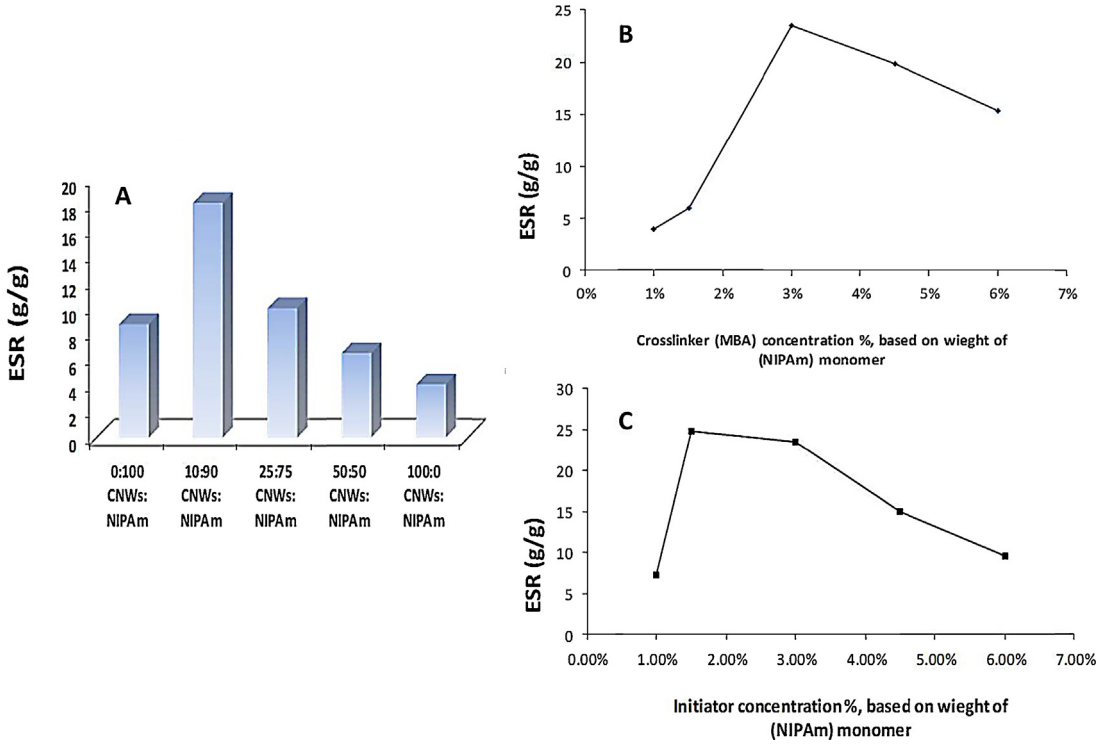


Fig. 4. (A) Effect of incorporation of CNWs into the hydrogel structures on ESR; (B) Effect of crosslinker concentration on ESR of the hydrogel prepared using a ratio 10:90 of CNWs%: NIPAm% for 1 h at 70 °C; and (C) Effect of initiator concentration on ESR of hydrogel with a ratio 10:90 of CNWs%: NIPAm% and 3% of crosslinker MBA for 1 h at 70 °C.

debased. Abundance of free radicals formed at higher initiator concentration causes fast rate of termination and consequently low molecular weight of the polymer (PNIPAm) besides terminating active sites on CNWs and MBA crosslinker. Once this is the case we are dealing with different hydrogels when compared with those formed at proper concentration of the initiator. In current situation, the initiator (KPS) concentration of 1.5% is regarded as optimal to hydrogels with high ESR values and complete polymerization.

3.2.3.4. Temperature responsive on swelling behavior of the hydrogel. Hydrogel of PNIPAm with the crosslinking structure in aqueous solution will swell below its lower critical solution temperature (LCST), which is around 32 °C, and shrink above this temperature. This property is the consequence of reversible breaking and formation of hydrogen bond between N—H or C═O group of PNIPAm and surrounding water molecules when temperature slightly changes. With this property, it is expected that the grafted PNIPAm on cellulose will display sensitivity measured by water absorption capacity of the grafted cellulose due to increased hydrophilicity of the NIPAm grafted cellulose (Suka & Simanjuntak, 2011).

Fig. 5 shows the temperature responsive property of the CNWs based nanocomposite hydrogel versus ESR of the hydrogel. Changes in the temperature responsive property was monitored by subjecting the hydrogel to water absorption experiments at different temperatures in the range of 20–60 °C. Results of Fig. 5 signify that, the ESR of the hydrogel sample decreases sharply from 23.6 g/g to 8.3 g/g when the temperature increases from 25 °C to 32 °C and remains practically constant from 35 °C and up to 60 °C. This implies that, the equilibrium swelling ratio is quite different at various swelling temperatures. Furthermore, the hydrogels exhibit good swelling behavior compared with that reported on using of carboxylated nanocellulose as a matrix materials in preparation of thermal sensitive hydrogels (Cha et al., 2012), and display

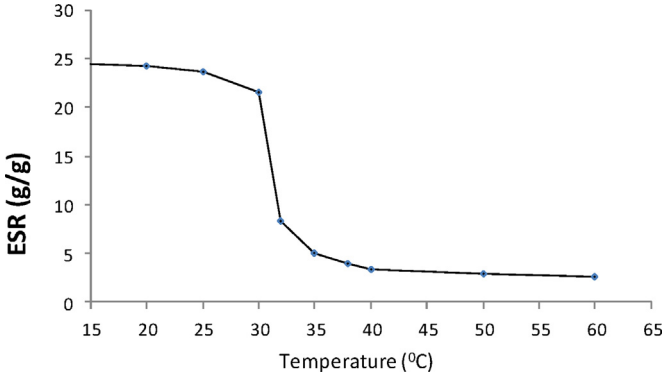


Fig. 5. Temperature responsive on swelling behavior of the hydrogel prepared using a ratio 10:90 of CNWs%: NIPAm%, 3% of crosslinker MBA and 1.5% of initiator KPS for 1 h at 70 °C.

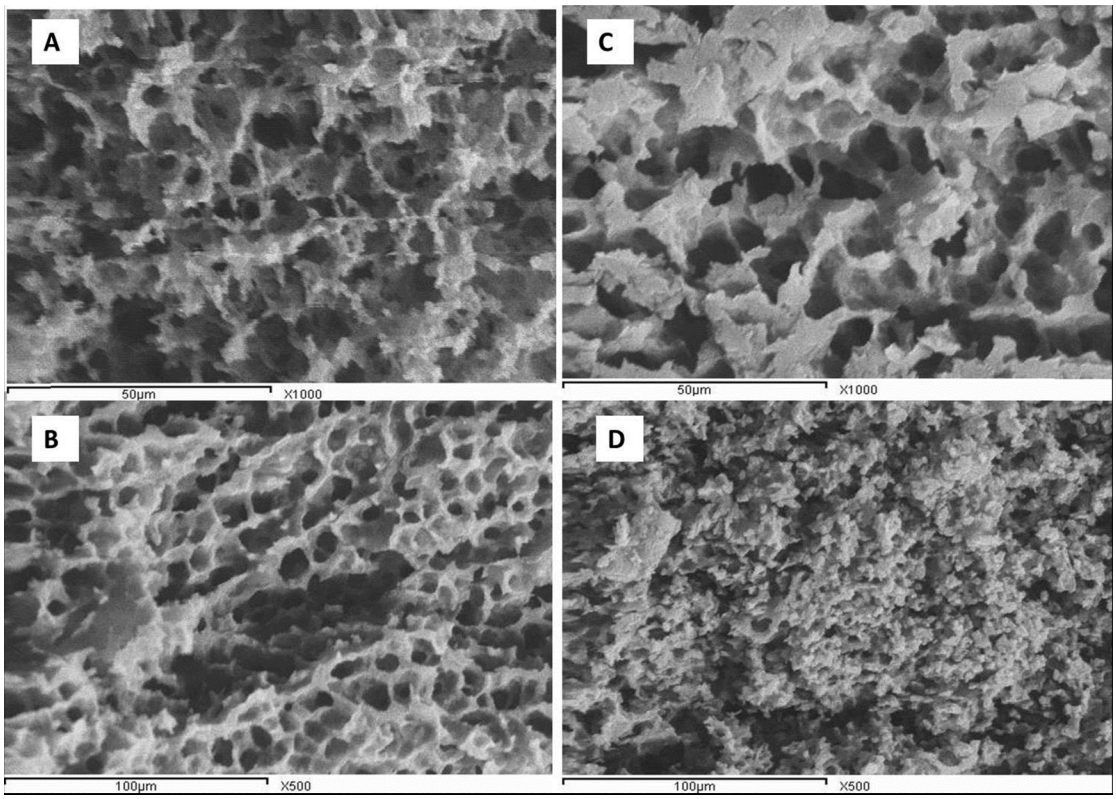


Fig. 6. SEM images of (A) cross-section of CNWs-PNIPAm hydrogel; (B) longitudinal section of CNWs-PNIPAm hydrogel; (C) longitudinal section cross-section of PNIPAm hydrogel; and (D) longitudinal section of PNIPAm hydrogel, crosslinker MBA (3%) and of initiator KPS (1.5%) for 1 h at 70 °C.

hydrophilicity at temperature lower than 32 °C, otherwise, these hydrogels exhibit very low ESR and become hydrophobic above 32 °C similar to LCST of pure PNIPAm. It can be, therefore, concluded that, CNWs based nanocomposite PNIPAm hydrogels acquire the good temperature stimuli.

3.2.4. Morphology of PNIPAm/CNWs semi IPN hydrogel using scanning electron microscopy (SEM)

The Scanning Electron microscope images of the internal structure of PNIPAm/CNWs semi IPN hydrogel and PNIPAm hydrogel in longitudinal section and cross section are shown in Fig. 6. SEM micrographs of PNIPAm/CNWs semi IPN hydrogel (Fig. 6A and B) confirm some findings which could be enumerated as follows: (a) the morphology of PNIPAm/CNWs hydrogels exhibits a homogeneous, well-proportioned network structure and dense architecture without any apparent microscopic phase separation of the polymeric constituents; (b) the hydrogels are covered by highly connected irregular pores with size ranging from 0.5 to 1.2 μm; (c) the pores were spherical in shape with circular interactions; and (d) the distribution of pores over the hydrogel appears more even and homogeneous throughout the surface area.

On the other hand, the SEM micrographs of PNIPAm hydrogel (Fig. 6C and D) shows that, a poor network interaction with uneven dispersions of pores throughout the surface area of the hydrogel. The pore sizes in PNIPAm are ranged around 3–10 μm. Furthermore, it seems that PNIPAm has the largest pore size than that observed with PNIPAm/CNWs hydrogel. Hence, PNIPAm/CNWs hydrogel appears to have the largest number of pores per unit area.

These findings certainly affect the swelling degree of hydrogel by enabling water molecules to be absorbed in every direction with faster response time. This would suggest that incorporation of CNWs in PNIPAm hydrogel enhances and improves the formation of pores and increase the permeability of pores within the hydrogel matrix thus improving its swelling properties.

4. Conclusions

Smart materials are those materials which have one or more properties can be response to changes produced by external stimuli. Smart hydrogel is a crosslinked network of hydrophilic polymers that can absorb and hold large amount of water, in addition, they are very sensitive to environmental stimulus, which is manifested by a sharp phase transition; a feature which is important for their application particularly in pharmaceutical field. Current work addresses the synthesis and characterization of novel hybrid hydrogels nanocomposites which are temperature responsive. The synthesis involves preparation of cellulose nanowhiskers (CNWs) followed by inserting them in a polymerization system containing NIPAm monomer and crosslinker, KPS initiator and water.

In this way PNIPAm/CNWs hydrogels nanocomposites are formed. Modulation of the properties of this hydrogel could be made through varying the factors affecting the structure of the hydrogel. Factors studied encompass CNWs%: NIPAm% ratio, concentration of both the crosslinker and initiator as well as temperature-responsive for swelling behavior of the hybrid hydrogels nanocomposites. Conclusions arrived at from these studies are summarized below.

1. CNWs produced through sulfuric acid hydrolysis are well stabilized polydispersed nanoparticles with size diameter ranging from 10 to 25 nm with a length range of 80–200 nm.
2. Incorporation of CNWs into PNIPAm enhances the values of equilibrium swelling ratio (ESR) provided that the concentration of

CNWs are within 10% using CNWs:PNIPAm ratio 10:90 and 25% using CNWs: PNIPAm ratio of 25:75.

3. ESR of the formed hydrogels displays a very fast increase by increasing the crosslinker (MBA) concentration from 1% to 3% then decreases upon further increase in the concentration up to 6%.
4. ESR exhibits high values within a very narrow range (1–1.5%) of initiator (KPS) concentration then decreases thereafter.
5. The hydrogels exhibit good swelling behavior and display hydrophilicity at temperature lower than 32 °C; above this temperature the hydrogels become hydrophobic (as evidence by the low value of ESR) similar to LCST of pure PNIPAm.
6. FTIR and TGA were employed to verify the ultrafine structure of the hydrogels under investigation.
7. Morphology of PNIPAm/CNWs hybrid hydrogels nanocomposites as revealed by SEM indicates: (a) the morphology exhibits a homogeneous, well-proportional network structure and dense architecture without apparent microscopic phase separation of the polymeric constituents, (b) the hydrogel are covered by highly connected irregular pores with size ranging from 0.5 to 1.2 μm, (c) the pores are spherical in shape with circular interactions, and (d) the distribution of the pores over the hydrogel appears more even and homogeneous throughout the surface area.

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