Synthesis and Characterization of Nanocomposite Based on Waste Polystyrene and Cellulose Nanowhiskers

Manal El Hefnawy [(a)], Samy Bader [(b)].
(a) Natural Science Department , Faculty of Engineering ,Benha University , shoubra, Egypt
(b)Chemistry Department, Faculty of Science, Benha University, Egypt.
* E-mail of the corresponding author: manalelhefnawy@yahoo.com

Abstract

A superabsorbent nanocomposite composed of waste polystyrene chitosan acrylic and cellulose nanowhiskers(CNWs) were synthesized and characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM).The effect of major factors on water absorbency were investigated to obtain optimum conditions with high swelling capacity.It was found that the incorporation of CNWs improved the swelling capacity as well as improved the mechanical properties.The composite showed responsive behavior in relation to pH and salt solution which make these smart materials suitable for several technological applications. Finally the use of waste polystyrene provided a new method for converting waste resources into variable products.

Keyword: waste polystyrene, cellulose nanowhiskers, chitosan, superabsorbent, hydrogel.

1. Introduction:

Polystyrene is a synthetic hydrophobic polymer that is not biodegradable. Thus it can cause environmental pollution [1]. There are different alternatives for reducing the problem of its disposal and for converting it into valuable product, including polymer modification and functionalization [2, 3]. The introduction of polar groups into synthetic polymers causes the induction of hydrophilicity [4, 5] functionalized polystyrene has different applications for instance, as a polyelectrolyte for water treatment processes [6].

Hydrogels are three dimensional networks of hydrophilic polymer that can swell to an equilibrium state that retains a significant amount of water and/ or biological fluid .Among the class of hydrogels, the superabsorbent ones can exhibit fast swelling rate, Absorbing extraordinary amounts of water [7, 8]. These properties are observed because the hydrogel pores disposed in interconnected networks with diameters of several hundred microns create upon channels that allow water movement inward the matrix for capillarity.

Studies have been reported on the preparation of superabsorbent hydrogels using natural polymer which could increase their biocompatibility, biodegradability, water uptake capacity as well as decrease the toxicity, broadening their potential of application [9, 10]. From the main polymers used in hydrogels preparation are chitosan .

Chitosan is a well known polymer derived from the biopolymer chitin, shows interesting physical, chemical and biological properties, antibacterial, haemostatic activities and chelating potential [11-13]. However, the use of chitosan to form superabsorbent materials has been limited because of their usually poor mechanical properties when compared to other polymer. The addition of reinforcing filler into the hydrogel matrix can enhance their mechanical properties and improve their handling.CNWs have been incorporated in a wide variety of materials to improve strength properties [14, 15]. Some works have reported that cross linked composites CNWs showed unique properties that were distinctly from the starting components and of special interest are the hydrogel [16, 17].

In this work the purpose was to prepared superabsorbent hydrogel using waste polystyrene, chitosan and cellulose nanowhiskers as a filler to reduce the cost of the final product, to help decrease environmental pollution with waste polystyrene also to study effect cause by the incorporation of CNWs into the hydrogel matrix on the water uptake capacity also on the mechanical properties.

2. Experimental

Materials

Potassium persulfate (KPS), benzoyl peroxide (BP), and Sodium hydroxide were obtained from Merck. Acrylic acid (AA) from Fluka was used without further purification. Toluene, n-hexane and ethylene acetate were obtained from Merck. Waste polystyrene foam (from food containers) was washed with distilled water before use. N.N methylene – bis-acrylamide (MBA) and span 60 were purchased from Aldrich. Chitosan (code KB-002) was purchased from Funakoshi Co, m LTD, Japan .Egyptian cotton fibers.

Preparation of Cellulose Nanowhiskers (CNWs)

Cotton fibers were firstly washed under mechanic stirring for 1h at room temperature to remove some impurities (waxy for instance).After this the fibers were soaked in deionizer water for 1h at 80 C^0 and then oven dried for 5h at 50 C^0 The cellulose nanowhiskers were obtained through acid hydrolysis reaction using concentrate HCL at $45C^0$ for 1h under vigorous magnetic stirring at cellulose HCL ratio 1/20 (g/mL).The resulting suspension was then treated as described in the literature to obtain the cellulose nanocrystals[18] in brief the resulting solution was centrifuged at 7.000 rpm for15min (three times)and washed using deionizer water up to pH = 7 . The resultant material was freeze -dried 48h). Then CNWs were characterized by Fourier transformed infrared spectroscopy technique.

Preparation of Polystyrene Grafting Poly (Acrylic Acid) –co-Chitosan / CNWs. (PS g PAA-co-CTS/ CNWs) superabsorbent hydrogel).

A proper amount of waste (PS) was dissolved in a mixture of solvents including n-hexane-toluene and ethyl acetate. Appropriate amount of span 60 (as emulsifier) and an oil soluble initiators benzoyl peroxide (BP), were added to the solution in a four- necked reaction flask equipped with a thermometer, a mechanical stirrer and a hydrogen line. A definite amount of acrylic acid (AA) was partially neutralized with NaOH solution (3M) with cooling (ice bath) then the solution was added to the reaction flask and heated to $45C^0$ for a few minutes. A proper amount of chitosan was solubilized under magnetic stirrer in 30 ml of acetic acid solution (V/V %), the chitosan solution was bubbled with N_2 (g) for 30 min to remove oxygen and then added to the reaction flask and the solution was heated to $60C^0$, appropriate amounts of cross linker (MBA), CNWs (5-20%), and initiator (KPS) were added to the solution after a few minutes. The temperature was increased to $70C^0$ for 2h then the sample were precipitated into the ethanol, filtrate and dried at $80C^0$ for 12hr.Acrylic acid homopolymers and unreacted monomers were extracted from the product by soxhlet extraction using an ethanol – water mixture (80: 20) for 8h [19] the extraction was carried out three times for the samples to obtain the constant weight of grafted samples. In addition, a blank sample, without CNWs was synthesized according to procedures described above.

Characterization Techniques

FTIR spectroscopy

All the dried samples were characterized by infrared spectroscopy technique using a transform infrared spectrophotometer (Shimadzu Scientific Instruments, Model 8300)operating in the range from 4000 to500 Cm^1.The dried material was blended with KBr powder and pressed into tablets before spectrum acquisition.

Scanning electron microscopy

The hydrogel nanocomposite morphologies were evaluated through SEM images obtained from scanning electron microscopy (Shimadza Model SS550super scan)

Water Absorbent Measurement

A certain amount of samples (0.15 ± 0.01 g) were placed in 30 mL filter crucibles (porosity no.0) pre moistened and with a dry outer wall. This set was inserted in water in such a way that the gel was completely submerged. The crucible/ composite hydrgel samples sets were removed at various time intervals, with the external wall of the set dried and the system weighed .For each sample 3 assays were performed (n=3).The swelling capacity of the samples was determined according to the Eq.(1) .

$$W = (m/m_o) - 1 \qquad (1)$$

Where w is the gained water mass (in grams) per gram of composite hydrogel, m is the mass of the swollen absorbent and m_o is the mass of the dry materials.

Effect of salt solution on the water uptake capacity

The hydrogel composite were immersed in distinct salt aqueous solutions (concentrations 0.15mol / L) and their swelling capabilities were determined according to the procedures described previously .Aqueous solutions of NaCl, $CaCl_2$ and $AlCl_3$ at $25C^0$, were used as swelling fluid. All solutions presented constant ionic strength (I=0.1M). All the procedures were done in triplicate (n=3).

Effect of pH on the water uptake capacity

The effect of pH on the water up take capacity was also evaluated using buffer solutions (pH=2-12) with constant ionic strength (I=0.1) the experimental procedures were the same described in the previous subsection, the procedures were done in triplicate (n=3)

Mechanical properties

The mechanical properties of the prepared hydrogel nanocomposite with different contents of CNWs were determined through compressive tests in aTexturometer equipments. All samples were previously swelled in distilled water overnight the superficial water excess was removed and then they were cut in small samples before the compression tests. The tests were performed at temp. ($25C^0$) and relative humidity (50%) The Young' modules were calculated according to the following equation:-

$$\text{Young's Modulus} = \frac{F \times L_1}{A \times (L_2 - L_1)} \qquad (2)$$

Where F is the force necessary to compress the sample (N) A is the area (m^2) of the transversal section of the samples, $L_1$is the samples initial length (mm) and L_2 is the samples length (mm) before the rupture point, respectively.

3. Results and discussion

Fig (1) a, b shows the FTIR spectra of raw cotton fibers and cellulose nanowhiskers respectively, which are quite similar. Both presented band at 3344, 2900 and 1646 cm^{-1} which are assigned to stretching of - OH groups, C-H stretching, and – OH bending of the adsorbed water. Therefore , the band of H-C-H and O-C-H in plane bending vibrations appeared at 1432 cm^{-1} and the C-H deformation vibration appeared at 1367 cm^{-1} , the C-O-C , C-C-O and C-C-H deformation modes and stretching vibrations, in which the motion of the C-5 and C-6 were observed at 897 cm^{-1} [20,21] and the band referent to the C-OH out of the plane bending at 670 cm^{-1}. From these FTIR spectra, it was found that the acid hydrolysis reaction performed to obtain the cellulose nanofibrilis did not affect the chemical structure of the cellulose fragment [22].

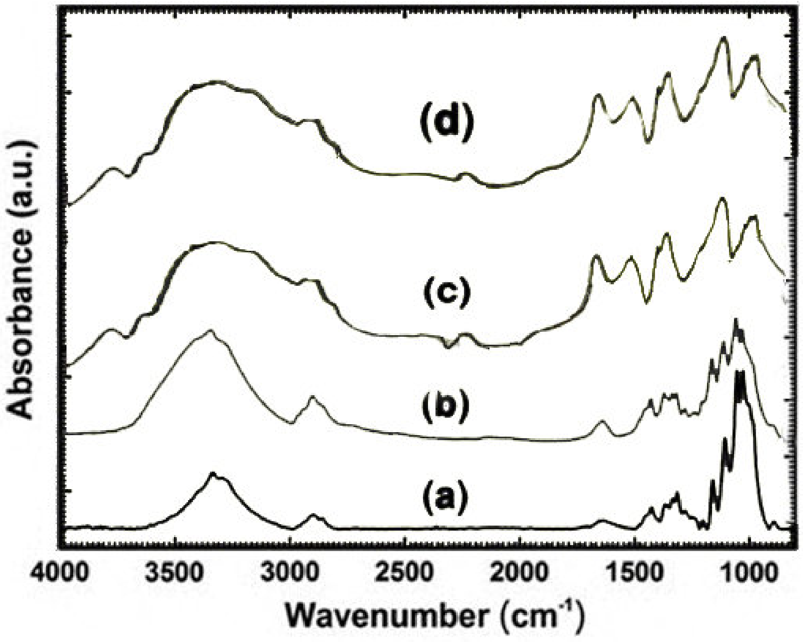

Fig (1) FTIR spectra of (a) a raw cotton fibers, (b) CNWs, (c) PS gPAA co CTS (d) PS g PAA co CTS/CNWs hydrogel

FTIR spectrum of the chitosan graft (poly AA co polystyrene) exhibited a characteristics shoulder at 1686 cm^{-1} assigned to –COOH stretching and bands at 1573 and 1410 cm^{-1} assigned to asymmetric and symmetric stretching of C=O .The band at 1326 cm^{-1} should contribute to the stretching and bending vibration of the C-N bond of the amide III band . The characteristic absorption band of chitosan [N-H 1598 and 1380 cm^{-1}] and C_3-OH (1094 cm^{-1}) could not be found [23] such information confirm that [NH_2-NH-CO and -OH] from chitosan took part in the grafting reaction with acrylic acid and polystyrene. According to FTIR spectra the bands of 2923 cm^{-1}, corresponds to the asymmetric and symmetric stretching vibrations of –CH_2 from PS. The peak at 1585 cm^{-1} is due to the C=C of the vinyl groups from PS while the band at 1452 cm^{-1} results from the deformational vibrations of –CH_2 and (B_1) of the benzene ring of the styrene molecule [24] .
FTIR spectrum of CTS g poly (AA CO PS) / CNWs exhibited a similarity with the FTIR spectrum of chitosan g poly (AA CO PS) as can be seen from fig (1c,d).Bands at 1169 and 1118 and 1056 cm^{-1}are assigned to C-O-C asymmetric valence vibration, vibrational stretching C-C and C-O asymmetric pyran ring and C-O deformation in secondary alcohols and aliphatic ether ,regarding to cellulose nanofibrils which confirms the hydrogl nanocomposite formation[20,21]

Morphologies of Hydrogel Composite

The change on morphology of chitosan graft PAA composite, hydrogel promoted by the addition of cellulose nanofibers were investigated through SEM image fig (2). As can be seen (CTS g PAA- co-PS) hyrogel fig (2a) show interlaced network and highly porous morphology. The pores should small average size and are homogeneously distributed into the hydrogel matrix which could be associated with the lower liquid uptake capacity of CTS g (PAA co PS) .The CTS g PAA co PS / CNWs hydrogel composite morphology fig (2b) seem to be more irregular with large pores and follaceous aspect. The presence of CNWs into the hydrogel matrix increases the amount of hydrophilic groups, which make diffusion of liquid inward the matrix easier and faster. This fact increases the average pore size as can be seen in SEM image.

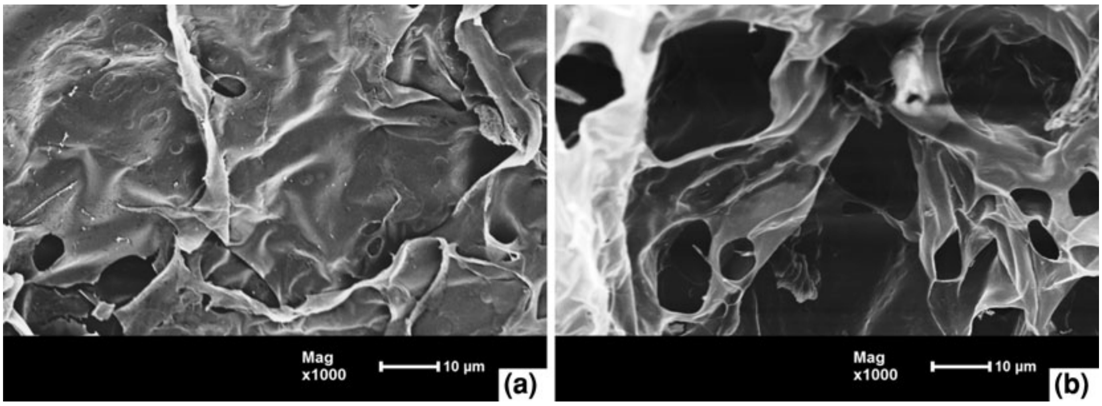

Fig (2) SEM images of (a) PS g PAA co CTS and (b) PS g PAA co CTS/CNWs

Evaluation of Water Uptake Capacity

Effect of the weight ratio of acrylic acid to polystyrene on water absorbency:

Table (1); shows that the water absorbency increased with increasing AA content. The maximum swelling capacity was obtained when the sample was synthesized with an AA to PS ratio of 10:1.This could be due to the fact that the increase in amount of AA from the ratio of 4:1 to 10:1 resulted in an increase in the molecular weight and grafting of poly acrylic acid chains [25]. With further increases in the AA content, the water absorbency decreased. This could be due to preferential homopolymerization of acrylic acid over graft copolymerization or increased medium viscosity which hinders the movement of the monomers molecules and free radicals [26].

Table (1)

Effect of Different Variables on the water absorbencies of PS g PAA co CTS superabsorbent composites

Sample	AA/PS	Neutralization degree of AA	Chitosan wt%	MBA wt%	KPSwt%	BP wt%	W_{H2O}
Effect of AA to PS weight ratio	4	60	0.15	0.07	0.8	0.6	260
	6	60	0.15	0.07	0.8	0.6	330
	8	60	0.15	0.07	0.8	0.6	360
	10	60	0.15	0.07	0.8	0.6	420
	12	60	0.15	0.07	0.8	0.6	320
	14	60	0.15	0.07	0.8	0.6	280
Effect of neutralization degree of AA	10	40	0.15	0.07	0.8	0.6	330
	10	50	0.15	0.07	0.8	0.6	360
	10	60	0.15	0.07	0.8	0.6	420
	10	70	0.15	0.07	0.8	0.6	280
	10	80	0.15	0.07	0.8	0.6	230
	10	90	0.15	0.07	0.8	0.6	210
Effect of chitosan	10	60	0.05	0.07	0.8	0.6	330
	10	60	0.1	0.07	0.8	0.6	390
	10	60	0.15	0.07	0.8	0.6	420
	10	60	0.2	0.07	0.8	0.6	280
	10	60	0.25	0.07	0.8	0.6	230
	10	60	0.3	0.07	0.8	0.6	190
Effect of cross linker contents	10	60	0.15	0.03	0.8	0.6	360
	10	60	0.15	0.05	0.8	0.6	390
	10	60	0.15	0.07	0.8	0.6	420
	10	60	0.15	0.09	0.8	0.6	320
	10	60	0.15	0.11	0.8	0.6	220
	10	60	0.15	0.13	0.8	0.6	190
Effect of water soluble initiator	10	60	0.15	0.07	0.2	0.6	190
	10	60	0.15	0.07	0.4	0.6	280
	10	60	0.15	0.07	0.6	0.6	310
	10	60	0.15	0.07	0.8	0.6	420
	10	60	0.15	0.07	1.00	0.6	380
	10	60	0.15	0.07	1.2	0.6	340
Effect of oil soluble initiator	10	60	0.15	0.07	0.8	0.2	170
	10	60	0.15	0.07	0.8	0.4	240
	10	60	0.15	0.07	0.8	0.6	420
	10	60	0.15	0.07	0.8	0.8	360
	10	60	0.15	0.07	0.8	1.00	340
	10	60	0.15	0.07	0.8	1.2	320

Effect of neutralization degree of AA on water absorbency

As shown from Table (1) the water absorbency increases as the neutralization degree increases from 40% to 60% and decreases with further increases in the neutralization degree of AA . The maximum water absorbency is obtained when the neutralization degree of AA is 60%. When acrylic acid was neutralized with sodium hydroxide solution the negatively charged carboxyl groups attached to the polymer chains produced on electrostatic repulsion resulting in an expansion of the network. The electrostatic repulsion raise as the neutralization degree increased from 40% to 60% leading to increased water absorbency. The further increase in the neutralization degree of AA resulted in the decreased water absorbency of the prepared superabsorbent. This behavior could be due to a rise in the chain stiffness and counter ion condensation on the polyion [27]. (as the amount of Na^+increase with increasing AA neutralization degree, the condensation of counter ion (Na^+)that cover COO^- ion increased ,resulting in a decreased formation of hydrogen bonds between the COO^- groups and H_2O.This phenomena causes the water absorbency of the superabsorbent hydrogel to decreased.

Effect of initiator content on water absorbency

Table (1) illustrates the effect of the oil soluble initiator and the water soluble initiator on the water absorbency of prepared sample. The water absorbency increases as BP and KPS content increase from 0.2 to 0.8 % and from 0.2 to 0.6% respectively, but decreases with further increases in BP and kPS content. The maximum water absorbency (420) is obtained when the total amount of initiator (KBS and BP) is 1.4%.which causes the graft polymerization rate to increase consequently, the final water absorbency increases. When the total amount of initiator is higher than the optimum value, the water absorbency is decrease. This phenomenon is most likely due to an increase in the number of radical centers, which increases the cross linking density .The greater cross linking density prevents the network from expanding to its greatest extent. Furthermore, an increase in the number of radical centers leads to a decrease in the chain length of the grafted AA co CTS of the hydrogel and a decrease in molecular weight of the grafted AA co CTS of the hydrogel. As a result, the water absorbency decreases. This may be due to the inverse relationship between the initiator content and the molecular weight [28].

Effect of cross linker content on water absorbency

Table (1) shows the effect of cross linker content on water absorbency. An increase in the cross linker content from 0.07 to 0.13% leads to a decreased water absorbency. This phenomenon due to the fact that as the amount of cross linker increases, more cross link points are produced during polymerization and the crosslinking density increases. The increased crosslinking density lead to a highly cross linked and rigid structure and the polymer network cannot expand enough to retain a large amount of water [25]. The maximum water absorbency is achieved when the amount of cross linker is 0.07% .

Effect of chitosan on water absorbency

Table (1) shows the effect of different amount of chitosan on water absorbency in distilled water .It can be seen that, the water absorbency increased from 330 to420 as the ratio of chitosan in the feed increased from0.05 to 0.15 wt% and further increase in the amount of chitosan in the feed decreased the water absorbency. First with the increasing of chitosan, there were many available monomer molecules around chitosan large molecular free radical chain that would be grafted onto chitosan backbone. Large molecular chain would grow and network structure of polymers extended and thus formed three dimensional structures at the same time, due to the increasing of the hydrophilic hydroxyl contents, hydrophilic properties of composite resins enhanced, and therefore, its water absorbency rate increased. When chitosan increased from 0.15 to 0.3 water absorbency rate reduced. This due to the generation of more crosslink point in the polymeric network which could cause the crosslink density of the superabsorbent hydrogel to increase therefore , there would be a decrease in the water absorbency [29] .

Effect of CNWs content on water absorbency

The influence of CNWs content on the water absorbency of PS g PAA co CTS/CNWs superabsorbent composite is shown in table (2). It is obvious that CNWs content has an important effect on the water absorbency of the superabsorbent composite. According to the result the water absorbency of the superabsorbent composite in distilled water increased from 420 to 540 g/g as 4% CNWs was introduced and when 8wt% CNWs was filling into the hydrogel matrix water absorbency achieved the highest value 580. This behavior can be attributed to the presence of hydroxyl groups which provides greater hydrophilic character. The increasing in the interaction of the hydrogel surface with the water molecules allows a higher absorption capacity. On the other hand a further increase in CNWs content to 12% leads to a decreased water absorbency of 510. The excess of CNWs into the hydrogel network avoids that greater amount of water could held. In this stage the CNWs shows a typical behavior of inert filler [30]. Greater amount of CNWs enhanced the crosslinking density of nanocomposite and minimized the network voids, responsible for adsorbing and holding water molecules [22]. In addition with the excess of CNWs the ratio of hydrophilic groups per volume unit decreased leading to nanocomposite with lower hydrophilic character.

Table (2) Effect of CNWs content on water absorbency

Reaction conditions : reaction temperature 70^0 C, 60% neutralization degree of AA , weight ratio of AA/PS in feed 10:1 , weight ratios of chitosan, water soluble intiator , oil soluble intiator and cross linker in the feed of 0.15 , 0.8 , 0.6 and 0.07 wt% respectively .

Sample	Cellulose Nanowhiskers wt%	W(g/g)
PS g PAA co CTS/$CNWS_0$	0	420
PS g PAA co CTS/$CNWS_1$	4	540
PS g PAA co CTS/$CNWS_2$	8	580
PS g PAA co CTS/$CNWS_3$	12	510
PS g PAA co CTS/$CNWS_4$	16	570
PS g PAA co CTS/$CNWS_5$	20	430

Effect of salt solution on water absorbency

The influence of some ions cations and anions on swelling capability of hydrogels was tested by the addition of different saline solution, including monovalent (NaCl), divalent ($CaCl_2$) and trivalent ($AlCl_3$) ions (concentration: 0.15 mol L^{-1}) and at 25.0 C^0 as the swelling fluid. To achieve a comparative measure of sensitivity of the hydrogel, a dimensionless salt sensitivity factors (f) [31] is defined as follow:

$$F = 1 - \frac{W_{saline}}{W_{water}} \qquad (3)$$

Where W_{saline} and W_{water} are the swelling capacity in saline solution and in deionized water, respectively. It is obvious that the swelling decreasing strongly depended on the type of salt added to the swelling medium. The effect of cation type (cation with different radius and charge) and sensitivity factor f on swelling behavior is shown in fig (3) The higher cation charges the higher degree of crosslinking and the smaller swelling value .Therefore the absorbency for the hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations .The (f) values indicate that the CTS g PAA Co PS /CNWs hydrogels undergo less influence to the presence of salt than CTS g (PAA Co PS). The increase in the ions strength reduces the difference in the concentration of movable ions between the polymer matrix and the external solution (osmotic swelling pressure) and leads to an immediate contraction of gel. The decreasing is more significant to Ca^{++} and Al^{+3} which can be additionally caused by the complex formation ability of carboxamide or carboxylate groups including interamolecular and intermolecular complex formation or because one multivalent ion is able to neutralize several charge inside the gel consequently the crosslinking density of the net work increased while water absorption capacity decreased .

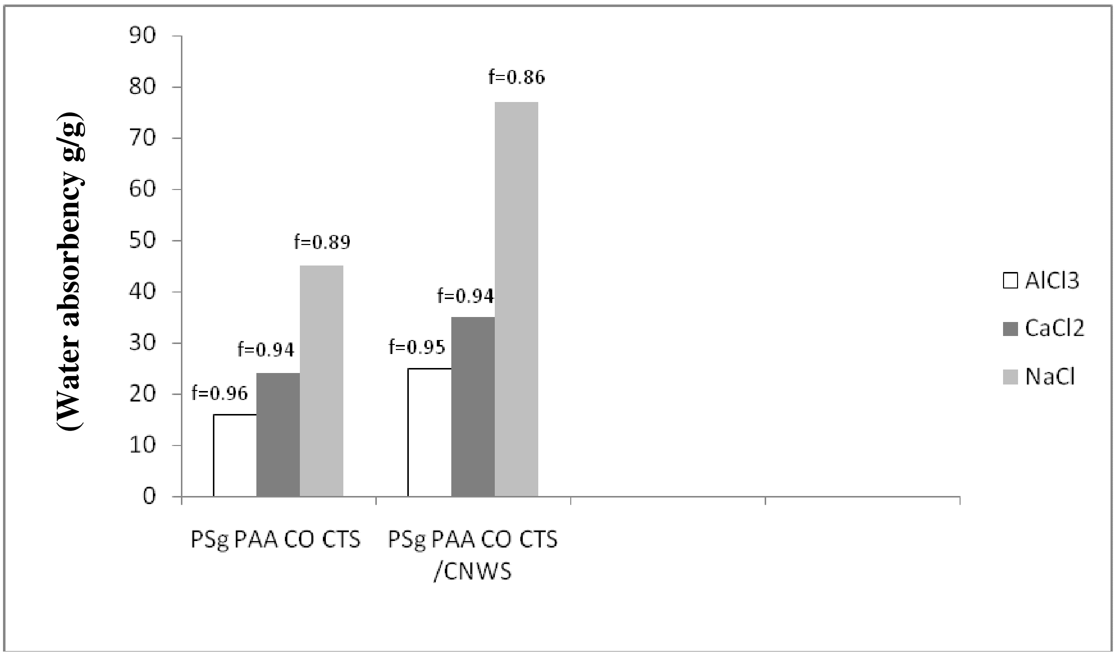

Fig (3): Water absorbency of PS g PAA co CTS and PSg PAA co CTS/CNWs hydrogel composites at aqueous solutions from different salt (conc. Equal 0.15 mg L^{-1})

Swelling behavior at various pH

The swelling behavior of PS g PAA co CTS/CNWs and PS g PAA co CTS hydrogel composite at various pHs were observed with the use of buffer solution at pHs 2-12 maintaining the ionic strength equal to 0.1.According to Fig(4) the absorbency increased as the pH increased from 2.0 to 8.0 and then decreased at pH higher than 8.0.The water absorption is low in acidic pH values($\leq$4) but dramatically increases until a plateau was reached when the pH $\geq$ 4 .In acidic medium –COO^- converted to COOH groups .The hydrogen bonding interaction among –OH and COOH groups was strengthened and the degree of physical cross linking was increased. As a result, the water absorption was decreased .However, as the pH increased to the basic medium –COOH groups transform into COO^- groups and the hydrogen bonding interaction was broken .In addition the electrostatic repulsion among polymer chains was increased due to the rapid increase in the number of negatively charged –COO^-groups .This effect causes to the hydrogel matrix an expansion and the amount of water absorbed increases considerably [32].

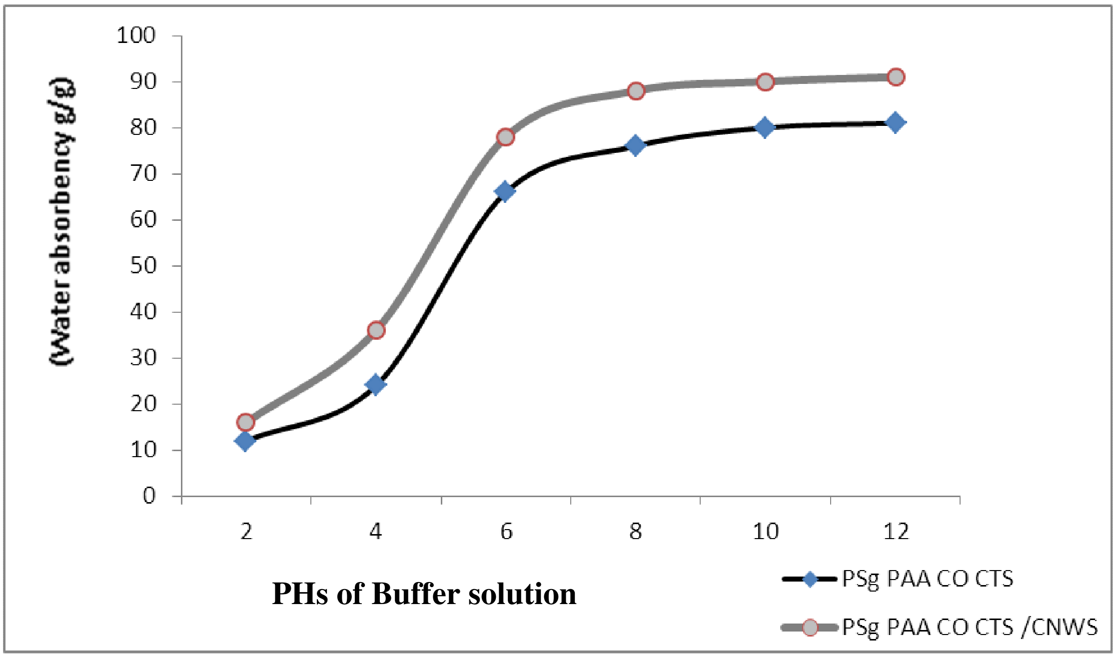

Fig (4): Effect of PH in the swelling properties of PSg PAA co CTS and PSg PAA co CTS/CNWs hydrogel composites with 8wt% of cellulose nanofibrils.

Mechanical Properties

Fig (5) shows the mechanical properties of CTS g PAA co PS hydrogl nanocomposite as a function of CNWs incorporated into the hydrogel matrix .As can be seen the incorporation of CNWs into the hydrogel decreased considerably the Young' modulus. This happen because the CNWs contributes to increase the water up take capacity which consequently became the hydrogel softer than the hydrogel without CNWs. Further increase in CNWs from 4% to 20% increases the Young's modulus again . The CNWs acts as efficient filler and contribute to improve the mechanical resistance against compressive stress.

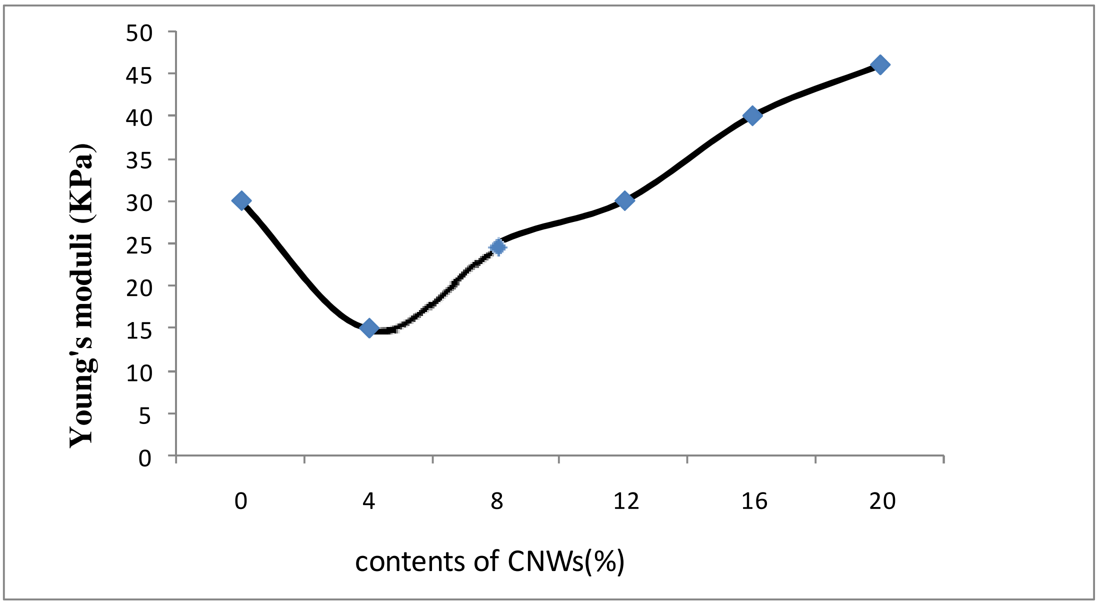

Fig (5): mechanical properties of PS g PAA co CTS/CNWs hydrogel nanocomposite as a function of % CNWs

4. Conclusion

A superabsorbent composed of waste polystyrene, chitosan ,acrylic acid and cellulose nanofibrils which were obtained from cotton linters was prepared through emulsion polymerization .The effect of major factors such as the weight ratio of acrylic acid to polystyrene,crosslinker,initiator and cellulose nanowhisker content on water absorbency were investigated to obtain optimum conditions with high swelling capacity, The superabsorbent hydrogel was characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope(SEM).The addition of cellulose nanowhiskers improved the swelling capacity as well as improved the mechanical properties of the hydrogel. SEM images showed that the hydrogel CNWs morphology changed due to the incorporation of cellulose nanowhiskers .The nanocomposite presented good responsive behavior in relation to pH and salt solution , such characteristics make these smart materials suitable for several technological applications .Furthermore , the use of waste polystyrene not only can reduce the production cost of superabsorbent hydrogel, but can also provide a new method for converting waste resources into valuable products.

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