Characterization of Cellulose Nano fibers re-enforced Polyvinyl Alcohol (PVA) /Poly Aniline Films



In the proposed work, for first time we have produced insoluble films by loading cellulose nanocrystals into PVA/ PANI films without using any toxic chemical. The CNC were prepared by physical method. Their mechanical and water absorption properties were also studied. poly(vinyl alcohol)/ PANI films have been prepared in the presence of cellulose nano crystals to yield films with enhanced stability in aqueous medium and fair tensile strength. Cellulose nano crystals were obtained by continuous ultra-sonication of cellulose power in water. The nano crystals had dimensions of 50 to 100 nm, .The CNC loaded films were characterized by XRD, SEM. The water absorption behavior of films was studied in the physiological fluid (PF) of pH 7.4. The films, loaded with 12, 24 and 30 wt % of CNC exhibited swelling ratio(SR) of 0.81, 1.32 and 0.95 g/g respectively, thus showing unusual trend.

Keywords: Hydrogel Films, Cross-Linking, Less-Fickian Swelling, Physiological Fluid (PF).

Introduction

Poly (aniline) (PANI) as a conducting polymer has an immense potential to be used in biomedical field [1-4]. MC is a non-ionic and water soluble polymer that has been incorporated into PAni through oxidative polymerization of aniline in acidic solution to produce water-soluble PAni. MC acts as a steric stabilizer and molecular template to help the dispersion of PAni. This work has been done successfully by Dipankar Chattopadhyay et al.7 and Bin Jia et al.[5]

This method has been investigated in the presence of water soluble polymers or tailor-made reactive copolymers (e.g., poly(2vinylpyridine-co-p-PVA,poly(N-vinylpyrrolidone), aminostyrene), PEO, cellulose derivatives, poly (methylvinylether) [6-11]. Yassar et al. [12] reported an alternative method to produce conducting colloid latexes, through pyrrole emulsion polymerization in sulfonated and carboxylated PS latexes, in which the particles were overcoated by Ppy. Ruckenstein et al. [13-15] developed emulsion pathways for the preparation of conductive PANI composites to produce PANI/PMMA and PANI/PS composites via an oxidative aniline polymerization. The composites obtained showed a percolation threshold of 2 to 10 vol% PANI. They also developed an inverted emulsion pathway to prepare PANI composites with SBS rubber at different molar ratios of aniline/dopant (sulfonic acids), oxidant/aniline, quantities of a surfactant, and nature of the solvent in the continuous phase [15]. Wiersma et al. [16] investigated the critical condition for stability of polyurethane (PU) latex particles of a chemically grafted nonionic polymeric stabilizer, such as PEO or hydroxymethylcellulose, and used transmission electron microscopy (TEM) to reveal a "coreshell" morphology of latex particles (core) coated by the conducting polymer (shell). These coated particles displayed the good film-forming properties of the parent PU at ambient temperature and revealed conductivity in the range of 1025 to 101 S/cm [16]. Banerjee and Mandal [17] synthesized a dispersion of nonspherical PANI particles with diameters of 150 to 300 nm, stabilized with poly(methylvinylether). These particles were disintegrated into nanosized particles with diameters less than 20 nm, which were used to prepare conducting blends with conventional polymers PVC, PS, PMMA, poly(vinylacetate), and PVA by sonicating a suspension of the preformed submicronic PANI HCI particles in solutions of the matrix polymers.Nguyen Dang Luong et al. employed cellulose nanofibrils in aqueous suspension as a stabilizer in aniline in-situ polymerization.[18] In addition, cellulose



J. M. Keller Profeesor, Dept. of Physics and Electronics, University Teaching Department, Rani Durgawati Vishwavidyalaya, Jabalpur, M.P.



Nema Mishra Research Scholar Dept. of Physics and Electronics, University Teaching Department, Rani Durgawati Vishwavidyalaya, Jabalpur, M.P.

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nanofibrils have many advantages such as low cost, non-toxicity, renewable nature, biodegradability, and able to form stable aqueous suspension.[19] C. Koul et al. [20] reported blends of conventional thermoplastic ABS copolymer with PANI doped with a specific ratio of mixed dopants, consisting of DBSA and TSA at dopant ratios from 1:1 to 9:1. It was observed that the blends had the best conductivity when PANI was doped by mixtures of DBSA and TSA in 1:1 and 9:1 ratio.

In the present work, we have used cellulose nano crystals as an additive to not only strengthen the PVA films but also to prevent them from dissolution. Cellulose is the most abundantly found bio-polymer in nature and is biocompatible and biodegradable.[21] It has frequently been used in a number of biomedical applications It is speculated that presence of a large number of hydroxyls along its backbone may bind to the -OH groups of PVA chains through H-bonding interactions to serve as additional crosslinks and provide stability to PVA hydrogels. Gangopadhyay et al. [22] prepared a PANI/PVA composite in an aqueous solution of PVA (1 g in 10 ml water), maintaining the molar ratio of aniline: APS 1:1 (at different quantities of aniline), and pH51 in the presence of HCl at 10 C. Xiang and Xie [23] revealed that aniline could be graft copolymerized onto the backbone of poly (acrylamide) (PAM) in aqueous HCI solution in the presence of APS as oxidant. Niyazi Bicak and co-workers reported that the introduction of new ionic liquid, 2-hydroxyethylammoniumformate (HAF) as a solvent in the polymerization of anilium chloride with APS can improve solubility of PAni in organic solvents such as acetone, tetrahydrofurane (THF), dioxane, dimethyformamide (DMF), and Nmethyl, 2-pyrrolidinone.[24] A.T. Ramaprasad and partner have worked on blended PAni with chitin to get better processability of PAni in common organic Pron et al. [26-27] synthesized solvents.[25] conductive PANI/ cellulose acetate (CA) composite films cast from m-cresol solutions and compared properties of the blends, either without plasticizer or with (dimethylphthalate, common plasticizers and triphenylphosphate). diethylphthalate, The addition of plasticizers not only improved the flexibility of the composite films, but also significantly lowered the percolation threshold: for the PANI-CSA/CA composite to 0:84 wt%, for other blends to values below 0.5 wt%.

Review of Literature

A review on polymeric hydrogel membranes for wound dressing applications: PVA-based hydrogel dressings. Kamoun EA, Kenawy ES, Chen X. J Adv Res. 2017 May;8(3):217-233. J Biomater Sci Polym Ed. 2017 May;28(7):664-678. Collagen-PVA aligned nanofiber on collagen sponge as bi-layered scaffold for surface cartilage repair. Lin H.Y, Tsai WC2, Chang S.H. Preparation and Application of Starch/Polyvinyl Alcohol/Citric Acid Ternary Blend Antimicrobial Functional Food Packaging Films ZhijunWu ,Jingjing Wu , TingtingPeng 2, Yutong Li 2, Derong Lin 2,*, Baoshan Xing 3,*, Chunxiao Li 2, Yuqiu Yang 2, Li Yang 2, Lihua Zhang 1, Rongchao Ma 1, Weixiong Wu 1, XiaorongLv 2, Jianwu Dai 2 and Guoquan Han, Polymers 2017, 9,102-121. Gangopadhyay R, De A, Ghosh G. Polyaniline-poly (vinyl alcohol) conducting composite: material with easy processability and novel application potential. Synth Met 2001;123(1):21-31. Xiang Q, Xie HQ. Preparation and characterization of alkalisoluble polyacrylamide-gpolyaniline. Eur Polym J 1996;32(7):865-8.

Lennartz et al. Lennartz W, Mietzner T, Nimtz G, Wessling B. Morphological changes in PANI/PMMA-blends during dispersion studied by SAXS. Synth Met 2001;119(1-3):425-6.showed that PANI-TSA particles agglomerated to 50 nm aggregates in a PMMA matrix.MC acts as a steric stabilizer and molecular template to help the dispersion of PAni. This work has been done successfully by Dipankar Chattopadhyay et al.7 and Bin Jia et al. Banerjee and Mandal synthesized a dispersion of nonspherical PANI particles with diameters of 150 to 300 nm, stabilized with poly(methylvinylether). Casado U.M., Quintanilla R.M., Aranguren M.I., and Marcovich N.E. (2012). Composite films based on shape memory polyurethanes and nanostructured polyaniline or cellulose-polyaniline particles. Synthetic Metals 162, 1654-1664. Neves and De Paoli produced PANI dispersed inside a microporous cellulose-acetate membrane structure.

Experimental

Materials

Poly(vinyl alcohol)(PVA; degree of substitution 95 %,), cellulose powder(Cell; molar mass), Polyaniline and other chemicals were purchased from Hi Media Chemicals, Mumbai, India . The double distilled water was used throughout the investigations.

Preparation of CNC/PVA/ PANI composite films

The CNC/PVA/PANI composite films were prepared by solvent evaporation method. We take Aniline soulition (3ml Aniline+2ml HCL) in a testube and ponder it in a beaker of ice for 1 hour.We make APS solution (5gm APS+50ml H₂O).We ponder Aniline and APS solution in a petri plate in dropping **CNC/PVA** film. The films, so prepared, were peeled off carefully and placed in a dust free chamber for further use.In all four samples were prepared, designated as CNC/PVA/PANI (x). The films shall be designated as CNC/PVA/PANI (1), CNC/PVA/PANI (2), CNC/PVA /PANI (3) and CNC/PVA/PANI (4).

Characterization of CNC/PVA/ PANI (x) films

The X-ray diffraction (XRD) method was used to measure the crystalline nature of the films. These measurements were carried out on a Rikagu Diffractometer (Cu radiation = 0.1546 nm) running at 40 kV and 40 mA. The diffractogram was recorded in the range of 2 from 3 to 50^{0} at the speed rate of 2 degree/ min.

In order to investigate the surface morphology of films, SEM.

Swelling studies

Swelling studies were carried out in the pseudo extracellular fluid (PEF) as described by Lin et al.[28] This simulated wound fluid has following

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composition : 2.2 g of KCl, 6.8 g of NaCl, 25 g of sodium bicarbonate and 3.5 g of sodium di-hydrogen phosphate in 1 liter. The pH of this solution was fond 7.36. The pre-weighed film sample was placed in 100 mL of PEF at 37^{0} C and it 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 placed back in water. The swelling Ratio(SR) determined at different time intervals using the following expression:

$$SR = \frac{(m_t - m_0)}{m}g/g$$
 ... (1)

Where m_0 and m_t are the initial mass and mass at different time intervals respectively .In orders to determine Equilibrium Swelling Ratio (ESR), m_t was replaced by m_e which is the weight of the swollen film at equilibrium.

Preparation of cellulose nano crystals

According to the literature available. cellulose nano crystals have been prepared by a number of methods such as acid hydrolysis[29] mechanical disintegration[30]enzymatic hydrolysis[31] etc.However, the mechanical disintegration appears to be the safest one as it is pro-ecofriendly approach. In this work, cellulose particles were ultrasonicated for total period of 5 days, with an exposure frequency of 5 h per day which enabled us to obtain cellulose nano crystals. The ultrasonic waves penetrate through the amorphous region of cellulose chains and break them in to smaller sized chains with dimension in the nano scale range. Aniline and APS soulition were poured into petri plates in dropping CNC/PVA film for a period of 30 min.

Characterization of Films

The diffraction pattern of native cellulose, shown in Fig. 3(a), confirm relatively suppressed peak at 2 θ = 14.62°(110) and a sharp peak at 22.48°(200), thus indicating the presence of cellulose I.[32]





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In addition a sharp peak also appears at $2\theta = 21.53$ (200), indicating presence of cellulose II structure[33] The XRD pattern of CNC/PVA, displayed in Fig.3(b) indicates presence of nearly all the peaks that exist in diffractogram of cellulose and PVA as mentioned above. Finally, the XRD pattern of CNC/PVA/PANI displayed in Fig.3(c) indicates presence of nearly all the peaks that exist in diffractogram of cellulose and PVA/PANI displayed in Fig.3(c) indicates presence of nearly all the Peaks that exist in diffractogram of cellulose and PVA/PANI as mentioned above.

SEM analysis



CNC/PVA/ PANI 20kv x2,000 CNC/PVA/ PANI 20kv x5,000 CNC/PVA/ PANI 20kv x10,000







CNC/PVA/ PANI 20kv x20,000 CNC/PVA/ PANI 20kv x25,000 CNC/PVA/ PANI 20kv x50,000 Swelling Kinetics of CNC/PVA/ PANI Composite Films

The water absorption behavior of plain PVA and CNC/PVA and **CNC/PVA**/ PANI films containing different cellulose contents were studied in the phosphate buffer saline (PBS) of medium 7.4.The results are shown in Fig.5. It can be seen that the plain PVA film shows a faster swelling and attains ESR of 2.1 in 15 min. However, thereafter it begins to lose weight and dissolves completely in next 5 min. On the other hand, the film samples PVA, CNC/PVA and CNC/PVA/PANI show total swelling ratios of 0.81, 1.32 and 0.95 g/g respectively. It took almost 45 to 80 min.





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Anilne	5ml+10cell+pva			
	TIME	% SWELLING		
	0	0	0	0
	5	0.475	0.1497	0.867
	10	0.487	0.4233	2.08
	15	0.541	0.6009	0
	20	0.547	0.6427	
	25	0.547	0.6782	
	30	0.566	0.6866	
	35	0.632	0.713	
	40	0.695	0.7256	
	45	0.706	0.7674	
	50	0.715		
	55	0.732		
	60	0.792		
	65	0.806		

The water penetration mechanism of the CNC/PVA/PANI films was best investigated using the well-known "Power function model", developed by Peppas [34] According to this model $\frac{M_t}{M_{\infty}} = k t^n$...(2)

Where M_t and M_{∞} are the masses of the

respectively; 'n' and 'k' are the swelling exponent and gel-characteristic constants respectively. The logarithmic form of the above equation may be written as

$$\ln \frac{M_t}{M_{\infty}} = \ln k + n \ln t \qquad ...(3)$$

hydrated film sample at time 't' and at equilibrium Fig.6 Power function model for dynamic water uptake of CNC/PVA/PANI samples in medium of pH 7.4 at 37°C.



the kinetic water absorption data. According to this model [35]

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Fig.7 Schott model for dynamic water uptake of CNC/PVA/PANI samples in medium of pH 7.4 at 37°C.



Where, M_t is the water uptake at time't' and 'k₂' is the second order rate constant for water absorption process. On integrating above equation within the limits t=0 M_t =0 and t= ∞ M= M_{∞} , following equation is obtained:

 $t/M_t = A + B t$... (5) Where, A and B are two coefficients whose physical meaning is interpreted as follows: At a long retention time Bt>> A and therefore B= 1/ M_∞, that is, B is reciprocal of the maximum water uptake. On the contrast, at a very short time interval B t << A and so, Lt (dMt/dt) = 1/A ... (6)

Lt (dMt/dt) = 1/A t→0

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/Mt and t as shown in Fig.6. 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. $r_{ini} = 1$ /A). All these parameters are shown in Table-II. A close look at the various parameters, obtained for the Schott model, reveals that for all the samples regressions are fairly high thus indicating the suitability of the Schott model. In addition, it may also be noticed that the theoretical and experimental SR values are quite close to each other, thus further confirming the validity of this model. **Conclusion**

It may be concluded from the above study that entrapment of cellulose microcrystals in to uncrosslinked poly(vinyl alcohol)/ Poly Aniline film renders it with fair stability in the physiological fluid while the un-crosslinked film dissolves within 20 min after its immersion. In addition, the water absorption behavior of CMC-reinforced PVA/ PANI films follows Fickian water transport mechanism. Since the PVA/ PANI films have been stabilized through entrapment of cellulose micro-crystals, and no toxic chemical has been used throughout the study, these films have great potential to be used for biomedical applications. **References**

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