

Mechanics and Pervaporation Performance of Ionic Liquid Modified CNT Based SBR Membranes - A Case Study for the Separation of Toluene/Heptane Mixtures

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Abstract: SBR/ionic liquid modified CNT Nanocomposites were prepared using different concentration of CNT. Nano scale dispersion of CNT affected the properties of SBR. The results have been compared with the unfilled SBR films. Cure characteristics and mechanical properties such as tensile strength, modulus, abrasion resistance and hardness were measured for different composites. Morphological behaviour and structural characteristics of the composites were investigated by AFM, TEM, FTIR and Raman spectroscopy. Microstructural development in presence of filler and interfacial interaction between modified CNT and polymer matrix led to enhanced properties. The pervaporation performances of membranes were analysed using a toluene/heptane mixture. Membranes displayed high selectivity towards heptane. The influence of feed composition on pervaporation was also analysed. The 5 phr CNT loaded membrane showed enhanced membrane permeance and selectivity value, an improvement of 18% over the neat polymer. A drop in selectivity and an increase in permeation rate were observed at higher CNT loadings.

Keywords: Ionic liquid modified CNT, Microstructure, Interfacial interaction, Flux, Separation factor.

1. INTRODUCTION

Polymer based nano composites serve as very promising, cost effective candidates for applications in wide range of fields which includes mechanical engineering, nano scale electronics, chemical sensing, tissue engineering, bio sensing and membrane fabrication [1, 2]. These materials consist of polymer matrix which contains various nano fillers such as clay, CNT, graphene, metal oxides etc [3, 4]. Among various nano fillers CNT has an excellent combination of mechanical, electrical and thermal properties which make CNT a potential candidate to replace the conventional nano fillers in the fabrication of multifunctional polymer nano composites [5, 6]. The major issues in the preparation of MWNT reinforced polymer nano composites are located in efficient dispersion of CNTs within the polymer matrix. CNTs have an inherent tendency to form agglomerates in the polymer matrix which diminishes the reinforcing effects [7]. So proper surface functionalization of CNT is inevitable for the preparation of multifunctional CNT based polymer composites. Non covalent functionalization of CNT using ionic liquid is a green and clean approach for the modification of CNT. Fukushima *et al.* succeeded to obtain a superior

dispersion of CNTs in room temperature ionic liquid (IL) by mixing single walled carbon nano tubes (SWCNTs) with 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) [8]. Ionic liquid modified CNT polymer composites with improved mechanical, thermal, electrical and oxidation resistance properties are prepared by various researchers [9-11].

Several studies have been reported on the effective pervaporation separation of various solvent mixtures by using CNT based composite membranes. Novel ploy(vinyl alcohol)/carbon nano tube hybrid membranes for pervaporation separation of benzene/cyclohexane mixtures was prepared by Peng *et al.* [12]. Choi *et al.* reported a facile method for the pervaporation of water ethanol mixtures by using multiwalled carbon nano tube based poly (vinylalcohol) membranes [13]. The pervaporation dehydration of ethanol by hybrid membranes incorporating Fe₃O₄@MWCNT nano fillers was fabricated by Gao *et al.* [14] This study demonstrated that decorating hydrophilic inorganic nano particles onto CNTs was a suitable method to improve the dispersion of CNTs in polymer matrix as well as the separation performance of water-selective polymer-CNTs hybrid membranes.

The styrene-butadiene rubber (SBR) is one of the most widely used rubbers due to its inexpensive cost and good mechanical property. Gum vulcanization of SBR leading to lower mechanical properties due to the

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lack of self-reinforcing ability. CNTs are widely used as the reinforcing agents for SBR to improve overall performance of composites. In this study, SBR and surface modified CNT composites with varying CNT loadings (1, 3, 5, 7 and 10 phr) were prepared. The pervaporation characteristics of these films using toluene – heptane (50/50) mixtures were analysed and then compared. Mechanical properties such as tensile strength, abrasion resistance and hardness values were compared for composites with different CNT loading. AFM, TEM, FTIR and Raman study was performed to evaluate the morphology and structural characteristics.

2. EXPERIMENTAL SECTION

2.1. Materials

Styrene Butadiene rubber (Synaprene 1502) with a 25% styrene content was used for this study. MWCNT obtained from Nanocyl, Belgium was used as the filler. The diameter of the tubes ranges from 10 to 20 nm and the average length is 1.5 μm . The carbon content of the material is 90% and the rest is metal oxide (impurity). The Ionic Liquid 1-Benzyl-3-methylimidazolium chloride (Fluka Germany) was used as received. The zinc oxide (ZnO), stearic acid, Tetramethylthiuram Disulfide (TMTD), 2, 2' Dibenzothiazyl Disulfide or 2,2'-Dithiobisbenzo Thiazole (MBTS) and Sulphur used in this study were of industrial grades.

2.2. Composite Preparation

Carbon nano tubes were surface modified by ionic liquid by simply grinding both in an agate mortar for 30 minutes. Unfilled and modified CNT filled SBR membranes were prepared. The mixing was done in laboratory scale two roll mixing mill at a nip gap of 1.3 mm and at a friction ratio of 1:1.4. The nip gap (1.3 mm), mill speed ratio (1:1.4), time of mixing (20 min) and temperature (28^oC) of the rolls were kept constant. First rubber was masticated for 2 minutes and then all the ingredients were added one by one and the mixing was completed within 20 minutes. Cure properties of the compounded samples were determined using a Moving Die Rheometer at a temperature of 160^oC. Samples were then moulded to a thin film by using an electrically heated hydraulic press under a pressure of 120 bars at 160^oC. Samples were prepared with different CNT contents and designated as ST₀l₀, ST₁l₁, ST₃l₁, ST₅l₁, ST₇l₁ and ST₁₀l₁.

2.3. Membrane Characterizations

The cure characteristics of the SBR composites were determined with a moving die rheometer (MDR 3000, Mon Tech, Germany) at 160^oC for 30 min. Atomic force microscopy observations were carried out in air on as-received sample surfaces using Agilent 5500 AFM operated in contact mode. Measurements were carried out using standard triangular silicon nitride cantilevers (MSCT from Bruker). Topography, deflection and friction data were collected simultaneously. The images were taken at 512 x 512 pixels resolution. The morphology of the composites was analysed by TEM (JEM-2100HRTEM). The cryocut specimens prepared using an ultra-microtome (Leica, Ultra cut UCT) were placed on a 300 mesh Cu grids (35 mm diameter) and were analysed. The transmission electron microscope was operated at an accelerating voltage of 200 kV. Stress–strain tests were performed with a universal material testing machine (Zwick model 1435) with a crosshead speed of 500 mm min⁻¹ according to the standard PN-ISO 37-2005

2.4. Pervaporation Studies

The permeation cell is assembled from two half cells of column couplers made of glass and tightened with locked clamps. The capacity of each cell was about 100 mL and the effective area of the membrane in contact with feed solution was 16.61 cm². The membrane was first swelled in the organic mixture to be separated and then mounted in the cell. The vacuum was then pumped out on the downstream side. Feed solution is introduced into the upper part of membrane which is maintained at atmospheric pressure. The membrane was kept in the pervaporation cell for about 1 h in each run to reach equilibrium conditions before collecting the permeate. Once steady state was reached permeate was collected in traps immersed in liquid nitrogen. The flux was calculated by weighing permeate on a digital microbalance Mettler Toledo (JB1603-C/FACT) with an accuracy ± 0.0001 g. The feed and permeate compositions of all of the mixtures were determined by measuring their refractive indexes with a refractometer. All the experiments were carried out at room temperature and were repeated to obtain reproducible results.

2.5. Pervaporation Characteristics

The pervaporation performance of each membrane can be analysed by calculating separation factor and total flux. The selectivity of membrane was demonstrated by separation factor and defined as [15]

$$\text{Separation factor, } \alpha = \frac{\left(\frac{Y_i}{Y_j}\right)}{\left(\frac{X_i}{X_j}\right)} \quad (1)$$

where, Y_i and Y_j represent the weight fractions of heptane and toluene in permeate and X_i and X_j represent those of heptane and toluene in the feed respectively.

The permeability was evaluated by the normalized flux, J ($\text{Kg m}^{-2} \text{hr}^{-1}$) as defined in Eq. (2) to compare pervaporation performances of membranes [16].

$$J = \frac{Q}{At} \quad (2)$$

where Q , is the quantity in kilograms of permeate collected after a time (t) and A is the effective area of the membrane.

Pervaporation Separation Index was calculated by the following equation, [17]

$$\text{PSI} = Q(\alpha - 1) \quad (3)$$

Component flux [18] for the separation of azeotropic composition of methanol and toluene mixture were calculated by using equation

$$J_{\text{Heptane}} = JX_{\text{Heptane}} \text{ and } J_{\text{Toluene}} = JX_{\text{Toluene}} \quad (4)$$

J_{Heptane} and J_{Toluene} are the component fluxes, J is the flux, X_{Heptane} and mX_{Toluene} are the permeate composition of the mixtures.

3. RESULTS AND DISCUSSION

3.1. Cure Rheographs

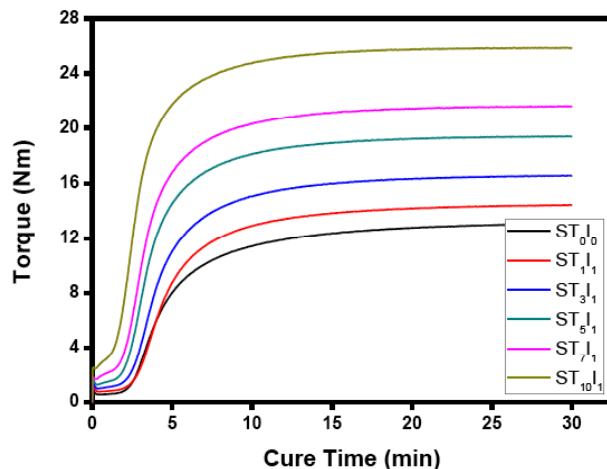


Figure.1: Rheographs of SBR composites.

Vulcanization curves of the neat SBR and SBR-CNT composites are represented in Figure 1. It can be observed that scorch time is decreased by the addition of CNT. The reason for this due to the improvement in the thermal conductivity of the SBR material because the thermal conductivity of the CNTs is 10^4 times greater than that of polymer materials, and thus could promote requirement of vulcanization [19]. Increment of CNT in the SBR matrix has reduced the mobility of the macromolecular chains of the SBR during vulcanization which in turn leads to the increase of torque with filler loading which clearly demonstrated the reinforcing nature of CNT due to the better interaction between ionic liquid modified CNT and rubber. The reason for the shorter cure time of the rubber composite containing ionic liquid modified CNT could be attributed to the increase of thermal transition of SBR in the presence of CNT due to the increased the specific surface area which gradually improves the filler-filler and filler-matrix interactions. Reports were available on the cure acceleration properties of ionic liquid in rubber nanocomposites which eliminates the use of different accelerators in rubber vulcanization [20, 21].

3.2 Mechanics

Table 1: Mechanical Characteristics of Composites

Sample	Tensile Strength (MPa)	Elongation at Break	Tensile Modulus
ST _{0/0}	1.296	145.7	2.58
ST _{1/1}	2.249	143.05	3.04
ST _{3/1}	3.42	132.74	4.106
ST _{5/1}	4.63	123.61	5.633
ST _{7/1}	5.78	116.07	7.432
ST _{10/1}	6.798	106.94	9.362

The tensile strength and young's modulus of the nano composites show higher values compared to the neat SBR. Composites containing 10 phr showed significant improvements in tensile strength (a 424% increase) and modulus (262%) as compared to unfilled rubber. Presence of ionic liquid prevents the aggregation tendency of CNT, and this resulted in a microstructural development which explains the improvement in the mechanical behaviour of filled composites compared to unfilled one [22]. The driving force behind the fine distribution of CNT in the matrix is the cation- π interaction between ionic liquid and CNT. In all cases CNT acts an effective reinforcement which facilitates the efficient load transfer from matrix to

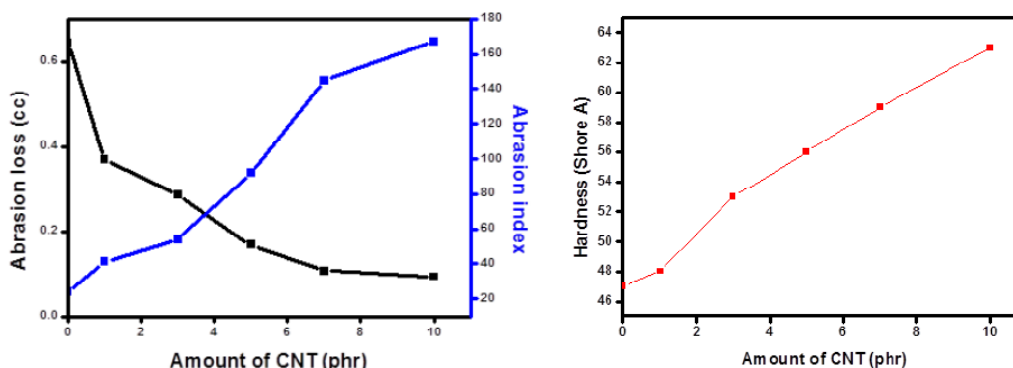


Figure.2: DIN abrasion test results and Shore A hardness of the rubber composites.

dispersed phase. Stronger interactions between modified CNT and polymer molecules associated with larger contact surface result in more effective constraint of the motion of polymer chains. A third phase between polymer matrix and CNT particles with different properties from both primary constituents is much necessary to understand the unexpected improvement in the mechanical behaviour of nano composites. A good interface will restrict the deformation of the polymer and lead to a higher tensile strength [23].

Abrasion resistance of SBR vulcanizates was determined in terms of DIN volume loss. Figure 2 shows DIN volume loss of ionic liquid modified CNT/SBR vulcanizates containing various amount of CNT. DIN volume loss of SBR vulcanizates reduced as filler content increased. Addition of reinforcing fillers (*i.e.*, carbon black) in conventional composites improves abrasion resistance by suppressing tearing of polymer matrix [24]. By incorporating reinforcing nano filler into the rubber matrix, abrasion resistance of unfilled rubber can be increased. The gliding movements of abrasives on a solid composite surface resulted in mass removal and its mechanism depend upon the hardness of the polymer, an important criterion which determines the amount of mass removal. The presence of rigid reinforcing CNT in the matrix increases the effective hardness of the composite, which acts to decrease the amount of mass elimination. There was a gradual increase in hardness value with increase in the CNT loading due to the increased filler- filler and filler-polymer interaction which in turn resulted in the high crosslink density [25, 26].

3.3. Raman Spectroscopy

Raman spectrum of neat SBR rubber is shown in Figures 3. And 4 shows a comparison of the 514.5 nm excited Raman spectra of MWCNTs and SBR/MWCNTs (5 phr). A band at approximately 1350

cm^{-1} in the Raman spectrum of MWCNTs was assigned to the D band which is due to the defects or disorders in the graphitic structure. The G band at 1580 cm^{-1} was attributed to the in-plane vibrations of the graphitic wall. G band for composites is used to investigate the load transfer in nanocomposites and the state of filler dispersion in the polymer matrix [27] Raman spectroscopy is identified to provide information on the structure, crystallinity and ageing of both components of a composite material by the careful evaluation of the associated vibrational features (band frequencies and widths). Variations in CNTs band spectral features have been also suggested as indicators of their dispersion/loading characterization. Several studies have been reported on the characterization of polymer nanocomposites dispersion state based on Raman spectroscopic characterizations. In most of the cases researchers found a shift of G band depending on the concentration of MWCNT. The shifts observed in the Raman bands of CNTs arise from three mechanisms: chemical interaction between CNTs and matrix, such as charge transfer or chemical bonds changes in the tube-tube interactions due to the van der waals force of attraction between individual tubes and mechanical compression from the polymer matrix.

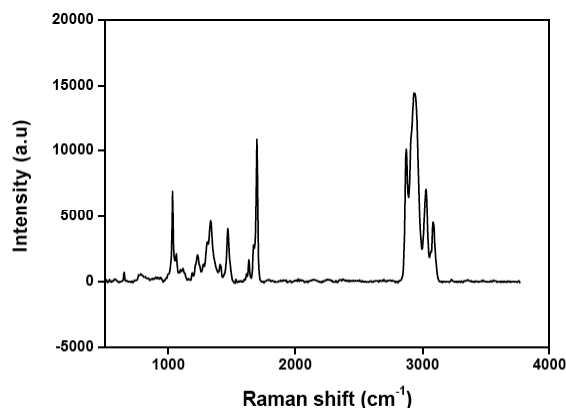


Figure 3: Raman Spectrum of Neat SBR.

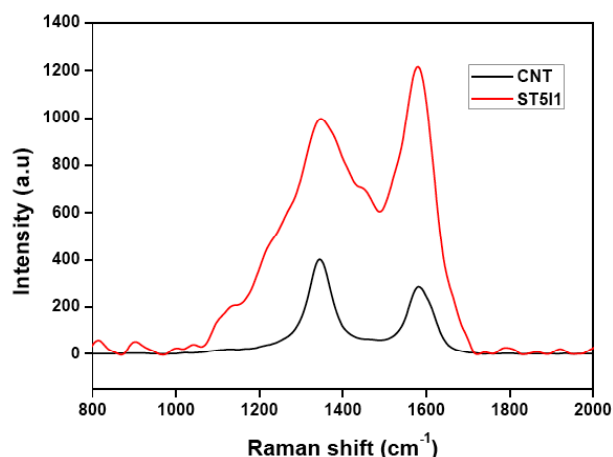


Figure 4: Raman spectra of pristine MWCNTs and the composites containing 5wt% loading of modified CNT.

3.3. FTIR

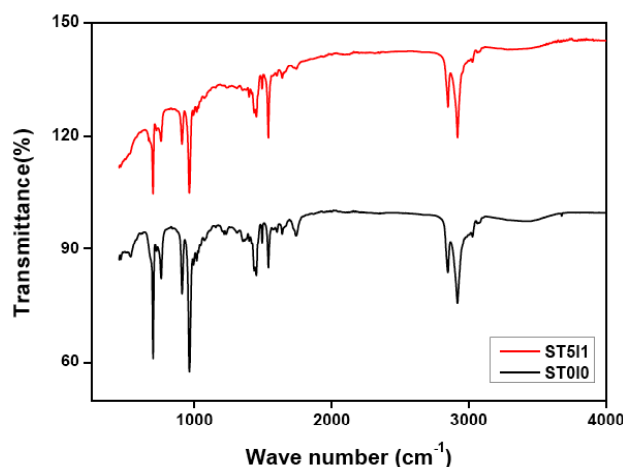


Figure 5: FTIR spectrum of Neat SBR and its composite loaded with 5 phr ionic liquid modified XNT.

From the FTIR spectrum of SBR it is clear that (Figure 5) showed a band at 699 cm^{-1} that is related to 1,4-cis, a band at 910 cm^{-1} to 1,2-vinyl double bonds, and a band at 969 cm^{-1} to 1,4-trans, respectively [28]. From the FTIR analysis it is revealed that there is no

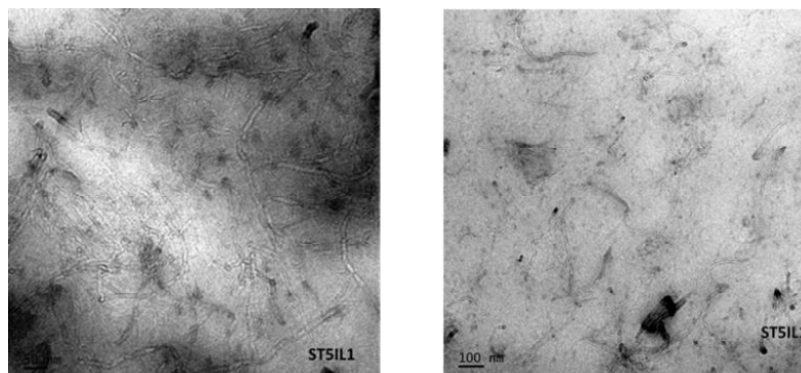


Figure 7: Transmission electron microscopy images of composites containing 5 phr CNT.

such huge variation in the appearance of spectrum of neat rubber and its CNT filled composite except in the intensity of each band. This is due to the secondary interaction between ionic liquid modified CNT and SBR [29].

3.5. Atomic Force Microscopy

The topographic features as well as the phase characteristics of surfaces were investigated using AFM in phase contrast tapping mode. The second image of Figure 6 show that the SBR film surface is thoroughly modified, and the incorporation of nano CNT strongly influences the film morphology. However, the distribution and the dimensions of the heaps/hills are almost homogeneous, indicating a good dispersion of nano CNT in the polymeric matrix.

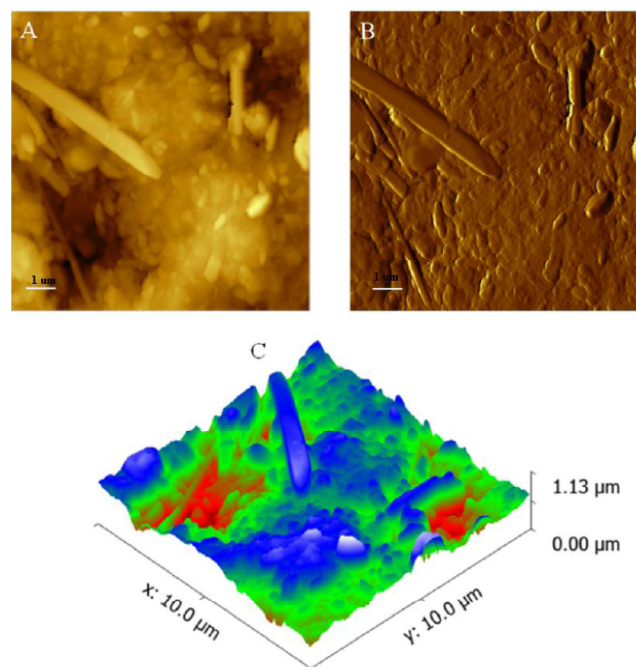


Figure 6: AFM topography (A) and deflection (B) images and the 3D view (C) of the sample with 5 phr CNT.

3.6. Transmission Electron Microscopy

The extent of dispersion of nano fillers in a rubber matrix is one of the most critical parameters which control the overall performance properties of the nanocomposites. Presence of aggregates or agglomeration of filler particles in the rubber matrix leads to stress concentration points resulting in early failure. This shows a substantial dispersion of modified CNT throughout the SBR matrix attributed to the molecular ordering of ionic liquids between individual tubes. It is well known that the shielding effect of ionic liquids on the π - π stacking interaction among MWCNTs takes the key role in dispersing the MWCNTs. The ionic liquids interact with MWCNTs through weak van der Waals interaction.

3.7. Pervaporation of Heptane-Toluene Mixture through SBR/CNT Nanocomposites

3.7.1. Effect of CNT Loading

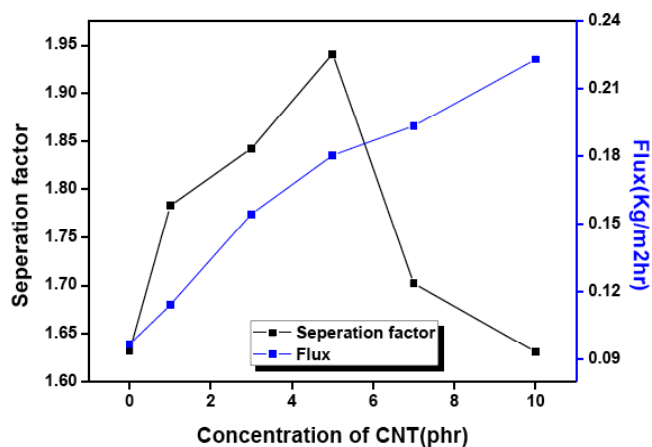


Figure 8: Variation of flux and separation factor with concentration of CNT for the separation of 50/50 composition of toluene/heptane mixture.

Results of the effect of CNT content on flux and separation factor of the membranes are given in Figure 8. As seen from Figure the separation factor of SBR membrane towards heptane was increased after adding CNT into SBR matrix upto 5 phr CNT and then gradually decreased. Membranes containing 5 phr CNT showed maximum heptane selectivity which is about 18% greater than that of unfilled membranes. The increased separation factor is due to the nano level dispersion of CNT in SBR rubber and the increased filler polymer interactions. The sorption and diffusion are considered as then rate-determining step of the mass transfer. The reason behind the high selectivity of

5 phr loaded SBR membrane is that when 5 phr CNT is introduced into SBR bulk, high aspect ratio of CNT and homogeneous distribution make the CNT maximize the possible attachment points with the polymer, that is, the cross linking density of the CNT and SBR chains can be effectively increased. Hence, higher separation factor is obtained. MWCNT could enhance sorption selectivity of SBR membranes towards heptane compared to toluene because membranes became more swollen in toluene which facilitates the retention of large number of heptane molecules on the permeate side as shown in schematic diagram (Figure 11). The overall pervaporation performance of the membranes was calculated using PSI it is shown in Figure 9. Maximum PSI and enrichment factor was shown by SBR membrane with 5 phr CNT due to the nano level dispersion of CNT in SBR with the aid of ionic liquid.

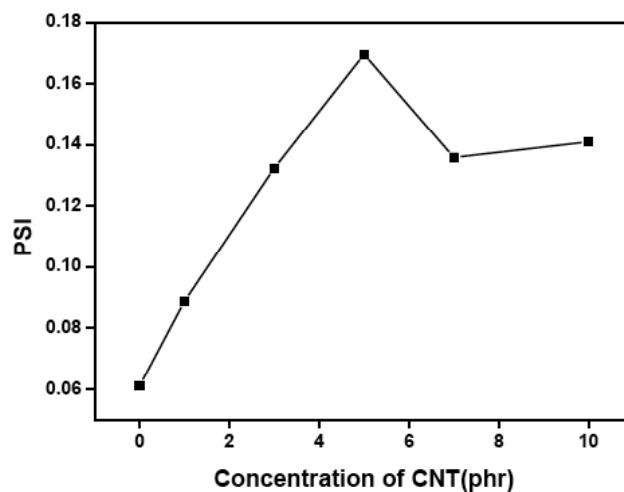


Figure 9: Variation in PSI with the concentration of CNT.

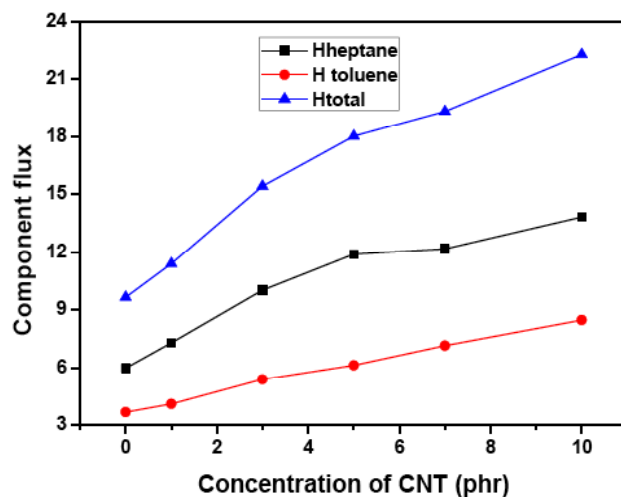


Figure 10: Variation in component flux and total flux with concentration of CNT.

Figure 10 shows the variation in component flux and total flux with filler loading. Total flux and component flux increases with increase in filler loading. Component flux for heptane is more and it is very close to total flux. It indicates the selective transport of heptane through the membrane.

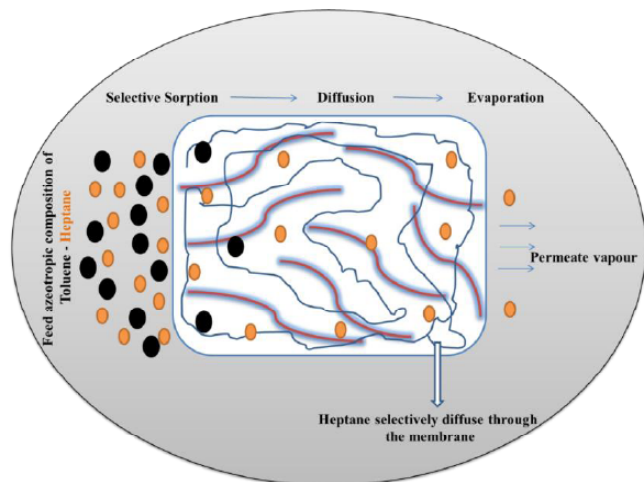


Figure 11: Schematic representation of the mechanism of pervaporation separation of liquid mixtures through CNT network structure.

3.7.2. Effect of Ionic Liquid Aoncentration

Table 2: Effect of Ionic Liquid Concentration on the Pervaporation Characteristics of SBR Membrane

Sample	Flux	Separation Factor	PSI
ST ₅ l ₀	0.1788	1.879	0.1571
ST ₅ l ₁	0.1803	1.941	0.1696
ST ₅ l ₅	.1780	1.900	0.1602

Effect of ionic liquid concentration used for the surface modification on the pervaporation performance of SBR/CNT composites is given in Table 2. From the tabulated values it is clear that there is an optimum concentration for ionic liquid at which membrane performance is maximum. At higher concentration of ionic liquid there is a drop in flux, separation factor and PSI values.

3.7.3. Influence of Feed Composition on Pervaporation

Separation factor increases with increase in concentration of toluene up to a certain concentration of toluene and then decreases. As the concentration of toluene in the feed is increased polymer membrane

became more swollen which helps in the easy passage of small heptane molecules through the membrane there by increasing the heptane selectivity. Flux is gradually increasing with increasing the toluene concentration. At higher loading polymer became more swollen so some toluene molecules are passing to the permeate side along with heptane molecules thereby decreasing separation factor and increasing flux at higher toluene concentration in the feed.

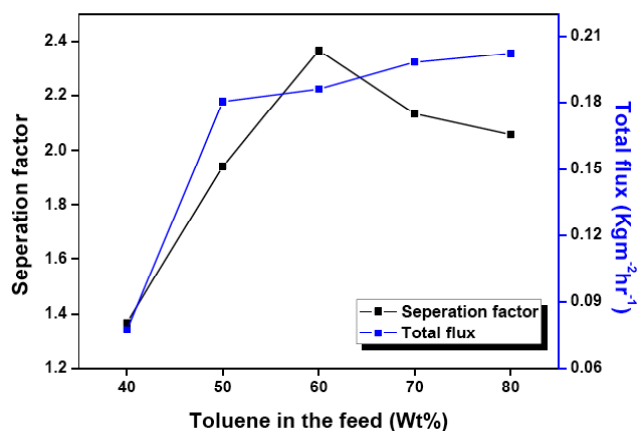


Figure 12: Influence of feed composition on pervaporation.

CONCLUSION

The present work investigated the influence of functionalized MWCNT on the pervaporation and mechanical properties of SBR nanocomposites. In corporation of modified CNT to SBR led to a dramatic improvement in the mechanical characteristics especially tensile strength and modulus of the composites due to the microstructural development and interfacial interaction between CNT and matrix. Raman and AFM analysis supports the microstructure development and role of interface in determining the behaviour of composites in presence of CNT. The pervaporation performances of membranes were analysed using a toluene/heptane mixture. Membranes displayed high selectivity towards heptane. The influence of feed composition on pervaporation was also analysed. The 5 phr CNT loaded membrane showed enhanced membrane permeance and selectivity value. A drop in selectivity and an increase in permeation rate were observed at higher CNT loadings.

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