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# Functionalized MWCNT and PVA Nanocomposite Membranes for Dielectric and Pervaporation Applications

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## Abstract

Novel PVA nanocomposite membranes were prepared with acid functionalized multiwalled carbon nanotubes (a-MWCNT) as the reinforcing material. The presence of functional groups on MWCNT is revealed by FTIR techniques. The excess swelling of poly (vinyl alcohol) (PVA) membranes were reduced by the crosslinking of glutraldehyde (GA). The functionalized MWCNT induces hydrophilicity to the PVA nanocomposites and the hydrophilic nature of the nanocomposites was revealed by the contact angle analysis. The effect of a-MWCNT concentration on the dielectric and DC conductivities of the PVA nanocomposites was studied very well. The electrical conductivity of the nanocomposites is increased with the concentration of MWCNT, and PVA with 1.5 wt% nanotube loaded membranes showed better dielectric properties. As the concentration of MWCNT increased to 1.5 wt%, the PVA nanocomposites got transformed from a region of insulator to semiconductor. DC conductivity also showed the same trend. The Voet model showed good agreement with the experimental results of the conductivity. We also found that the developed PVA/a-MWCNT nanocomposite membranes can be used to separate the azeotropic composition of water-ethanol mixtures. The pervaporation (PV) performance of the membranes is studied in terms of permeance and intrinsic selectivity. PVA with 0.5 wt% nanotube loaded nanocomposite membranes achieved 340% increment in intrinsic selectivity. The pervaporation performance of the membranes were in good agreement with the permeation ratio model, and the separation efficiency is influenced by the morphology of the membranes and the interaction of the filler and the permeates. It is also observed that the dielectric properties of the membranes were correlated with the concentration of the conductive nanofillers. Thus the present study provides good information on dielectric and the pervaporation performance of PVA/a-MWCNT nanocomposite membranes.

**Keyword:** Nanofillers; Nanocomposite; Microscopy

## Introduction

"Membrane technique" is an area in which effective and innovative research is undertaken now-a-days. Since CNTs are multifunctional nanofillers, it is used to develop nanocomposite membranes [1-3]. But the application of CNT is limited due to the improper dispersion in the polymer matrix. Henceforth the dispersion and interaction of CNTs are increased by adding suitable functional groups [4-6]. Moreover, it is selected by majority of researchers to develop nanocomposite membranes because of its high aspect ratio, chemical stability, Young's modulus, electrical conductivity and especially high permittivity. Several nanocomposite membranes are developed using CNTs, but the electrical as well as the pervaporation studies were not done. Therefore a membrane with these two applications can be used simultaneously to create a good impact in the membrane techniques.

PVA is a widely used polymer in the membrane technique on which several studies were done [7,8]. The hydrophilicity and chemical resistivity make it more attractive for developing membrane materials, but the excess solubility in aqueous solution limits its applicability. In order to overcome this drawback, crosslinking, blending or grafting can be used. Due to the difficulty in the dispersion of CNT in PVA, the studies of CNT incorporated PVA nanocomposite membranes were not explored very well. The commonly used functionalization methods are acid or amine functionalization. Choi et al. [9] used acid functionalized MWCNT/PVA nanocomposite membranes to separate 90/10 wt% ethanol/water mixture and achieved better flux and separation factor. Peng et al. [10] developed β-CD modified CNT–PVA nanocomposite membranes and effectively used for the separation of benzene/cyclohexane mixture.

Pervaporation separation of water- ethanol mixture is an industrially interesting area of research. Most of the studies were done to separate water- ethanol mixtures, but to the best of our knowledge, no reports are available on the field of PV separation of azeotropic composition of water - ethanol (4.37- 95.63 wt%) mixtures. Therefore, in the present study, we developed crosslinked PVA/a-MWCNT nanocomposite membranes via solution casting method with varying concentration of nanotubes. The effect of MWCNT concentration on the pervaporation performance and the dielectric and conductivity properties of the PVA membranes are investigated.

## Experimental

### Materials

In this study, MWCNT is purchased from Nanocyl, Belgium. Poly (vinyl alcohol) with number average molecular weight 1,25,000 g/mol was obtained from S.D Fine chemicals, Mumbai, India. Glutraldehyde (25 vol%) and all other chemicals were reagent grade and used without further purification, and supplied by Merck India Pvt. Ltd, Mumbai, India.

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## Membrane preparation

The dispersion of nanofiller in polymer matrix is one of the important factors to get better properties. The dispersion of pristine MWCNT in the PVA matrix is very difficult without suitable functionalization. In order to disperse the MWCNT to the PVA matrix, the pristine MWCNT was acid functionalized with $H_2SO_4$ and $HNO_3$ [11,12]. For preparing acid functionalized MWCNT, the pristine MWCNT was treated with 2:3 ratio $H_2SO_4$ and $HNO_3$ mixture. 1 g MWCNT was sonicated in a mixture of 100 mL $H_2SO_4$ and 150 mL $HNO_3$ for 16 h at room temperature. Then the mixture was washed with deionized water up to neutral pH. After attaining the neutral pH, the mixture was filtered and dried in a hot air oven at 40°C. The acid functionalized MWCNT is denoted as a–MWCNT. The schematic representation of the functionalization reaction is shown in Figure 1.

PVA/MWCNT nanocomposites were prepared by solution casting method. 5 g PVA was dissolved in 95 mL water using a mechanical stirrer at a temperature of 40°C. To this 0.5 wt% a–MWCNT was added slowly and sonicated for 2 h. The homogeneous mixture was cooled to room temperature. To this 1 vol% HCl added as a catalyst and then 5 vol% glutraldehyde was added slowly. It is then mechanically stirred for 1 h. The mechanically stirred solution is kept for 30 min for removing the air bubbles. Then it poured on a clean glass plate and dried in a laboratory oven at 40°C for 2 days. Dried membranes were peeled off carefully. Different set of PVA/MWCNT nanocomposite membranes were prepared by varying the concentration of a-MWCNT as 0.5, 1, 1.5 and 2 wt% and the membranes were denoted as PCr MWCNT (0.5), PCr MWCNT (1), PCr MWCNT (1.5), PCr MWCNT (2) respectively. For comparing the properties pure crosslinked PVA (5 vol% GA) membranes were also prepared.

## Characterization

**Fourier Transform Infrared spectroscopy (FT-IR):** The presence of different groups in the crosslinked nanocomposites were studied by FT-IR analysis. The FTIR spectrum was obtained from the Perkin Elmer analyzer at a spectrum range of 400-4000 $cm^{-1}$.

**Contact angle analysis:** Contact angle measurements were carried out using SEO phoenix 300 contact angle analyzer. Measurements were carried out with water as the liquid and the volume of the sessile drop was maintained as 5 µL in all cases using a micro syringe. The contact angle measurements were recorded as snap shots with definite time intervals for a single water drop.

**Optical micrographs**: Optical images of the sample are obtained from optical microscope XJL- 17 with resolution 400 × and 600 ×.

**DC conductance of the PVA nanocomposite membranes:** The DC Conductance of the nanocomposite membranes was studied using Keithley Electrometer. All conductance values are measured at a current range -70 to +70 µA with measurable voltage range 10 V.

## Pervaporation performance of the PVA nanocomposite membranes

PVA-MWCNT nanocomposite membranes were effectively used for the pervaporation separation of azeotropic composition of water and ethanol mixtures. The pervaporation experiments were carried under room temperature and the details are available in our earlier works [13].

An azeotropic mixture of water and ethanol (4.37-95.63 wt%) was taken as feed solution and all the experiments were carried out at room temperature with vacuum pressure 2 mm Hg. The selective component is transported through the membrane by applying the pressure. The desorbed permeate was condensed and collected in a liquid nitrogen trap. The flux was calculated by weighing permeate on a digital microbalance Mettler Toledo (JB1603-C/FACT) having an accuracy ±0.0001 g. The feed and permeate compositions were analyzed by gas liquid chromatography. All the experiments were repeated three times and the results were averaged to assess the experimental errors.

The pervaporation performance of the PVA membranes was evaluated by the separation factor (α), [14] and the separation flux (J) by following expressions:

$$\alpha = \left( \frac{X_B / Y_B}{X_A / Y_A} \right) \quad (1)$$

$X_A$ and $X_B$ are the composition of water in the feed and permeate respectively. $Y_A$ and $Y_B$ are the composition of ethanol in the feed and permeate respectively.

$$J = Q / A\,t \quad (2)$$

J is the molar flux of the membrane in $kgm^{-2}hr^{-1}$, Q is the quantity of permeate in kilograms, A is the effective area of the membrane in $m^2$ used for separation; 't' is time in hours.

The overall PV performance was calculated by pervaporation separation index (PSI). PSI was calculated using the equation:

$$PSI = J(\alpha - 1) \quad (3)$$

Component fluxes [15] for the separation of azeotropic composition of ethanol and water mixture were calculated by using the equation:

$$J_{H_2O} = J\,X_{H_2O} \text{ and } J_{ethanol} = J\,Y_{ethanol} \quad (4)$$

$J_{H_2O}$ and $J_{ethanol}$ are the component fluxes, J is the flux, $X_{H_2O}$ and $X_{ethanol}$ are the permeate composition of the mixtures.

## Membrane permeance and intrinsic selectivity

The partial pressure difference between either sides of the membrane is the real driving force for the transport of components through the membranes. The real intrinsic properties of the membranes are obtained from membrane permeance, permeability and selectivity values and are calculated using the Equations (5), (6) and (7) respectively. Most common ways to express the permeance as gas permeation unit (gpu).

$$Permeabilty\,(P_i^G) = J_i \frac{l}{P_{i0} - Pil} \quad (5)$$

$$Permeance\,(P_i^G / l) = \frac{J_i}{P_{i0} - P_{il}} \quad (6)$$

The membrane intrinsic selectivity is the ratio of permeabilities or permeance of the components i and j through the membrane and can be obtained from the expression

$$\alpha_{ij} = \frac{P_i^G}{P_j^G} \quad (7)$$

# Results and Discussion

## FT-IR analysis

The presence of different functional groups on a-MWCNT was characterized by FT-IR spectroscopy. The spectra of the pristine MWCNT and a-MWCNT are shown in Figure 2.

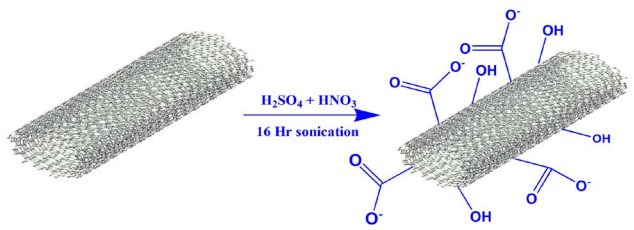


**Figure 1:** Schematic representation of side wall functionalisation of MWCNT.

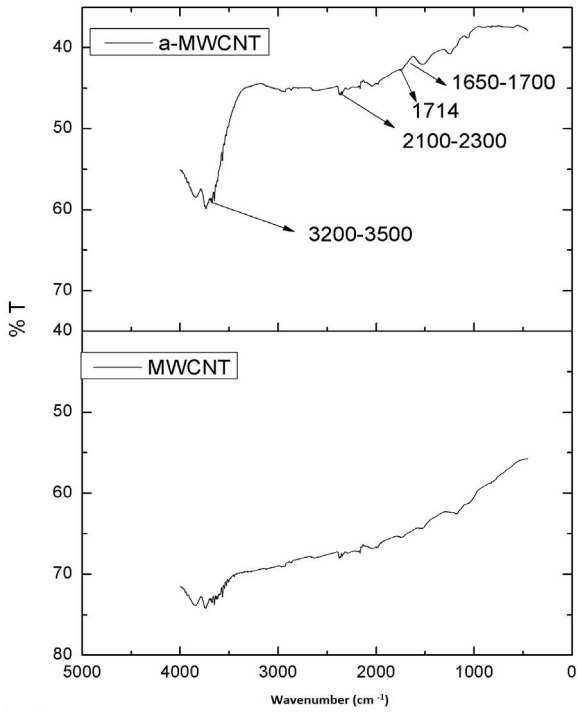


**Figure 2:** FT-IR spectra of MWCNT and a-MWCNT.

Introduction of functional groups such as hydroxyl (–OH), carbonyl (–C=O) and carboxyl (–COOH) groups can be obtained by the oxidation of nanotube with a $HNO_3/H_2SO_4$ mixture [16]. The peak around 3200 $cm^{-1}$ corresponds to –OH groups, which are always present in the MWCNT samples, and the peak intensity in this region is increased after the chemical treatment. The carbonyl stretching peak is obtained around 1714 $cm^{-1}$ and the peak at 1650 $cm^{-1}$ corresponds to the carboxylic peak, and the peak intensity increases with chemical treatment [17]. There was significant difference between the spectra before and after acid treatment.

The presence of a-MWCNT in the PVA nanocomposites is clearly obtained from the FT-IR spectra of the nanocomposites (Figure 3). The broad peak around 3300 $cm^{-1}$ indicates the presence of –OH functional group present in the a-MWCNT. Compared to cross linked PVA membranes, there is a presence of new peak at 1700 $cm^{-1}$ due to the –C–O group present in the a-MWCNT. Peak around 1140 $cm^{-1}$ correspond to the crystalline peak of PVA which changes in filler loading. One small peak at 1400 $cm^{-1}$ is associated with –O–H bending deformation of carboxylic acid groups, and peak at 1192 $cm^{-1}$ is associated with the –C–O stretching band. Thus the improved interaction of a-MWCNT with PVA matrix is clearly evident from FT-IR studies.

## Contact angle analysis

Contact angle measurements of the nanocomposite membranes were done at room temperature with water as the contact liquid. The hydrophilic- hydrophobic nature, work of adhesion of a - MWCNT reinforced nanocomposite membranes were studied using contact angle analysis. The contact angles were measured for each specimen of a sample for at least six to ten times and the average is taken as the contact angle for the particular specimen. The contact angle results are summarized in Table 1.

Crosslinked PVA membranes showed a water contact angle of 72°. While increasing the a-MWCNT content up to 2 wt%, the contact angle decreased to 51°. The crosslinked PVA membranes show a hydrophobic nature with high value of contact angle but by the addition of functionalized MWCNT to the crosslinked matrix the contact angle decreased. This means that the hydrophilicity increased in the crosslinked PVA matrix due to the presence of acid functional groups. The surface of the nanocomposite contains acid functionalized MWCNTs and this eventually decreases the hydrophobic nature of the crosslinked PVA membranes.

The work of adhesion, $W_A$, for the PVA nanocomposite membranes is shown in Table 1. $W_A$ is actually the work required to separate the solid and liquid depends on the contact angle and surface tension of the liquid. Normally $W_A$ can be correlated to the filler - matrix interaction of the filler with a liquid and which is comparable with the matrix polymer. From the table it is clear that the work of adhesion increases with the a-MWCNT concentration. Thus the effective dispersion of nanofillers into the matrix might have caused an increase in the work of adhesion which is the work required to separate the liquid from the solid surface [18].

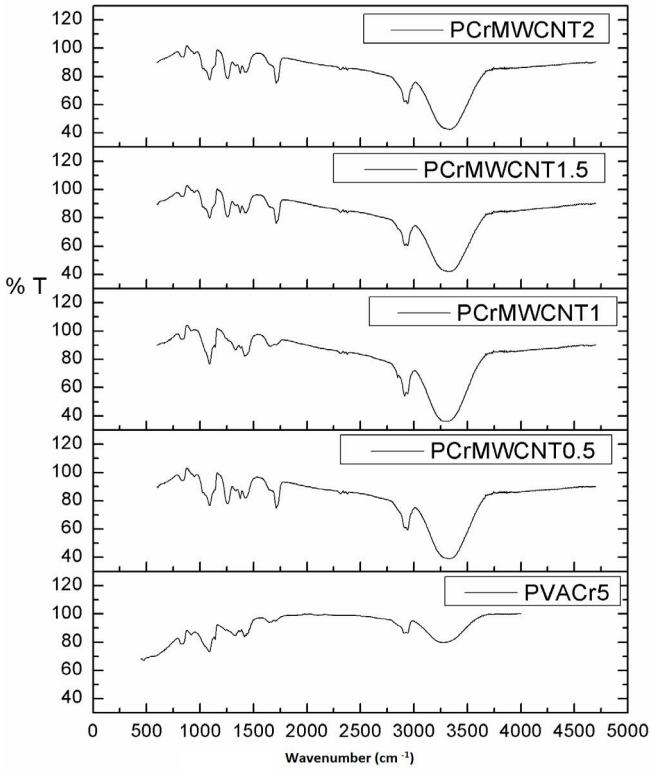


**Figure 3:** FT-IR spectra of the PVA/CNT nanocomposite membranes.

| Sample | Contact angle (θ) | Work of adhesion $W_A=(1+\cos\theta)\gamma_l$ mJ/m² |
|---|---|---|
| PCr5 | 72 | 95.29 |
| PCr5 a-CNT 0.5 | 63 | 105.85 |
| PCr5 a-CNT 1 | 58 | 111.38 |
| PCr5 a-CNT 1.5 | 53 | 116.61 |
| PCr5 a-CNT 2 | 51 | 118.61 |

**Table 1**: Contact angle analysis of PVA nanocomposite membranes.

## High resolution optical microscopy

The dispersion and interaction of MWCNT on the polymeric matrix are revealed by high resolution optical microscopy technique. The incorporation of MWCNT into the PVA matrix should form a network like structure. The filler-filler interaction would be the reason for the network formation and is clearly obtained from the Figure 4. Eventually at lower filler loading the interconnected structure of the tubes will no longer exist and the MWCNT are distributed uniformly as fine dispersion (Figure 4a). As the concentration increases, the network formation of the MWCNT is occurs in the matrix and is clearly evident from Figures 4b and 4c. But at higher filler loading, the MWCNT get agglomerates easily. (Figure 4d). The prolonged treatment of MWCNT with $H_2SO_4/HNO_3$ would cut some of the long-tubes into short tubes. This is due to the electrophilic attack by an acid mixture on the hexagon structure of nanotube which possibly cut the nanotubes to short tubes [19]. The filler-filler interaction is clearly evident from the optical images.

## Electrical conductivity of PVA/a-MWCNT nanocomposite membranes

The AC conductivity ($\sigma_{AC}$) against frequency of PVA with different a-MWCNT content is presented in Figure 5. The AC conductivity is increased for all nanocomposite membranes with filler concentration. The MWCNT is conducting filler and therefore there is a formation of conducting network on the insulating polymer matrix. Generally nanofillers particularly MWCNTs are very difficult to disperse in the polymer matrix because of its fine size and aggregating nature. This can be overcome by the suitable functionalization of the side walls of the MWCNT. So the conductivity of crosslinked PVA nanocomposite membranes with a-MWCNT is increased with filler loading. Crosslinked PVA with 1.5 wt% nanotubes shows optimum $\sigma_{AC}$ conductivity value in the range $10^{-6}$ S/m. The high aspect ratio of the nanotube is mainly responsible for the sudden rise in the conductivity at lower filler loading. The dispersion of MWCNT was considerably improved by the fuctionalization as evident from the optical photographs and thus leading to the formation of a MWCNT network with smaller amount of filler.

The AC-conductivity of nanocomposite membranes shows a frequency independent behavior with filler concentration. All the nanocomposite membranes except 1.5 wt% a-MWCNT shows frequency independent behavior at lower frequency and progressively increased with increasing the frequency. The increase in AC-conductivity with increasing frequency is in accordance with the equation [20-21].

$$\sigma_{AC} = \sigma_{DC} + 2\pi f \varepsilon'' \quad (8)$$

where, $\sigma_{AC}$ is the AC-conductivity, $\sigma_{DC}$ is the DC-conductivity, $f$ is the measurement frequency and $\varepsilon''$ is the loss factor.

The DC conductivity is the frequency independent conductivity and is related to the ionic or electronic conductivity. But the AC conductivity is proportional to the frequency, i.e, $2\pi f\varepsilon''$ and arises due to the accumulated charges at the filler-polymer interface. All composites are multiphase systems and therefore net polarization is due to the interfacial polarization originates at the interface of electrically different materials. In the present system the interfacial polarization arises due to the presence of MWCNT, which is electrically very much different from the base polymer, PVA.

The variation of dielectric permittivity as a function of frequency is shown in Figure 6. The $\varepsilon'$ values decrease linearly with frequency and then it leveled off. At the lower filler loading, then $\varepsilon'$ of the nanocomposite membrane exhibits a slow decrease trend along with increasing frequency. But when the filler content is at 1.5 wt%, there is a percolation transition from insulator region to conductor region, which is accompanied by an increased dielectric permittivity. The conductive nanotube in the polymeric matrix generates lots of micro capacitor structure throughout the matrix, which increase the intensity of the electric field. According to Dang et al. [22] the increment in dielectric permittivity of conductive filler-polymer systems near percolation threshold is due to the micro capacitor effect. Hence 1.5 wt% nanotube loaded membranes showed optimum dielectric behavior. After that the conductivity of the nanocomposite membranes decreased due to the fine agglomeration tendency of the CNTs.

## Direct current (DC) electrical conductivity

The DC conductivity of modified MWCNT nanocomposite membranes is shown in Figure 7. Due to the large aspect ratio and unique graphite structure, the nanotubes are considered as ideal conductive fillers and are used to prepare conductive nanocomposites with low percolation threshold. The conductivity of the PVA/a-MWCNT membranes increases with filler concentrations, and PVA with 1.5 wt%

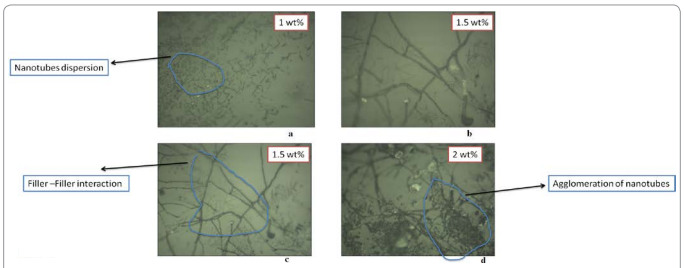


**Figure 4:** High resolution optical images of PVA/MWCNT nanocomposites, (a) 1 wt% (b) 1.5 wt% (400 ×) (c) 1.5 wt% (600 ×) (d) 2 wt%.

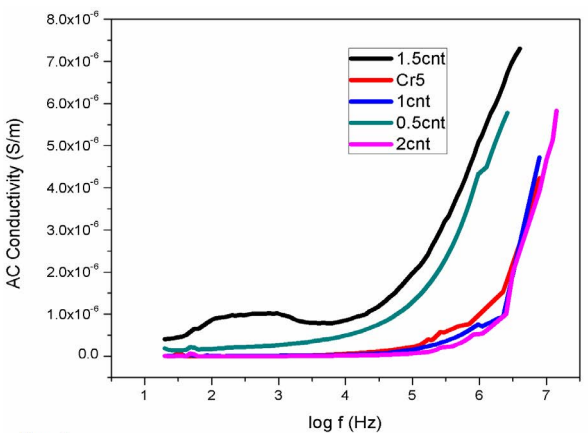


**Figure 5:** Variation of AC conductivity of the PVA nanocomposites with the frequency.

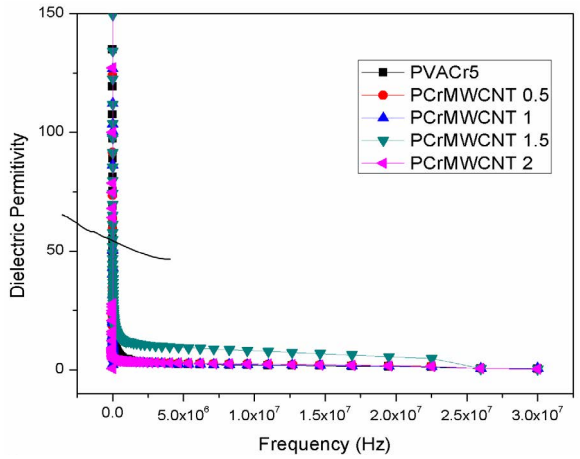


**Figure 6:** Variations of dielectric permittivity of the PVA nanocomposite with frequency.

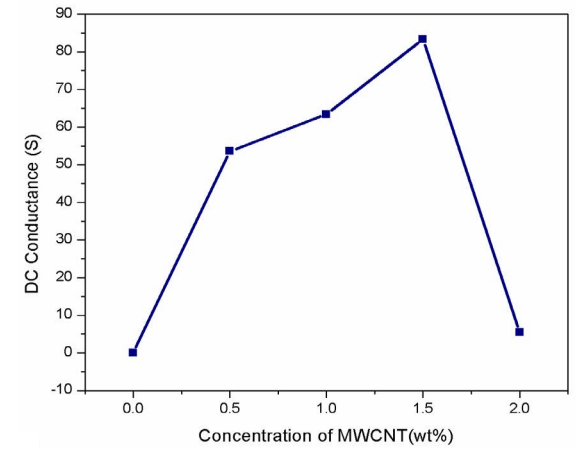


**Figure 7:** Variation of DC conductance of the PVA nanocomposite with filler loading.

a-MWCNT loaded membranes showed higher conductivity values around 83 Siemens. With an increase in the concentration of nanotubes, the filler particles form a conductive path in the polymer matrix. This would enhance the conductivity of the resultant PVA nanocomposite membranes. Due to the aggregating tendency of nanotubes at higher filler loading, the conductivity of the nanocomposites reduces. The aggregating tendency reduced the conductive network formation in the polymer matrix. So the DC conductivity of the PVA nanocomposites with 2 wt% a-MWCNT is decreased.

## Applicability of the models for the theoretical calculation of electrical conductivity

**Voet model:** The effect of filler concentration on the conductivity of polymer composite with conducting filler is described by Voet model [23]. According to the model prediction, the electrical conductivity is due to the electron emission phenomena. The Voet theory derived an equation in the form:

$$\log \sigma = k\phi^{1/3} \quad (9)$$

Where K is a constant, φ is the volume fraction of filler in the composite and σ is the conductivity of the composite.

According to Voet model, the plot log σ against $\varphi^{(1/3)}$ should be a straight line. Figure 8 shows the plots of logσ vs $\varphi^{(1/3)}$ for PVA/a-MWCNT nanocomposite membranes. In the present system, conductivity shows a sudden increase with lower filler loading, and then it forms almost constant values with further increase in the filler loading. According to the Voet model this straight line portion being conductive with the concentration of a-MWCNT such as 0.5, 1 and 1.5 wt%, respectively [24] and beyond that the conductivity reduces with increasing the filler loading. Thus, up to 1.5 wt% of filler loading, the PVA nanocomposite systems behaves as a conductive system and after that the constancy losses due to the agglomeration of nanotube at higher filler loading. The PVA with 0.5, 1, 1.5 wt% a-MWCNT loaded membrane forms a conductive system with a conductive polymer-filler network.

**Pervaporation performance:** The PVA/MWCNT nanocomposite membranes were used for the separation of azeotropic composition of water- ethanol mixture. The variation of flux and separation factor is shown in Figure 9. Initially at lower concentration, the separation factor values increased from 36 to 160 as compared to pure crosslinked PVA membranes, and decreased when the a-MWCNT content increased 0.5 to 2 wt%. The separation factor increased 344% for 0.5 wt% nanotube loading as compared to pure crosslinked PVA membranes. The reasons were, firstly a-MWCNT could enhance sorption selectivity of PVA membranes towards water compared to ethanol due to the hydrophilic interaction of acid functionalized MWCNT and water molecules. The decrease in the separation factor with increase in the MWCNT content is the characteristics of the MWCNTs, such as empty inner space and the hydrophilic functional groups attached to the surface of the a-MWCNT [25].

The permeation flux is drastically decreased upon the addition of a-MWCNT. The better interaction of PVA and a-MWCNT reduces the transport of water molecules and ethanol molecules through the membranes, which in turn reduce the permeation flux of the membranes. The effective free volume in PVA membranes is reduced with the addition of a-MWCNT, and so the permeation flux of the membranes decreased. Thus the membranes become stiff upon the addition of nanotube, and the permeation rate decreases on filler loading and correspondingly the flux. The selective permeation of both components is shown in Figure 10. The water component flux is more compared to ethanol component flux, and this indicates the selective transport of water molecules through the membranes. The water component flux shows the same trend as that of total component

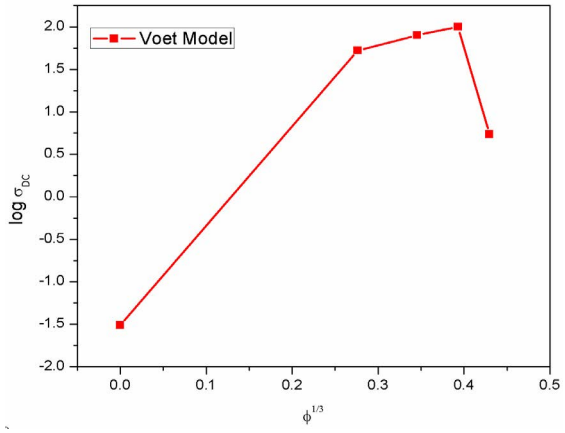


**Figure 8:** Theoretical prediction of the conduction with Voet model.

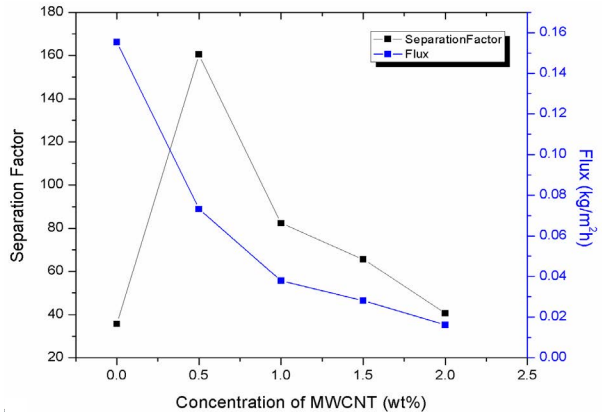


**Figure 9:** Variation of flux and separation factor of the PVA nanocomposites with filler loading.

flux. The hydrophilic nature of a-MWCNT reinforced membranes showed permselectivity towards water molecules, which selectively transport the water molecules. Hence the water component flux is more compared to the ethanol flux.

The overall pervaporation performance of the membranes was calculated using PSI and the enrichment factor (Figure 11). PVA with 0.5 wt% a-MWCNT membranes shows optimum PV performance. Thus, at lower filler loading, the dispersed MWCNT is more selective towards the water and the separation efficiency is increased due to the hydrophilic interaction of water and acid functionalized MWCNT present in the PVA matrix. According to Gonzalez-Velasco et al. [26] the content of the preferred component in the mixture is lower; the selectivity of the process is higher because of the reduced swelling. In the present system, i.e the azeotropic composition of water and ethanol, the ethanol concentration is more and water concentration is very less. The present PVA/a-MWCNT nanocomposite membranes are hydrophilic in nature and so the water is preferentially sorbed component. So the excessive swelling of the membranes in water is reduced and the membranes become more selective towards the water. Hence the PVA with lower filler loading showed better PV performance.

**Intrinsic properties of the PVA/MWCNT nanocomposites:** The conventional flux and separation factor data were converted to permeance and selectivity values for analyzing the real intrinsic properties of the membranes.

The water permeance of the azeotropic composition of water and ethanol mixture was decreased to 316 gpu from 3034 gpu for 2 wt% a-MWCNT concentration (Figure 12). The a-MWCNT content in the PVA matrix reduces the transport of the different component through the membranes, and so the water permeance decreased linearly. We also observed that the intrinsic selectivity, the ratio of the water permeance and the ethanol permeance, is increased to 3 to 13 for 0.5 wt% nanotube content. The intrinsic selectivity showed more than 300% enhancement than that of pure crosslinked membranes. The intrinsic selectivity for the PV separation of azeotropic composition of water-ethanol is increased at lower nanotube content. The hydrophilicity, a-MWCNT dispersion, and the interaction between the nanotube and the polymer matrix play significant role in the final performance of the permeants in the nanocomposite membranes.

At the higher filler loading, the acid functionalized CNT induces more hydrophilicity to the polymeric matrix (contact angle decreases), and so the water permeation through the membrane decreases. Also the interaction of polymer and filler is increased upon the addition of more filler content (work of adhesion increases), and this also reduces the selective permeation of water molecules through the membranes. These selective interactions might occur because of the increased swelling at higher filler loading and higher mobility of polymer chains. This accelerates the transport of ethanol along with water molecules. This sorption of ethanol results in a decreased selectivity at higher nanotube loading. The interaction and dispersion of PVA and a-MWCNT can be explained by schematic illustration depicted in Figure 13. In this scheme, the –OH group of PVA interacts with $–COO^-$ and -OH groups present in the a-MWCNT. Thus the separation performance of the resultant composite materials increased with filler loading.

**Permeation ratio (θ): Comparison of experimental result with theoretical data:** Total permeation ratio ($\theta_t$) is a measure of the division of the actual total permeation flux ($Q_t$) from the ideal permeation flux ($Q_t^0$) for a binary mixture. It describes the interaction between the polymers and permeates [27-28].

$$\theta_t = \frac{Q_t}{Q_t^0} \tag{10}$$

The permeation rate for an ideal binary mixture can be expressed in terms of permeation rates of the pure components and it is given by the equation:

$$Q_t^0 = X_1 Q_1^0 + X_2 Q_2^0 \tag{11}$$

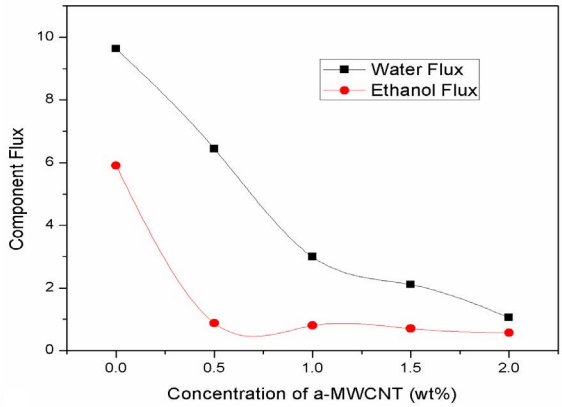


**Figure 10:** Variations of component flux of the PVA nanocomposites with filler loading.

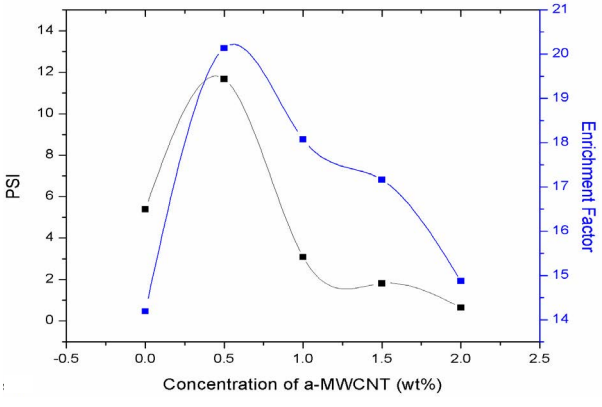


**Figure 11:** Variations of PSI and the enrichment factor of the PVA nanocomposites with a concentration of a-MWCNT

Where $X_1$ and $X_2$ are the weight fractions of water and ethanol in the feed mixture and $Q_1^0$ and $Q_2^0$ are the permeation rate of pure water and ethanol respectively. The permeation of each component is independent of the existence of the other components in the feed mixture, and then the ideal permeation flux occurs corresponds to the ideal situation.

The permeation can be classified into three according to the value of the permeation ratio. When the permeation ratio is equal to unity, then the feed alcohol solution exhibits the ideal behavior. If the permeation is non-ideal in nature, then the value of the permeation ratio is higher or lower than unity. There is 'permeation enhancement effect' and 'permeation depression effect' depends on the value of permeation ratio. If the permeation ratio of a system is lower than unity, the system can be said to exhibit a 'permeation depression effect', while a value higher than unity indicates a 'permeation enhancement effect'.

Figure 14 shows the permeation ratio against concentration of nanotube content. The total permeation ratio values of the PVA/a-MWCNT nanocomposite membranes are less than unity, indicating that the actual permeation rate is smaller than the ideal permeation rate. The permeation ratio value less than unity indicates the interaction of permeates and the membranes [29]. Thus, it shows the existence of interactions between the permeates and the PVA nanocomposite membranes. At lower filler loading, the value of permeation ratio is close to unity and it deviates as the concentration of a-MWCNT increases. So the selective interaction of permeates and membranes is increased at lower filler loading. Therefore at lower filler loading, PVA/a-MWCNT system is more favorable for the separation of water-ethanol azeotropic mixtures.

PVA/a-MWCNT nanocomposite membranes were effectively used to separate the azeotropic composition of water-ethanol mixtures. The various industrial applications of ethanol get considerable interest to the dehydration of ethanol by many of the researchers. PVA nanocomposite membranes of this study are much better in performance in terms of intrinsic selectivity and water permeance. It is noticed in the present study that the separation factor shows significant improvement by the addition of nanotubes. The real factor behind the PV performance is the partial pressure difference; which revealed from membrane permeance and intrinsic selectivity.

## Conclusion

The present work investigated the influence of functionalized MWCNT on the pervaporation and dielectric properties of PVA nanocomposites. The dielectric and conductivity properties of the PVA/a-MWCNT membranes were explored very well in this study. The electrical properties increase with an increase in the concentration of nanotube content. High resolution optical images showed the interaction and filler-filler network formation of MWCNT in the a-MWCNT/PVA nanocomposites. PVA with 1.5 wt% nanotube loaded membranes showed optimum conductivity performance with AC conductivity in the range of $10^{-6}$ and DC conductance of 83 Siemens. The conductivity of PVA composites increased from the region of insulator to semiconductor.

In addition to the dielectric properties, the pervaporation performance of PVA/MWCNT nanocomposites was studied very well. The nanocomposite membranes and GA crosslinked membranes appear to have promising potential for separation of azeotropic composition of water and ethanol mixtures. At lower filler loading, especially PVA with 0.5 wt% a-MWCNT loaded membranes showed promising performance for separation of water and ethanol. The intrinsic selectivity of the membranes was increased to 300% than that of pure crosslinked PVA membranes. The hydrophilic nature of the PVA/a-MWCNT membranes caused enhancement in the intrinsic selectivity of the membrane. The hydrophilic nature of the PVA nanocomposites obtained from the contact angle analysis. Thus the

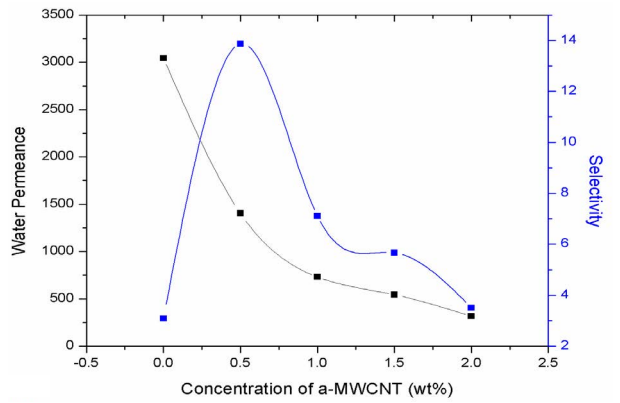


**Figure 12:** Variations of water permeance and selectivity of the PVA nanocomposites with a concentration of a-MWCNT.

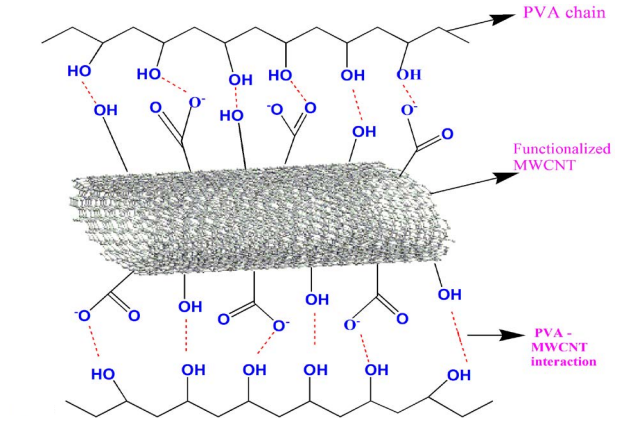


**Figure 13:** Schematic representation for the interaction and dispersion of a-MWCNT and PVA in the polymeric matrix.

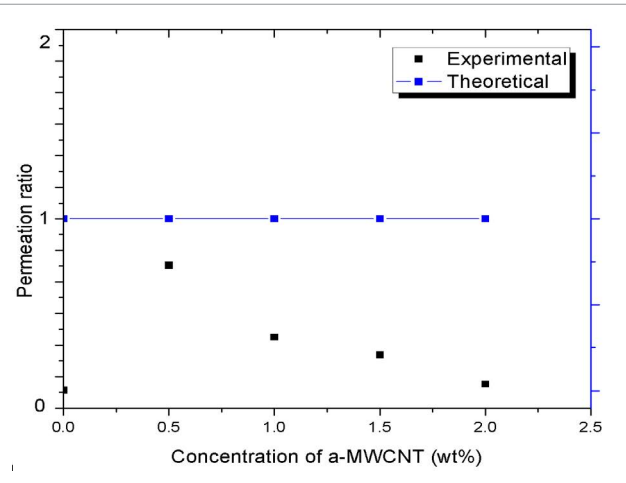


**Figure 14:** Permeation ratio of the nanocomposite membranes.

developed PVA/a-MWCNT nanocomposite membranes are potential membranes for both pervaporation and electrical applications.

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