WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 7.523
Volume 7, Issue 8, 59-73. Conference Article ISSN 2277– 7105

SYNTHESIS AND CHARACTERIZATION OF CHITOSAN (CS)/ CELLULOSE ACETATE (CA) /POLYVINYL ALCOHOL (PVA) TERNARY BLEND

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Article Received on
05 March 2018,
Revised on 25 March 2018,
Accepted on 15 April 2018
DOI: 10.20959/wjpr20188-10933

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ABSTRACT

In this study, a novel chitosan(CS)/celloluse acetate(CA)/polyvinyl alcohol(PVA) ternary biopolymeric blend in 1:1:2 ratio were synthesized and characterized by the universal tester like the Fourier transform infra red spectroscopy (FT-IR), X-Ray diffractogram (XRD), Thermo gravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Scanning electron microscopic (SEM) studies. Appearance of certain strong peaks due to the presence of various functional groups (-OH, NH_2, COO^- in ester) was evident from FT-IR results. These observed results clearly suggest that the chitosan biopolymer gets blended effectively with polyvinyl aclcohol and cellulose acetate. X-ray diffraction and SEM studies clearly indicate that the prepared chitosan (CS)/ celloluse acetate(CA)/polyvinyl alcohol (PVA) ternary biopolymeric blend possesses highly amorphous nature and rough surface morphology suitable for adsorption process. Also the TGA and DSC studies showed that the prepared chitosan/polyvinyl alcohol/cellulose acetate ternary biopolymeric blend has highly thermally stable behavior. The results were investigated.

KEYWORDS: chitosan, polyvinyl alcohol, cellulose acetate, characterization, ternary blend.

INTRODUCTION

Water is one of the fundamental essentials in our everyday life but in recent years especially due to the excessive industrialization process the water now gets polluted by so many ways. The contamination of water by toxic heavy metals is a worldwide problem.[1][2] The development of membrane technology has geared up in recent years to overcome water pollution effectively and especially this membrane has been used for water treatment for

more than 45 years. Statistics show that membrane technologies contribute up to 53% of the total world processes for clean water production.[3] In order to fabricate the membranes wide range of materials has been used and these materials can generally be grouped into two types namely ceramic-based and polymeric-based membranes. Ceramic-based membranes are thermally and chemically more stable, have high porosity, and have a longer life span but it is more expensive and brittle whereas the polymer-based membranes offer flexibility in design, are cheaper and can remove dissolved ions and organics more efficiently.[4] Due to these advantages majority of the research works were focused on synthetic polymers.

Basically the membrane is actually a thin selective permeable layer helps in separating two phases and acting as an active or passive barrier to the transport of matter between the phases adjacent to it.[5] The membrane permits mass transport to pass through it based on the pore size. Because of its favorable permeaselectivity, solvent stability and as well as good film forming properties the biopolymer chitosan was chosen as the suitable material for membrane preparation.[6] Chitosan, the deacetylated product of chitn which is a linear polysaccharide composed of randomly distributed β (1,4) linked D-glucosamine and N-acetyl-D-glucosamine used in a number of applications such as a flu coating agent, a wound healing agent, a sizing, prevention of water pollution, in membrane separation, in medicine and biotechnology (a delivery vehicle for pharamaetucials and genes), food technology and strengthing agent for a paper.[7][8]

T-sai and his coworkers reported that the chitosan is a good membrane material for reverse osmosis, ultrafiltration and microfiltration membrane.[9] Due to the poor mechanical strength and chemical stability the scope of preparing pure chitosan membranes has been largely limited.[10] One of the most popular methods of natural membranes preparation is the modification of natural polymers by combination with another polymer. In order to improve the stability and mechanical properties of chitosan based membranes, certain solving methods had been done such as blending chitosan with other polymers like cellulose acetate and polyvinyl alcohol, bringing crosslinked structure to membranes, casting chitosan on another polymer substrate to form composite membranes, and adding inorganic reinforcements into chitosan membranes.

Polyvinyl alcohol is a non-toxic, water soluble synthetic polymer which has good physical and chemical properties (film-formation ability). The use of this polymer is important in many applications, such as controlled drug delivery systems, membrane preparation,

recycling of polymers and packaging. Polyvinyl alcohol (PVA) and its derivatives are hydrophilic and have reactive hydroxyl groups[11] and hence can be easily modified with other reactive functional groups to obtain adsorptive membranes. When compared to the hydroxyl group, the amine groups are however much more reactive and can be used directly as affinity adsorption sites under mild conditions and hence, one of the choices to prepare adsorptive membranes is to introduce some amine groups into PVA or its derivatives. Mirzadeh and Mahadavi reported that the combined form of PVA and chitosan provide new materials with biological functions and unique physical and mechanical properties.[12] Hence based on the reported works the polyvinyl alcohol has been selected for membrane preparation.

Cellulose acetate is the classic membrane material used by the pioneers of modern membrane technology to create skinned membranes. Cellulose and its derivatives are generally linear, rod like and rather inflexible molecules, which are considered as a fairly membrane characteristics of reverse osmosis (RO) and ultra filtration (UF) applications. Due to its desirable thermal, mechanical and chemical properties the cellulose acetate (CA) has been used as an excellent polymeric material for UF membrane synthesis.[13] However, pure CA membranes suffer from the limitation of lower fluxes[14] and hence it can be blended with other materials resulting in the production of membrane with improved physical properties.[15] Reports about the preparation of cellulose nanocrystals reinforced cellulose acetate ultrafiltration membranes by phase inversion technique was given by Jian jun Zhou and his coworkers. The study demonstrated the importance of cellulose acetate ultrafiltration membranes and provided an efficient method for preparing high-performance membranes.[16]

Jun Yin and his coworkers reported about the preparation and antifouling properties of cellulose acetate (CA)/poly(vinyl alcohol) (PVA)/Poly vinyl pyrrollidone (PVP) blend membranes and glutaraldehyde cross linked cellulose acetate (CA)/poly(vinyl alcohol) (PVA) /PVPblend membranes by non-solvent induced phase separation process. The obtained result indicated that all CA/PVA/PVP blend membranes had better antifouling property than CA/PVA membrane.[17] Hence based on the literature survey in the present research work, the ternary chitosan/cellulose acetate/polyvinyl alcohol blend membranes were prepared, characterized and the results were investigated.

MATERIALS AND METHODS

Materials

Chitosan was purchased from India Sea Foods, Cochin, Kerala, which is 92% deacetylated. The commercial grade cellulose acetate was procured from Chenchems, Chennai. The chemicals such as polyvinyl alcohol, N-N dimethyl formamide and sodium lauryl sulphate was obtained from Central Drug House private Limited, New Delhi and SD-fine chemicals, India. All the chemicals used in the present research work were of analytical reagent grade.

Preparation of chitosan/cellulose acetate/polyvinyl alcohol ternary blend

The chitosan/cellulose acetate/polyvinyl alcohol ternary blend was prepared as follows. Initially the homogeneous chitosan solution was prepared by dissolving 1g of chitosan in 30 ml of 2% acetic acid solution by magnetic stirring process for over a period of 30 mins. To the above prepared chitosan solution, the mixture of cellulose acetate solution (1g cellulose acetate solution dissolved in 30ml of N, N dimethyl formamide (DMF)) and the polyvinyl alcohol solution (2g of polyvinyl alcohol in 60 ml of water) was added. These three solutions were blended well with constant continuous mechanical stirring process for a period of 60 minutes at room temperature.

After this stirring process is over, the above prepared blended homogeneous mixture of chitosan, cellulose acetate and polyvinyl alcohol solution was allowed to stand for few hours before casting in order to eliminate air bubbles. The blended mixture of chitosan, cellulose acetate and polyvinyl alcohol was then finally poured into petridish and after a day the solvent was evaporated in the casting chamber. The membrane was taken from petridish and stored in gelation bath. (The gelation bath was prepared by dissolving 2.5 g of dimethyl formamide and 0.2g of sodium lauryl sulphate in distilled water (acts as a non solvent) taken in a 1000ml standard flask which was then made upto the mark). Finally the soaked membranes was then cooled to 15^0C and stored in refrigerator. The photograph of the prepared chitosan/cellulose acetate/polyvinyl alcohol membrane was given in Fig. A.

Figure. A: Photograph of chitosan/cellulose acetate/polyvinyl alcohol membrane *Characterization.*

Fourier Transform Infra Red Spectroscopy Studies

The FT-IR spectrum of the chitosan/cellulose acetate/polyvinyl alcohol membrane was recorded using Perkin Elmer 200 FTIR spectrophotometer instrument in the wave number range from 4000 cm^{-1} to 450 cm^{-1} during 64 scans, with 2 cm^{-1} resolution.

X-Ray diffraction Studies

X-ray powder diffractometer (XRD- SHIMADUZ XD-D1) with Ni filter Cu Kα radiation source (λ=0.154nm), set at scan rate of10º/min, using a voltage of 40kv and current of 30 mA was utilized for recording the X-ray diffraction patterns of chitosan/cellulose acetate/polyvinyl alcohol membrane.

Thermogravimetric Analysis

Thermogravimetric analysis of the prepared samples was performed using SDT Q600 V8.0 Build 95 instrument. The range of temperature used is between 30ºC to 750ºC with a heating rate of 10ºC/min under nitrogen atmosphere.

Differential scanning calorimetric analysis

The DSC studies of the prepared samples were carried out using DSC Q10 V 9.0 Build 275 instrument in the temperature range between 30°C to 350°C with the heating rate of 10°C/min.

Scanning electron microscopic studies

The surface morphology of the prepared samples was examined with the Scanning Electron Microscope (Zeiss EVO 40). The photographs of the various cross sectional morphologies of the CS/CA/PVA ternary blend membrane samples were taken at different magnifications.

RESULTS AND DISCUSSION

FT-IR spectral analysis

The FT-IR spectrum mainly helps to identity the molecular structures and the functional groups. The FTIR spectral details of pure chitosan and chitosan/cellulose acetate/polyvinyl alcohol (1:1:2) membrane was represented in Fig.1 and Fig. 2.

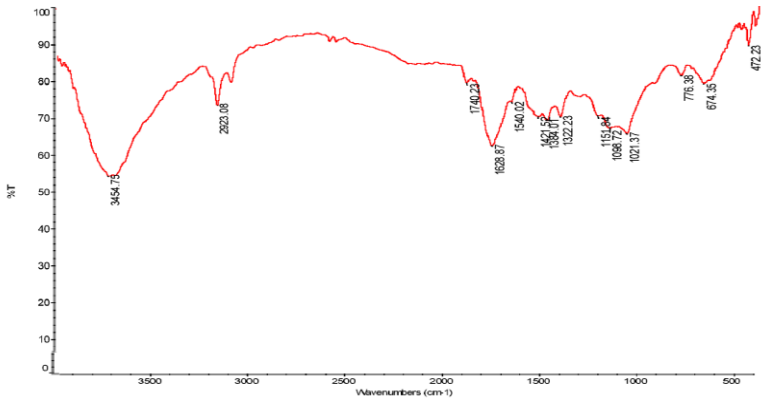

Figure 1: FT-IR spectrum of pure chitosan.

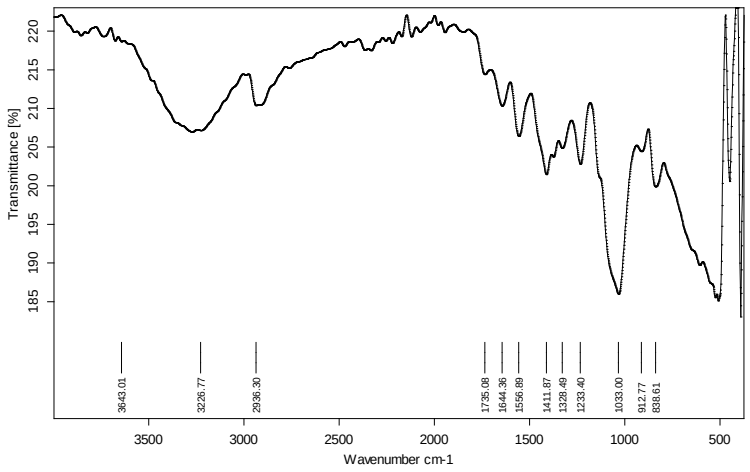

Figure 2: FT-IR spectrum of chitosan/cellulose acetate/polyvinyl alcohol (1:1:2) blend membrane.

The prominent peak observed at 3454.75 cm^{-1}, 2923.08 cm^{-1} in case of pure chitosan (Fig.1) corresponds to the intermolecular hydrogen bonded –OH stretching of axial OH group, -NH stretching of primary amine[18] and aliphatic methylenic–CH stretching. The peaks observed at various wavenumbers such as 1628.87 cm^{-1}, 1421.52 cm^{-1}, 1283.16 cm^{-1}, 1087.88 cm^{-1}, revealed the presence of C=O stretching, N-H bending, C-H bending, O-H bending and C-O-C stretching in cyclic ethers.

The chitosan/cellulose acetate/polyvinyl alcohol (1:1:2) ternary blend membranes (Fig.2) shows sharp peaks at 3226.77 cm^{-1}, 2936.30 cm^{-1}, 1735.08 cm^{-1}, 1644.36 cm^{-1} and so on. These observed peaks indicate the presence of intermolecular hydrogen bonded –OH stretching, –NH stretching for primary amine, aliphatic methylenic –CH stretching, C=O stretching in esters, N-H bending respectively. Certain absorption bands observed at 1328.49 cm^{-1}, 1233.40 cm^{-1}, 1033.40 cm^{-1} and 838.61 cm^{-1} was attributed to twisting and wagging in CH_2 vibration, C-(C=O)-O stretching in esters , C-N stretching in esters and NH wagging respectively.[19][20]

On comparing the FT-IR spectral details of chitosan/cellulose acetate/ polyvinyl alcohol membrane prepared in 1:1:2 ratio with pure chitosan it was observed that so many additional bands were obtained at various wave number such as 1735.08 cm^{-1}, 1233.40 cm^{-1},1033.00 cm^{-1} which corresponds to C=O stretching of esters, C-O stretching in alcohol. The appearance of these new peaks in case of ternary blend membrane confirms that the blending had taken place effectively between chitosan, cellulose acetate and polyvinyl alcohol.

X-Ray Diffraction (XRD) studies

X-ray diffraction is commonly used to determine the polymorphic forms of a compound having different crystalline structures. These patterns are indicative of different spacing of the crystal planes, which provide strong evidence for polymorphic differences.[21] Table-1 and Fig.3 and Fig.4 represents the X-ray diffractogram details of pure chitosan and chitosan/cellulose acetate/polyvinyl alcohol (1:1:2) ternary blend membrane.

Table-1: X-ray diffractogram details of pure chitosan and CS/CA/PVA ternary blended membrane.

Sample	2-Theta	Percentage of crystallinity (%)
Pure chitosan	10^0, 20^0	7.52
CS/CA/PVA (1:1:2) ternary blend membrane	19^0, 22^0	4.58

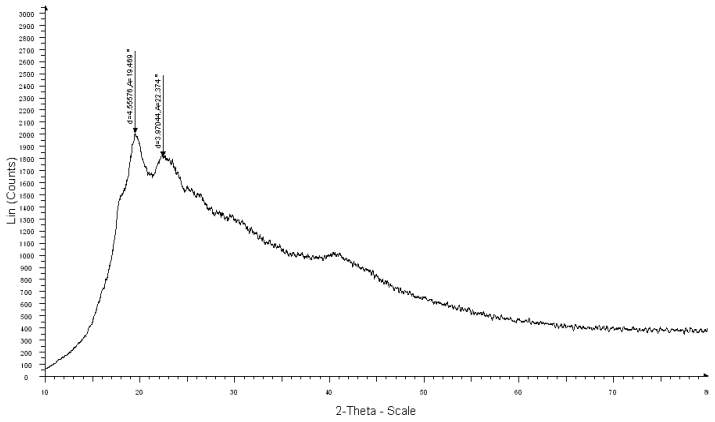

Figure 3: X-ray diffractogram of pure chitosan.

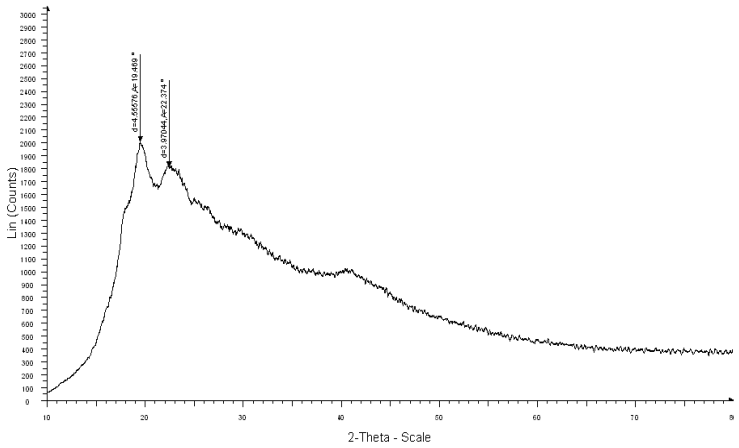

Figure 4: X-ray diffractogram of chitosan/cellulose acetate/ polyvinyl alcohol (1:1:2) ternary blend membrane.

The X-ray diffractogram of pure chitosan (Fig.3)displays two sharp peaks at around 2Ɵ= 10° and 20° indicating the semicrystalline nature whereas the X-ray diffractyogram of chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane (Fig.4) shows two broad peaks at around 2Ɵ= 19° and 22° showing the highly amorphous nature. The comparison X-ray diffractogram details of pure chitosan with chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane reveals that the chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane prepared in (1:1:2) ratio shows broad peak and lower percentage of crystallinity values when compared to pure chitosan. These observed results suggests that the chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane has highly amorphous nature than pure chitosan and this might be due to hydrogen bond formation and greater miscibility. The blending of two or more polymers makes the resulting materials more amorphous, which explains the disappearance of sharp diffraction peak from individual one.[22]

Thermo gravimetric (TGA) analysis

Thermogravimetric analysis is a method of thermal analysis which deals with the measurement of changes in physical and chemical properties of materials as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).[23] The TGA thermogram details of pure chitosan and chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane was represented in Fig. 5 and Fig.6.

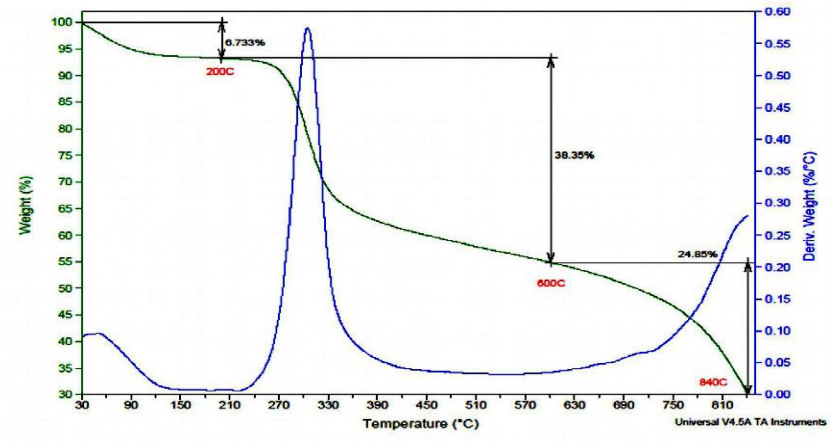

Figure 5: TGA thermogram of pure chitosan.

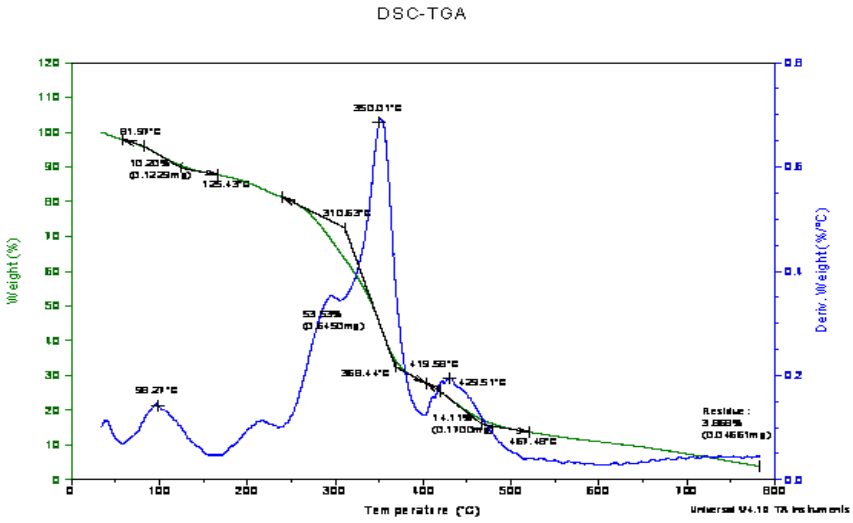

Figure 6: TGA thermogram of chitosan/ cellulose acetate/polyvinyl alcohol (1:1:2) ternary blend membrane.

The TGA thermogram of chitosan presented in Fig.5 shows mainly two major weight losses one before 200º C and another after 270ºC in polymer mass. The first one is due to the elimination of water molecules bound to the two polar groups in chitosan and the second one

is due to the dehydration of saccharide rings, depolymerisation and decomposition of volatile products.[24] Maximum weight loss occurs at the temperature range of 217°C – 450°C and the residual temperature was found to be 850ºC. At the end of the experiment around 69.933 % of the chitosan gets disintegrated within 840°C leaving behind 30.067% of the sample as residue showing higher thermal stability.

Fig. 6 represents the TGA thermogram details of chitosan / cellulose acetate / polyvinyl alcohol (1: 1: 2) ternary blend membrane. The results presented in the Fig-6 indicate that the 90% of the sample was decomposed at 580^0C. Maximum weight loss was observed from 330^0C to 380^0C which may be due to breaking of hydrogen bonds between polymers. The residual temperature of the blend was found to be 782^0C. At the end of the experiment 3.868% of the blend remained as residue and the gradual weight loss was observed from 415^0. From the comparison of TGA results of the chitosan/cellulose acetate/polyvinyl alcohol (1: 1: 2) ternary blend membrane with pure chitosan it was concluded that the chitosan/ cellulose acetate/ polyvinyl alcohol (1:1:2) membrane was found to be thermally more stable and this was concluded from the obtained higher initial decomposition temperature (180°C).

Differential Scanning calorimetric (DSC) analysis

Differential scanning calorimetric measurements were carried out by a heating-cooling-heating cycle. DSC is a technique which involves the measurement of the difference in the amount of heat required to increase the temperature of a sample and reference as function of temperature. By observing the difference in heat flow between the sample and reference, DSC is able to measure the amount of heat absorbs or release during such transition.[25] Fig.7 and Fig. 8 represents the TGA thermogram details of pure chitosan and chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane.

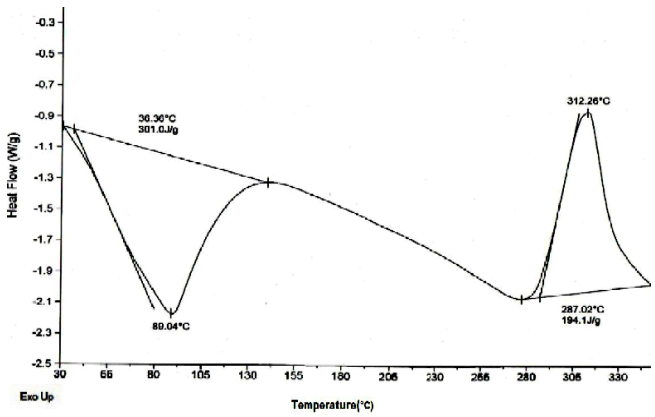

Figure 7: DSC thermogram of pure chitosan.

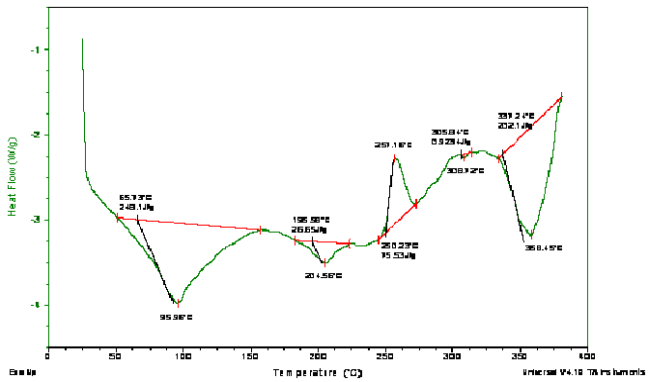

Figure 8: DSC thermogram of chitosan/ cellulose acetate/polyvinyl alcohol (1:1:2) ternary blend membrane.

The DSC thermogram of pure chitosan (Fig.7) shows a broad endothermic peak at 89.04°C and sharp exothermic peak at 312.26°C which indicate the crystallization and the melting process of polymer at different temperatures. A wide endothermic peak obtained at 89.04°C is attributed to the elimination of absorbed water and a sharp exothermic peak at 312.26°C is due to the decomposition of chitosan chains.[26] The glass transition temperature of the polymer is observed at 203°C and an exothermic peak obtained at 313.26°C indicating that certain chemical changes had taken place in this temperature range.

DSC curve of chitosan/cellulose acetate/polyvinyl alcohol (1:1:2) ternary blend membrane (Fig.8) show three endothermic peaks at 95.96^0 C, 204.56^{0}C and 358.45^{0}C. This endothermic peak explains strong crystallization of polymer blends. An exothermic peak which was observed at 257^{0}C shows that the blend has undergone some chemical changes like decomposition. The glass transition temperature of the ternary blend polymer membrane was found to be 240^{0}C.

The comparison of DSC thermogranm details of chitosan/cellulose acetate/polyvinyl alcohol (1: 1: 2) ternary blend membrane and pure chitosan indicate that the chitosan/cellulose acetate/ polyvinyl alcohol (1:1:2) membrane was also found to be highly thermally more stable and this was concluded from the observed higher glass transition temperature.

Scanning electron microscopic (SEM) studies

Scanning electron microscopy (SEM) studies reveals about the microstructure of the various components of the membrane and this technique can be regarded as a useful tool when interpreting durability and function values. The morphology of membranes is impressively

complex, diverse and irregular. The scanning electron microscopic (SEM) images of pure chitosan and chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane taken under various cross sections to investigate the surface morphology was shown in Fig.9 and Fig.10.

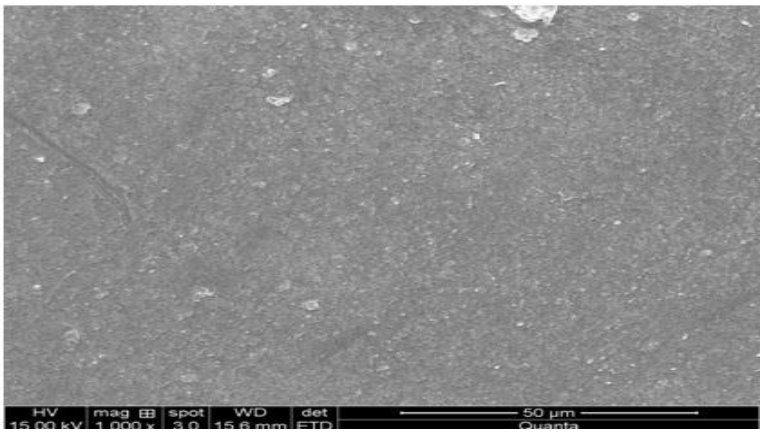

Figure 9: Scanning electron micrograph of pure chitosan.

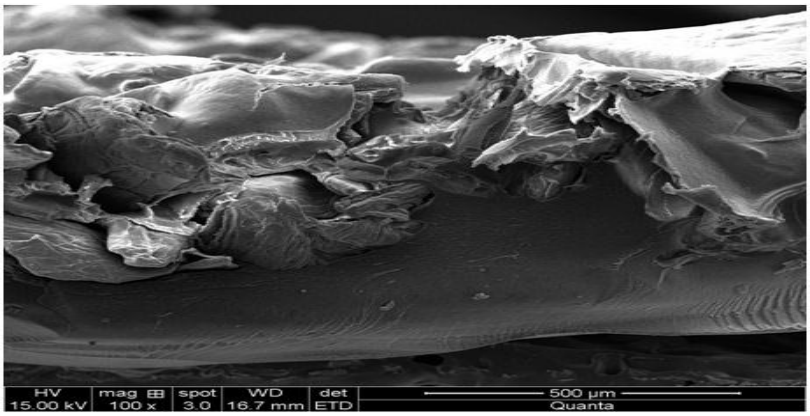

Figure 10: Scanning electron micrograph of chitosan/cellulose acetate/polyvinyl alcohol (1:1:2) ternary blend membrane.

The SEM micrograph of pure chitosan represented in Fig. 9 indicated the smooth surface morphology, the texture is plain without pores showing compact and homogeneous even surface structure whereas the SEM micrograph of chitosan/cellulose acetate/polyvinyl alcohol membrane presented in Fig.10 shows the rough irregular surface morphology. The chitosan/cellulose acetate/polyvinyl alcohol membrane exhibits large-scale surface roughness of ridge-and-valley structure which will be suitable for adsorption process. This result may be attributed to the high thickness of the cast film and long drying time. In the process of drying the water evaporated and the high molecular weight polymer in the membrane first dissolves out which caused the uneven section.[27]

CONCLUSION

The chitosan/cellulose acetate/polyvinyl alcohol ternary blend membrane were successfully prepared and characterized. From FT-IR results it was evident that, the certain new peaks were observed due to the various functional groups (NH, C=O stretching in esters, OH) in case of ternary blend membrane and these observed results suggest that the strong interaction had taken place effectively between the molecular chains of chitosan, cellulose acetate and polyvinyl alcohol which may lead to the miscibility at 1:1:2 ratios of the three components. The XRD studies elucidate the highly amorphous nature of the CS/CA/PVA ternary blend membrane. The TGA, DSC studies clearly indicate that the prepared CS/CA/PVA ternary blend membrane was found to be highly thermally stable and the rough surface morphology of the CS/CA/PVA ternary blend membrane was identified from the SEM studies. These new findings of CS/CA/PVA ultrafiltration membranes strengthen our research and can open a new path for further research in the wastewater treatment.

ACKNOWLEDGMENT

The authors would like to thank the Chemistry Department of D.K.M College for Women and special thanks to VIT University, TBI for their great support.

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