

## Development and characterization of polyvinyl chloride-graphite membrane

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Graphite dispersed polyvinyl chloride membrane has been prepared by scalable solution blending technique in different compositions. The obtained composite has been characterized by infrared spectroscopy, X-ray diffraction and microscopic techniques. Results reveal the formation of intercalated composite with improved properties like solvent retaining capacity, porosity, swelling capacity, hardness, and tensile strength. Further, ion exchange ability has been determined by ASTM method and observed values are in range  $10^{-1}$  (meq/g), which is comparable to industrial membrane and indicate its suitability for commercial application. Further, durability and mechanical strength is studied and compared with standard membrane, which reveals compatible to the commercially available membrane and confirms suitability for technical applications.

**Keywords:** Polymer composite, Membrane, Ion exchange capacity, Physical properties

Polymer composite based membranes (PM) have been considered an important polymeric structure for gas separation, water purification, filtration and fuel cell. Basic advantages of PM over conventional alternatives include their low cost, stability, better mechanical properties and low energy consumption. Since the polymers are susceptible to high temperature and harsh chemical environments. Therefore, enhancing mechanical and chemical stability of PM in industrial environments is essential. The various steps taken to address this issue like incorporation different filler materials. In this regard many types of filler such as zeolites<sup>1</sup>, heteropolyacids<sup>2</sup>, carbon nanotubes<sup>3</sup>, graphenes<sup>4</sup> and graphite<sup>5</sup>, have been used. Among these fillers, graphite is very important due to its layered structure, conductivity and ability to interact with the polymer matrix. It also enhances the mechanical, electrical and thermal properties of the membrane<sup>6-8</sup>.

Graphite has been extensively utilized as electronically and thermally conducting filler for formulating conductive polymer composites membranes. These membranes have been used in fuel cell as bipolar plates<sup>9-12</sup>, zero-emission power source required in environmentally friendly transportation and stationary applications<sup>13</sup>. The use of graphite imparts notable lubrication behaviour to the polymer matrix since it has a solid, lubricant and anisotropic structure. The different polymer graphite membranes

has been prepared and used for different properties like electrical conductivity, chemical resistance and mechanical strength<sup>14</sup>. However, the optimisation of structure property relationship in graphite polymer is still missing and shall need intensive study. In the light of above development, present work report the preparation of polyvinyl chloride(PVC) and graphite composite membrane with proton exchange capacity and improved performance. The properties of the PVC/graphite composite membranes include thermal stability, mechanical strength, water-uptake, dimensional change, proton conductivity, as well as ion exchange ability were investigated.

### Experimental Section

#### Materials

Graphite powder (200 mesh, SPECKPURE, India), Polyvinyl chloride, Tetrahydrofuran (CDH, India) was used without any further purification. However triple distilled water and analytical grade solvents were used in entire investigation.

#### Preparation of Polymer/Graphite composite membrane

Initially, PVC (2 g) was dissolved in a minimum amount of tetrahydrofuran (THF) at 22°C after stirring on a magnetic stirrer for 40 min. In the resultant solution, different amount of graphite powder was slowly added along with stirring, which was continued for 4 h. The obtained solution was

casted onto a clean glass petri-dish with diameter of 4 inch and allowed to dry in hot air stream until no residual solvent remained. The film was then demolded and obtained membrane was stored in air tight poly bags.

#### Characterizations

The structural and morphological characterization of PVC/graphite composite was done by Fourier transform infrared (FTIR) spectrometer (Bruker alpha model) in ATR mode in 600 to 4000  $\text{cm}^{-1}$  range. The spectra were recorded with an accumulation of 16 scan and resolution of 2  $\text{cm}^{-1}$ . X-ray diffraction (XRD) was performed on Rigaku Rotaflex, RAD/Max-200B for phase characterization using Cu Ka radiation ( $\lambda = 1.5405 \text{ \AA}$ ) generated at 40 KV and 50 mA with scanning rate of 2° per min. The surface morphology and homogeneity were examined by JEOL (USA) scanning electron microscopy (SEM) and optical microscope. The samples were sputter-coated with thin layer of gold prior to analysis to avoid charge accumulation in SEM analysis. Further, mechanical properties (water uptake, ion exchange capacity) were tested as reported ASTM methods<sup>15</sup>.

#### Water uptake (WU)

The membranes in completely dried state weighed using microbalance (Sartorius, sensitivity of 1  $\mu\text{g}$  mass capacity). Water uptake capacity measurement was carried out by weight of the membranes (0.2-0.3g/sheet) in dry state (dried in vacuum oven at 100 °C for 24 h) and after immersing in deionized water at room temperature for 20 h. Then the membranes were taken out and wiped with tissue paper and quickly weighed over a microbalance. The WU was calculated by Eq. (1):

$$\text{WU (\%)} = (\text{W}_s - \text{W}_o) / \text{W}_o \times 100 \quad \dots (1)$$

Where  $\text{W}_s$  and  $\text{W}_o$  refer to the weight of the wet and dry membranes respectively.

#### Ion Exchange Capacity (IEC)

IEC was measured by well-known volumetric titration. The membranes were carefully washed with deionized water for many times, dried and were soaked in 0.1 M NaCl solution for 18-20 h. The protons released due to exchange reaction with  $\text{Na}^+$  ions were titrated against 0.01M NaOH solution by using phenolphthalein as an indicator. The IEC was determined from the following Eq (2):

$$\text{IEC (meq/g)} = X \times (\text{N/W}) \quad \dots (1)$$

where X is the volume of the NaOH consumed in mL and N is the normality of NaOH solution and W is weight of membrane in g.

#### Electrical conductivity ( $\sigma$ )

The electrical conductivity of membranes was measured by two probe method using Rish max multimeter. A sheet of composite membrane (1 cm  $\times$  1 cm  $\times$  0.5 mm) cut from surgical blade and electrical contacts were made on a pair of opposite edges by applying silver paste. Finally, the membrane was placed in controlled humidity chamber and multimeter was connected at silver paste through clamp. Electrical conductivity ( $\sigma$ ) was calculated from the following Eq (3):

$$\Sigma (\text{S/cm}) = 1/\Omega \times d/A \quad \dots (3)$$

where d is the distance between the electrodes and A,  $\Omega$  are the area and resistance of the composite membranes respectively.

## Results and Discussion

#### Preparation and characterizations

The composite film was prepared by solution blending method. The observed parameters during dissolution are given in Table 1. The observed data indicate that the presence of graphite facilitates the miscibility, because the interaction between PVC and graphite is exothermic in nature which supports the facilitated dispersion of graphite in PVC matrix. A tentative scheme is shown in Fig. 1.

The optical photograph of PVC and graphite PVC composites are shown in Fig. 2, which indicates that the maximum dispersion is feasible upto 15 phr after that aggregates of graphite are found.

The morphology of graphite/composite membranes was probed by SEM and the micrographs are shown in Fig. 3. Figure 3a is indicating flakes like structure of graphite, while Fig. 3b indicates the formation of binary structure types in the composite with graphite flakes were dispersed in PVC matrix. The comparison in size of graphite indicates the sharp reduction in size. It is because the matrix interaction reduces the size of graphite.

The structures of the graphite/PVC composites were studied by FTIR spectra and graph in shown in

Sample	Time for completion (min)	Change in temperature (°C)
PVC	19	2.8
PVC-Graphite	23	1.7

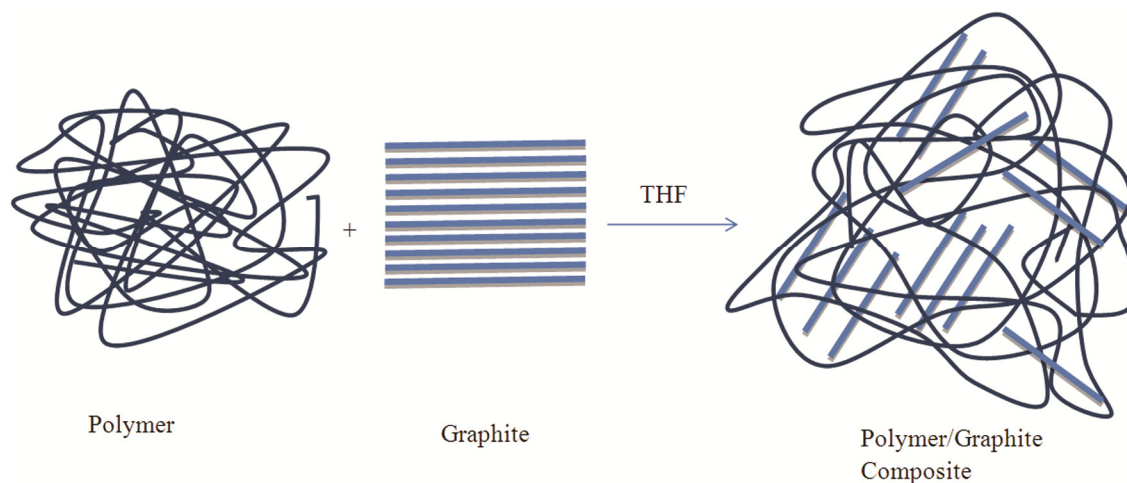


Fig. 1 — Dispersion mechanism of PVC/graphite composite

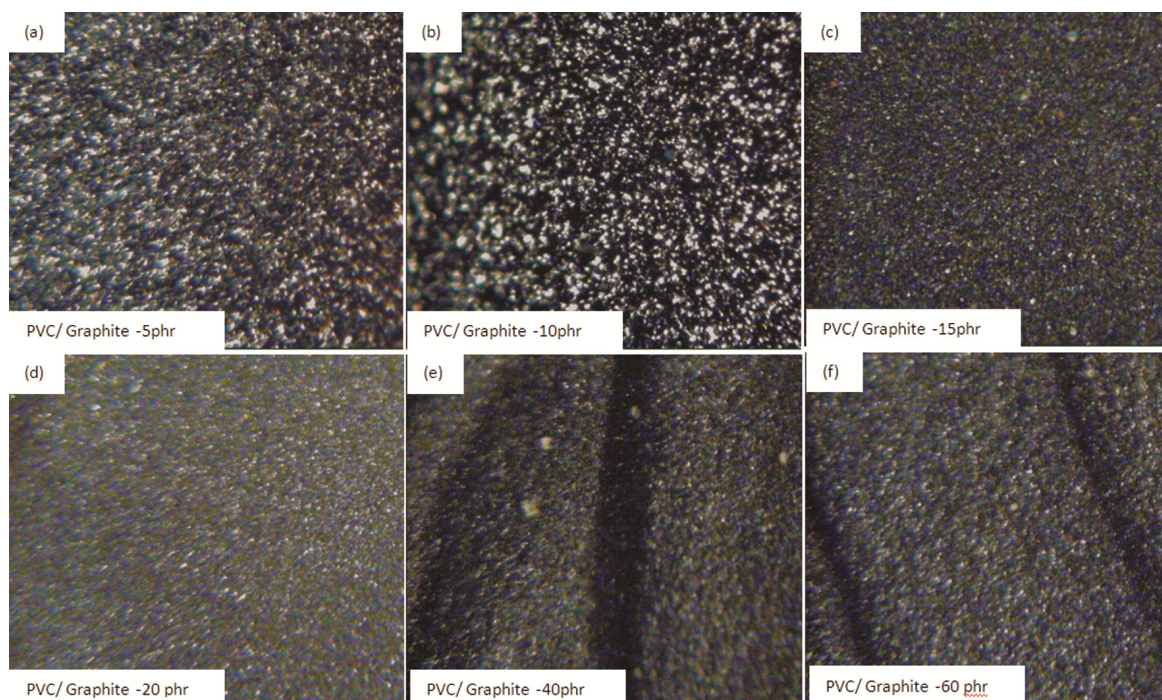


Fig. 2 — Optical microscopic pictures of PVC/graphite composite membrane at (a) 5 phr (b) 10 phr (c) 15 phr (d) 20 phr (e) 40 phr (f) 60 phr

Fig. 4. The spectra of composite show the characteristic bands of both graphite and PVC. The peaks at  $740, 677, 635 \text{ cm}^{-1}$  are characteristic of  $\text{C-Cl}_{\text{stretching}}$  which is not present in graphite but present in composite clearly give the confirmation for its synthesis,  $1350\text{-}1480 \text{ cm}^{-1}$  bands are characteristic of alkane  $\text{C-H}_{\text{stretching}}$ ,  $1600\text{-}1680 \text{ cm}^{-1}$  bands are characteristic of  $\text{C=C}_{\text{stretching}}$  of graphite rings,  $2850\text{-}3000 \text{ cm}^{-1}$  bands are characteristic  $\text{C-H}_{\text{stretching}}$  of alkane in PVC.

XRD spectrum of graphite/PVC composite is shown in Fig. 5. The Fig. 5 of composite film is indicating the red shift in the peak of graphite which indicates the expansion in the PVC matrix due to intercalation of graphite.

#### Physical characteristics of membrane

The physical properties of PVC and composites are given in Table 2.

The result indicates that the properties change due to addition of graphite in PVC and also depends on

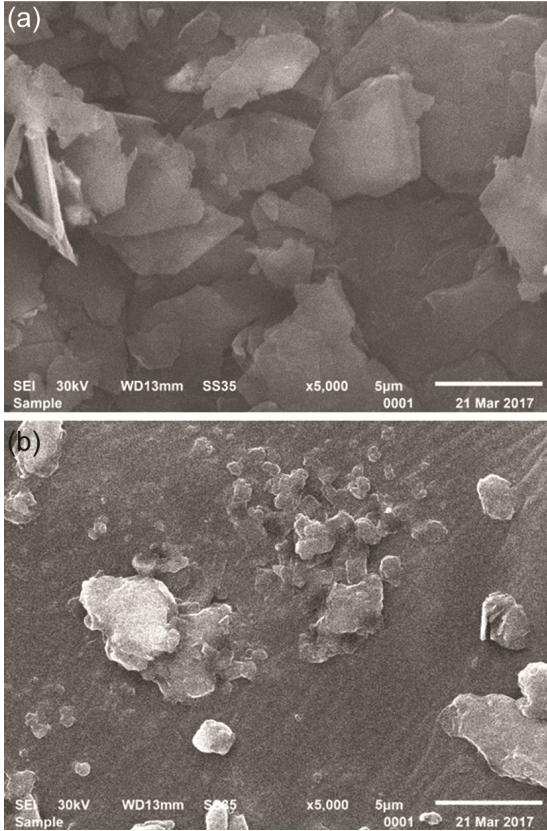


Fig. 3 — SEM image of pure (a) PVC (b) PVC- graphite (15%) composite

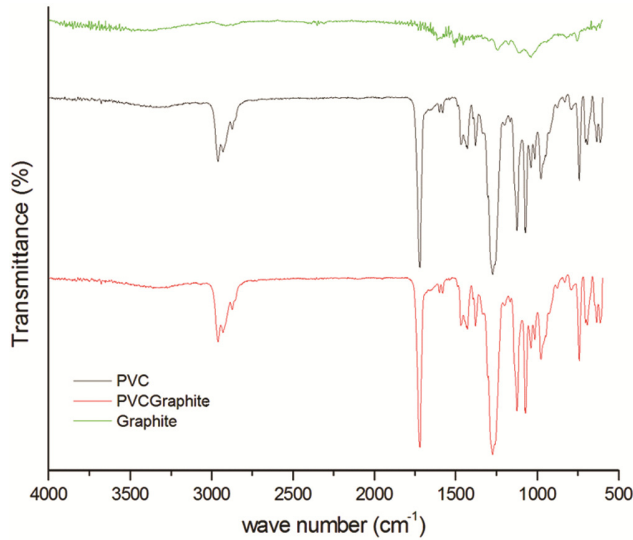


Fig. 4 — FT-IR spectra of PVC – graphite composite

the amount of graphite. The swelling behaviour and dimensional flexibility indicates that the graphite reduces the cross linking in PVC chain, which is responsible for electrical conductivity.

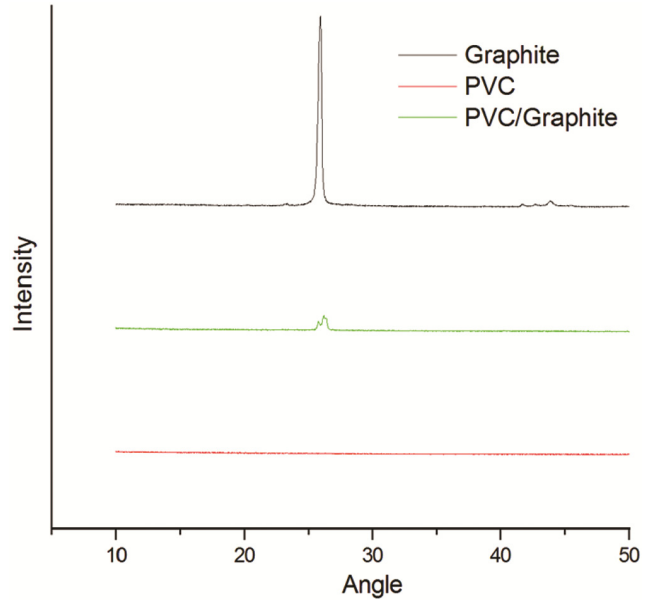


Fig. 5 — XRD spectra of graphite, PVC and graphite/PVC composite

Table 2 — Physico-chemical properties of the membranes

Name	Hardness (shore-A)	Solvent Content (%)	Porosity
Pure PVC	23	3.63	0.050
PVC-Graphite (5 phr)	24.5	3.39	0.024
PVC-Graphite (10 phr)	10	5.1	0.058
PVC-Graphite (15 phr)	15	5.5	0.034
PVC-Graphite (20 phr)	20	2.1	0.024
PVC-Graphite (40 phr)	21	2.9	0.028
PVC-Graphite (60 phr)	22	4.15	0.052

**Electrical and proton conductivity**

To further understand the functions of graphite in proton transfer, the proton conductivities of the membranes were measured at various RH conditions at 80°C, as shown in Table 3.

As expected, the composite membranes exhibit higher proton conductivities over the entire RH range than the pristine polymer. The pristine polymer membrane only displays a low conductivity, which is considered unsatisfactory for the fuel cell operation under medium or low RH states. The proton conductivities dramatically increase in the membranes containing graphite. Notably, the polymer/graphite composite 15 phr displays a high proton conductivity of  $1.72 \times 10^{-7} \text{ S cm}^{-1}$  under 50% RH, which is almost

Table 3 — Electrical conductivity and ion exchange capacity of the membranes

Name	$\sigma$ (S $\text{cm}^{-1}$ )			IEC (mequiv/g)
	RT (22 °C)	50 % RH	95% RH	
Pure PVC	-	-	-	0.032
PVC-graphite (5 phr)	-	-	-	0.0251
PVC-graphite (10 phr)	-	-	-	0.028
PVC-graphite (15 phr)	$7 \times 10^{-8}$	$1.72 \times 10^{-7}$	$2.38 \times 10^{-7}$	0.059
PVC-graphite (20 phr)	$7.3 \times 10^{-8}$	$1 \times 10^{-7}$	$1.1 \times 10^{-7}$	0.067
PVC-graphite (40 phr)	$6.99 \times 10^{-7}$	$1 \times 10^{-6}$	$4 \times 10^{-6}$	0.073
PVC-graphite (60 phr)	$1 \times 10^{-6}$	$8.5 \times 10^{-6}$	$2 \times 10^{-5}$	0.080

$10^7$ -  $10^8$  times<sup>16</sup> higher than the polymer control membrane. Due to the presence of polar groups in PVC, it allows the homogeneous dispersion of graphite layers producing high conductivity in composites. Although, they have similar IEC values in the range of  $10^{-1}$  mequiv/g. PVC/Graphite membranes are far economical than other commercially available membranes in industrial applications. So, it indicates its suitability for commercial application.

### Conclusion

PVC/graphite composite membranes are prepared by incorporation of graphite as fillers in solution method. The composite membranes also exhibited improved mechanical strength, proton conductivity. It is because, graphite effectively lowers the proton transfer barrier, all the composite membranes showed better proton conductivities than the pristine

polymers. Also PVC/Graphite membranes have potent application as ion exchange membrane which is economical for many industrial applications. So, PVC/graphite composite membrane indicates its potential in practical fuel cell applications as the substitute of commercial membrane.

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