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Preparation and Characterization of Chitosan-Wrapped Silver Nanoparticles Incorporated Poly (Vinyl Alcohol) Membranes for Purification of Biogas

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Abstract

A solution technique was adopted to develop membranes in which chitosan-wrapped silver nanoparticles (CS-wrapped Ag nanoparticles) were incorporated in poly(vinyl alcohol) (PVA). The morphological studies and the chemical compositions of the prepared membranes were investigated using the characterization techniques like Infrared Spectroscopy, Differential scanning colorimetry, Wide Angle X-ray Diffraction, Thermogravimetric analysis and scanning electron microscopy. The effects of CS-wrapped Ag nanoparticles on membrane swelling were systematically studied to know the gas separation performance of the membranes. TGA showed increased thermal stability of Ag-nanoparticles incorporated PVA membranes nearly twice that of plane PVA membranes. Further, SEM revealed that CS-wrapped Ag nanoparticles incorporation into the PVA membrane matrix showed good compatibility and high swelling properties. Copyright © VBRI Press.

Keywords: Poly (vinyl alcohol), chitosan, silver nanoparticles, membranes, glass transition temperature.

Introduction

The major challenge of the world in modern time is to meet the ever growing energy requirements. It is not only essential to find the long term and renewable energy sources but also to find the eco friendly energy sources. Considering these factors biomass is one of the prominent energy sources to the ever growing energy needs of the world. Biomass includes trees, crops, agriculture residue wastes, forest residue wastes and all the kinds of other organic wastes of plants and animal origin [**1**]. Ethanol fermentation, biodiesel production and anaerobic digestion are the three main biochemical technologies developed for biogas production or biomass. Anaerobic digestion (AD) is a process in which methanogenic bacteria is used to synthesize biogas from organic wastes in presence of limited supply of oxygen [**2**]. This method is natural and eco friendly but still the use of biogas has some draw backs like presence of carbon dioxide (20-45 vol. %) and hydrogen sulfide (0-1 vol. %) along with the major component methane (55-80 vol. %).

In order to utilize biogas as a proficient energy source, enrichment of methane concentration is essential. Liquefaction of bio gas is vital in order to use it as a fuel for automobiles and household applications. This is possible only after compressing the biogas followed by the removal of impurities like CO_2, H_2S and water vapors. The removal of these impurities also helps to increase the calorific value of the biogas which is an important parameter for any fuel to be used efficiently at a larger scale. Some of the modern biogas purification techniques include physico-chemical techniques such as membrane separation, adsorption as well as cryogenic separation.

In recent times, membrane separation technique has emerged as a prominent way to purify the biogas due to the advantages over usual separation methods like scrubbing, amine treatment and distillation [**3**]. Membrane separation process offer numerous advantages like the membrane separation devices are compact as well as modular, membrane separation processes can be carried out at normal conditions with simple instruments and membrane processes are highly energy efficient when it comes to power consumption.

Inorganic and polymer membranes are the two majorly used membranes for CO_2 separation and they follow different routes in transport mechanism. Polymer membranes, which follow solution diffusion route have demonstrated high permeance of up to ~2000 GPU for CO_2 [**4-6**], but they have also shown low CH_4/CO_2 selectivities (generally less than 30 at 57 ^oC) [**7, 8**].

On the other hand, membranes following facilitated transport route provide good permeance for CO_2 as well as high CH_4/CO_2 selectivity. In these amine containing polymer membranes, molecules of CO_2 first react with amine carriers (polyallylamine [**9-13**], polyethylenimine [**9, 14**] and polyvinylamine [**15-18**]) and then the products of these reactions transfer across the membrane leaving the CO_2 molecules in the permeate section. Through this route solubility of CO_2 is enhanced in the membrane matrix. On the other hand, CH_4 molecules are non reactive towards these amine carriers so they diffuse through the solution diffusion mechanism. Therefore facilitated transport membranes provide high CH_4/CO_2 selectivity.

In the inorganic membranes like Zeolite Y, the gas transport follows both molecular sieving and surface diffusion mechanisms. The molecular size of CO_2 (3.3 Å) favors it's diffusion through the membrane while CH_4 (molecular size 4 Å) gets blocked. By combining these mechanisms, high CH_4/CO_2 selectivity and good CO_2 permeance can be obtained by using inorganic membranes [**19-22**]. But it is difficult to modify the inorganic membranes chemically to enhance the permeability and selectivity due to trade off phenomenon.

An alternative method to increase the separation performance of the polymer membranes is the inclusion of nano particles like zeolite, carbon blacks, silica and metal oxides in the membrane matrix to form hybrid membranes [**23-32**]. These membranes show subsequently enhanced permeability without decreasing the selectivity which provides enhanced separation performance [**33**].

In view of this an attempt has been made to develop membranes for CH_4/CO_2 separation by adding different fractions of chitosan wrapped silver nano-particles in PVA matrix. The prime reason for selecting chitosan to wrap the silver nano particles is to enhance the permeability without decreasing the selectivity. Solubility and dispersion behavior of Ag nanoparticles were drastically improved after the chitosan wrapping due to the emulsifying ability of chitosan [**34**]. To examine the changes in the peak intensities of the FTIR relating to the fraction of chitosan wrapped silver nanoparticles present in the PVA matrix, the FTIR spectra were recorded by keeping the amount of KBr and the membrane sample constant.

To investigate the physico-chemical properties of the resulting membranes thoroughly, they are characterized using WAXD, TGA, DSC, SEM and FTIR. The hydrophilicity of the membranes was investigated using contact angle meter and the swelling measurements were carried out by considering the different compositions of water –isopropanol mixtures.

Materials section

Materials

Chitosan having the molecular weight ~ 200,000 and silver nanoparticles were procured from Sigma Alderich Chemicals, USA. Poly (vinyl alcohol) having the molecular weight ~ 125,000 (degree of hydrolysis 86 – 89%), acetic acid (HAc) and isopropanol (IPA) were purchased from E. Merck. Ltd., India. Chemicals used for the preparation of membrane are of reagent grade and double distilled, deaerated water was used for the analysis.

Preparation of chitosan-wrapped silver nanoparticles

Chitosan wrapped silver nanoparticles were prepared mainly to increase the gas performance of the PVA membranes. The process of preparation is as follows: In 50 cc of water (double distilled) containing 2 % of Acetic acid, 1 g of chitosan was added with consistent stirring at room temperature for one day. The preapared PVA solution was then filtered to remove the undissolved chitosan and a homogenous solution was obtained. In this solution 0.25 g of silver nanoparticles were mixed and constantly stirred for a day at 90 ^oC to get the suspension of chitosan wrapped silver nanoparticles. This suspension was further sonicated in ultrasonic bath (Grant XB6, UK) at constant frequency of 38 KHz for half an hour in order to break the possible aggregates of silver nanoparticles.

Membrane preparation

4 g of poly (vinyl alcohol) was dissolved in 96 cc of distilled water at room temperature with uniform stirring for one day. The solution was then filtered to remove the undissolved particles to get the homogenous solution. This solution was then casted on a glass plate by using a membrane casting knife in dustless environment. Casted solution was dried for about three days. Finally, the membrane was peeled and designated as M.

The preparation of chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membrane was carried out as follows: To homogenous PVA solution a known amount of chitosan wrapped silver nanoparticles suspension was added and stirred for a day. The above mixture was then sonicated at uniform frequency of 38 KHz for half an hour to increase the dispersion of chitosan wrapped silver nanoparticles in PVA matrix. The resultant solution was then poured on a clean glass plate and the remaining procedure was similar to the procedure followed for the preparation of membrane M. The quantity of chitosan wrapped silver nanoparticles added relating to the PVA was changed as 0.5, 1.0, 1.5 and 2.0 mass%. Obtained membranes were then correspondingly designated as M-1, M-2, M-3 and M-4 as well as investigated for the thickness by means of a Peacock dial thickness gauge of Ozaki manufacturing company, Japan. The obtained thickness was uniform at the different points of the membrane and was measured with the accuracy of ± 2 μm. The uniform thickness of all the membranes was found to be 40 ± 2 μm. the scheme of the preparation of chitosan wrapped silver nanoparticles incorporated PVA membranes is shown in **Fig. 1**.

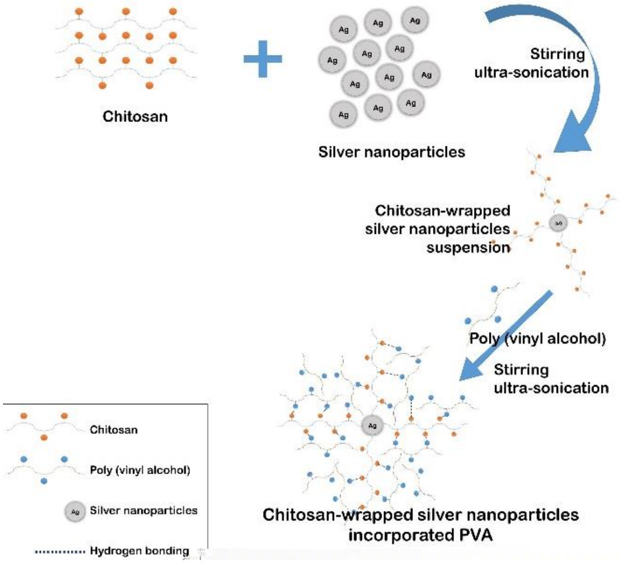

Fig. 1. Scheme of preparation of Chitosan-wrapped silver nanoparticles incorporated PVA membranes.

Fourier Transform Infrared (FTIR) Spectroscopy

Molecular finger printing of PVA and chitosan wrapped silver nanoparticles incorporated PVA membranes was carried out using FTIR spectrometer (Nicolet 6700). Range of the recorded spectra was from 400 to 4000 cm^{-1}.

Wide-Angle X-ray Diffraction (WAXD)

Morphological analysis of the PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes were done at normal conditions using Wide Angle X-ray Diffraction technique in a Philips Analytical X-ray Diffractometer. Dry membrane samples with uniform thickness (~40 μm) were scanned at an angle 2θ. The range was from 5° to 75° with the speed of 80/min.

Differential Scanning Calorimetry (DSC)

PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes were tested for their glass transition temperature using differential scanning colorimeter (DSC Q20, USA). The analysis was carried out under nitrogen atmosphere and at the heating rate of 10 °C/min.

Thermogravimetric Analysis (TGA)

The thermal analysis of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes were carried out using thermogravimetric analyzer (DSC Q20, USA). The analysis was carried out under nitrogen atmosphere and at the heating rate of 10° C/min.

Scanning Electron Microscopy (SEM)

Surface morphology of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes were studied by means of a scanning electron microscope named JSM-400 Å from Japan. Vacuum dried membranes were properly coated with sputtered gold conductive layer of 400 Å before the analysis.

Swelling measurement

Swelling measurements (equilibrium sorption) were carried out by considering various compositions of water-isopropanol mixtures by means of an oven (WTB Binder from Germany). First the dry weights of the membranes were determined. Weighed membranes were then immersed in different compositions of water-isopropanol mixtures and left for a day in a sealed vessel to achieve equilibrium. The temperature of the vessels was maintained at 30°C throughout the analysis. Swollen membranes were then weighed soon after blotting them on a digital micro balance with an accuracy of ± 0.01 mg. The percentage of degree of swelling was then analyzed using the following equation:

$$DS\,(\%) = \left(\frac{W_s - W_d}{W_d}\right) x100 \qquad (1)$$

where W_s = Mass of the swollen membrane and W_d = Mass of the dry membrane.

Contact angle meter

In order to measure the hydrophilicity of the membranes, static contact angle (CA) between the surface of the membranes and the distilled water was analyzed by means of a contact angle meter (Laben Instrument, Bangalore, India). Measurements of the angles were done at five different points on individual membranes. Entire analysis was carried out at room temperature.

Results and discussion

Membrane characterization

FTIR studies

Fig. 2 illustrates the FTIR spectra of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes.

In FTIR studies of the pure PVA membrane, a broad peak visible at around 3372 cm^{-1} corresponds to the O-H stretching vibrations. Multiple bands visible between 1000 to 1200 cm^{-1} corresponds to C-O stretching vibrations. All these peaks are similar to the ones reported in the research article by Karidurgannavar *et al.* [**35**]. In case of pure chitosan, presence of O-H group is confirmed by the appearance of broad peak at 3444 cm^{-1}. Multiple bands emerged at around 1645 to 1570 cm^{-1} are due to the presence of amide I and amide II (NH) functional groups respectively, and the bands appeared between 900 to 1200 cm^{-1} corresponds to C-O stretching which are evident for the presence of chitosan [**36, 37**].

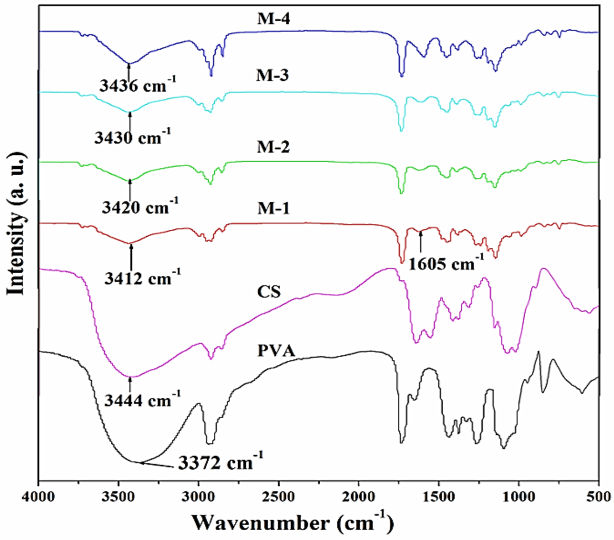

Fig. 2. FTIR spectra of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes (M to M-4).

In case of chitosan wrapped silver nanoparticles incorporated PVA membranes, broad band was appeared at around 3412 cm^{-1} and the intensity of the bands enhanced as we move from M-1 to M-4 with the peaks gradually moving towards the higher wave number. A new band was appeared at 1603 cm^{-1}. The band intensity increased as the amount of chitosan wrapped silver nano particle increased from M-1 to M-4. This is primarily due to increased hydrogen bonding between chitosan wrapped silver nano particles and poly (vinyl alcohol), which is evident for the good compatibility between the two chemicals.

WAXD studies

The illustrations of WAXD patterns of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes are shown in **Fig. 3**. The peak appearing at $2\theta = 20^{\circ}$ in diffraction pattern of pure PVA indicated that it contains both amorphous and crystalline domains in the membrane matrix [**38**]. The diffraction peak intensity is decreased as the incorporation of chitosan wrapped silver nanoparticles into the PVA matrix was increased. This decrement in the intensity is due to the increasing hydrogen bonding between PVA and chitosan wrapped silver nanoparticles. The peaks appeared at $2\theta = 27^{\circ}$, 38° and 55° also confirm the presence of silver nanoparticles which are responsible for increased gas separation performance since amorphous nature supports the movement of selective permeants [**39**].

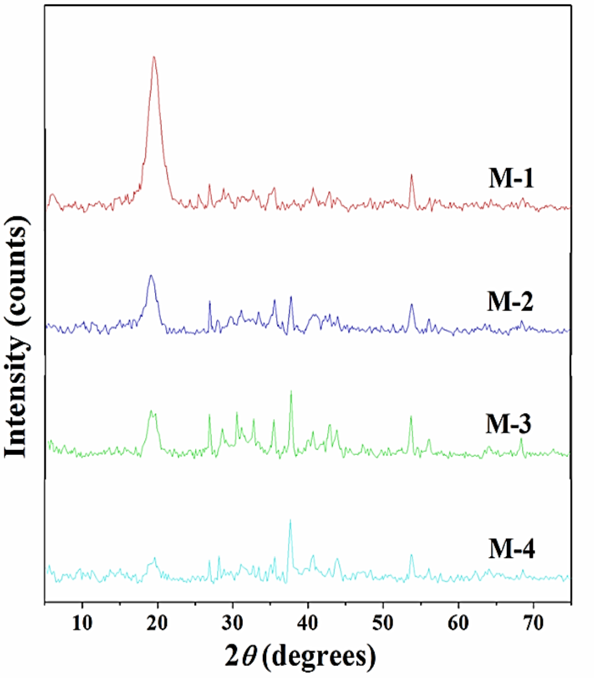

Fig. 3. XRD pattern of CS wrapped Ag nanoparticles incorporated poly (vinyl alcohol) membranes (M-1 to M-4).

DSC studies

Analysis of glass transition temperature (T_g) was carried out in order to assess the thermal behavior of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes. DSC analysis was done in the temperature range 27 ºC to 250 ºC to get the thermograms of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes. Two times the membranes were heated and cooled to eliminate moisture as the moisture affects the transitions. This temperature variation was also made to ensure that the membranes are not undergoing thermal degradation in first thermal cycle [**39**].

Fig. 4. Shows the thermograms of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes. According to these thermograms, T_g of the plane PVA membrane is around 85 ºC, then slowly enhanced from 90 ºC to 101 ºC as the quantity of chitosan wrapped silver nanoparticles was increased in the PVA matrix from M-1 to M-4.

This increase in T_g is primarily due to hindrance of chain movement because of the interaction between PVA and chitosan wrapped silver nanoparticles. Increased T_g values from M to M-4 indicate that the PVA membranes achieved greater stability when the concentration of chitosan wrapped silver nanoparticles increased in the membrane matrix.

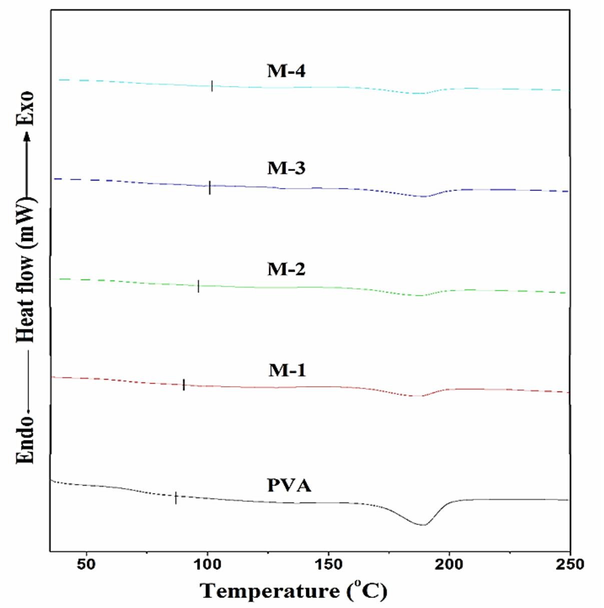

Fig. 4. DSC thermograms of PVA and CS wrapped Ag nanoparticles incorporated poly (vinyl alcohol) membranes (M to M-4).

TGA studies

Chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes were examined for their thermal stability and degradation nature under nitrogen flow by means of a thermo gravimetric analyzer. Recorded thermograms are illustrated in **Fig. 5**. To analyze thermal degradation, 30% weight loss and the corresponding temperature was considered as measuring point. According to the obtained thermograms it is clear that the chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes demonstrated around 20 to 36 ºC higher temperature than that of plane PVA at 30% weight loss. It clearly shows that thermal decomposition temperatures of chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes is higher compared to plane PVA membrane.

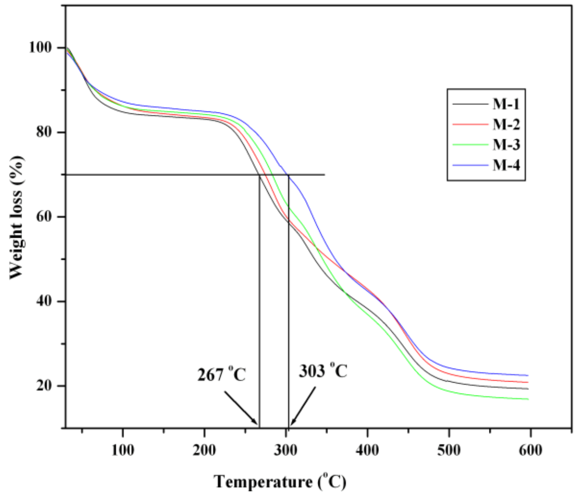

Fig. 5. Thermo gramogravimetric analysis of CS wrapped Ag nanoparticles incorporated poly (vinyl alcohol) membranes (M-1 to M-4).

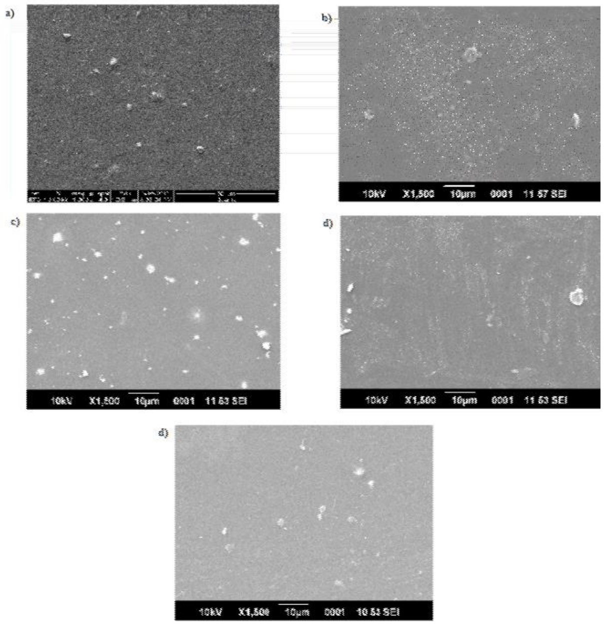

Fig. 6. SEM microgrames of (a) Plain PVA (b) M-1 (c) M-2 (d) M-3 (e) M-4 of Cs wrapped Ag nanoparticles incorporated poly (vinyl alcohol) membranes.

SEM studies

Scanning electron microscope images of PVA and chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes are shown in **Fig. 6**. From the photographs it is evident that the bright regions were increased as we move from M-1 to M-4 due to increase in the chitosan wrapped silver nanoparticles content in membrane matrix. The distribution of the chitosan wrapped silver nanoparticles in the membrane matrix was found without any cluster formation. These images also depicted that all the chitosan wrapped silver nanoparticles are individually dispersed in the membrane matrix and the membranes were homogenous and free from the defects. Further these images confirmed good compatibility between PVA and chitosan wrapped silver nanoparticles which are in accordance with WAXD and FTIR results. This confirms the incorporation of chitosan wrapped silver nanoparticles into the PVA matrix.

Effects of chitosan wrapped silver nanoparticles and feed composition on the swelling of membrane

Membrane sorption depends on factors like membrane structure, mutual interaction between the permeants and the interaction of the permeants with the membrane [**40**]. Membrane separation performance generally depends on the swelling studies of the membranes in different feed compositions. Swelling behavior of the membranes at 30 ºC in different proportions of water-isopropanol mixtures is shown in **Fig. 7**. Swelling of the membranes was increasing as the mass% of water was increased in the water-isopropanol mixture. This swelling behavior is due to the hydrophilic groups (-OH and –NH_2) present in the membranes. However, water being more polar, interacts with hydrophilic groups, as a result of this swelling of the membranes was increased.

The chitosan wrapped silver nanoparticles incorporation in PVA membrane matrix further increased the sorption selectivity. Therefore it was observed that the swelling of membranes increased as the amount of chitosan wrapped silver nanoparticles increased from the membrane M-1 to M-4. Presence of chitosan wrapped silver nanoparticles also enhanced hydrogen bonding which weakens the interaction in PVA matrix. Therefore free volume in the membrane was increased due to the decreased crystallanity. The changed structure of the membrane and the increase in the volume were the two factors accountable for the higher degree of swelling in chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes.

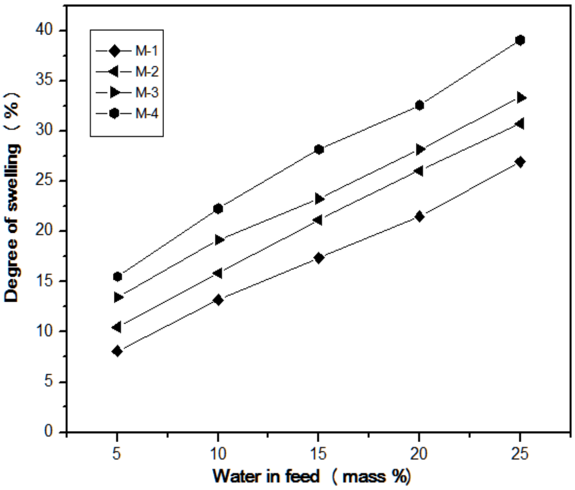

Fig. 7. Degree of swelling variation at different mass% of water in the feed for CS wrapped Ag nanoparticles incorporated poly (vinyl alcohol) membranes (M-1 to M-4).

Contact angle measurements

To investigate the surface properties of the membranes, contact angle technique was used.

Table 1. Contact angles of water for all the membranes at 10 second.

Membranes	Contact angle (°)
M-1	87.73
M-2	85.64
M-3	82.53
M-4	80.23

Contact angle allows to measure angle formed at the intersection of the surface of the membrane and the liquid. This provides information about the wettability of the surface [**41**]. The contact angle measurements of chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes are illustrated in **Table 1**. From the values observed, it is clear that the contact angle is decreasing as the concentration of chitosan wrapped silver nanoparticles is increased in the PVA membrane matrix. This is due to presence of more number of hydrophilic groups and silver nano particles present in the membrane. This demonstrates that the hydrophilicity of the developed membrane was enhanced as the presence of chitosan wrapped silver nanoparticles elevated in the PVA membrane matrix.

Conclusions

In this research paper, chitosan wrapped silver nanoparticles incorporated poly (vinyl alcohol) membranes were prepared using membrane casting method. These membranes were characterized by means of various characterizing techniques. FTIR shows interaction between PVA and chitosan wrapped silver nanoparticles and the peak intensity is increased with increase in the content of chitosan wrapped silver nanoparticles. WAXD demonstrates the predominant amorphous nature of the membranes. DSC gave the information about the increased T_g values from 85 to 101 °C as the content of chitosan wrapped silver nanoparticles in the membrane matrix. SEM images shown the compatibility between the PVA and chitosan wrapped silver nanoparticles along with the surface of the membrane. Degree of swelling is enhanced as the amount of chitosan wrapped silver nanoparticles increased in the membrane matrix which is due to the increased free volume and change in the structure of the membranes. Therefore the membranes can be used effectively to separate CO_2 from biogas.

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