

Novel functionalized graphene enhanced membranes for drinking water and waste water treatment

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ABSTRACT

Currently a variety of membranes are commercially available for both drinking water and wastewater treatment, where application of polymeric membranes is one of the most popular treatment methods. Polyvinylidene fluoride (PVDF) membranes exhibit high mechanical strength, thermal stability, chemical resistance and superior antifouling properties in comparison to other available polymeric membranes. This work focused on modification of PVDF membranes using raw and functionalized graphene. A range of graphene concentrations and their effect on the membrane properties can be investigated; in current article only 2% wt graphene membranes were studied. The membranes were manufactured via the phase inversion method. The resulting membranes were first characterized using a number of techniques such as SEM, FTIR, contact angle and mechanical stress-strain testing. Majority of changes within the modified membranes can be accredited to good interactions between the graphene and PVDF polymer, where oxygen functionalised graphene showed the most change due to superior dispersion and stability within the membrane matrix. The addition of graphene introduced changes in membrane pore network and structure, producing a more porous membrane with larger pores. By addition of graphene to the membrane matrix, it increased the oxygen containing groups on membrane surface giving rise to superior hydrophilic character compared to pure PVDF membrane. Thus, enhanced hydrophilicity of the graphene membranes resulted in raised antifouling ability of the membranes. The enlargement of pores, more porous membrane structure and improved hydrophilicity benefited membrane's pure water permeation and flux performance. In comparison to pure PVDF membrane, the improvement in flux was 51.3% for GNP-R and 91.3% for GNP-O membranes. Mechanical strength data also showed drastic improvement in Young's modulus, producing modified membranes with superior resistance to elongation.

1. Introduction

According to a recent fact sheet by The World Health Organisation [1] half of the world population will be living within water-stressed areas by the year 2025. Compared to

data collected in 2015, approximately 71% of the world population had access to safe and easily-reached drinking water. This drastic change in water availability is believed to be due to growing population which in turn leads to rise in use of water for food production, household and industrial purposes as well as increase in water quality degradation and contamination [2]. Over the years, the water pollution and poor water quality issues have been dealt with using reliable and effective technologies available at the time. Whilst some of the old technologies still in use there is growing need for novel more cost efficient and effective technologies.

One of the most commonly used methods for water purification is membrane technology. Currently, a variety of membranes are commercially available for both drinking water and wastewater treatment, where ceramic and polymeric membranes are the most widely applied. Although ceramic membranes are very effective, polymeric membranes tend to be more preferable due to their flexibility, ubiquity and low cost [3]. However, they are not protected from drawbacks such as subjectivity to mechanical damage, hydrophobicity, poor chemical resistance and antifouling properties [4]. Polyvinylidene fluoride (PVDF) membranes have gained popularity in the recent years due to their high thermal and chemical stability, mechanical strength and satisfactory antifouling ability in comparison to other commercially available polymeric membranes [3]. However, the PVDF membranes suffer from high hydrophobicity, fouling and absorption of organics, surface roughness and low surface energy [5]. Therefore modification of membrane is essential to overcome these problems and achieve production of more efficient membranes. Three different approaches can be applied for membrane modification: modification during membrane synthesis and formation process, change the application parameters of the membrane and post-synthesis modification of membrane [6]. Most common membrane modifications involve incorporation of additives to the membrane mixture or modification of membrane surface via grafting or surface deposition of molecules [7, 8].

In current work, the PVDF membranes are modified by blending graphene nanoparticles in the polymer matrix with following membrane production via phase inversion method. Zhao et al [9] used this technique to produce graphene oxide enhanced PVDF membranes. Their resulting membranes showed improved pure water permeability, minimised biofouling and reduced cleaning frequency in comparison to pristine PVDF membranes. Another example of similar work has been carried out by Whang et al [10], where graphene oxide was also used to enhance PVDF membranes. Their work suggested that the graphene oxide improved hydrophilicity of the membrane which resulted in higher pure water permeation and fluxes. It was also mentioned that the graphene oxide affected the membrane structure increasing the sublayer pore size as well as improvement in mechanical strength and antifouling ability.

In this article, raw graphene nanoplatelets (GNP-R) and oxygen functionalised graphene nanoplatelets (GNP-O) were used to successfully manufacture PVDF membranes using phase inversion method. The membranes were characterised by a number of techniques such as SEM, EDS, XPS, FTIR and mechanical strength. To evaluate the membrane performance, pure water permeation, flux and antifouling properties were investigated intensively through comparison with a pristine PVDF membrane.

2. Experimental

2.1. Materials

PVDF Kynar polymer powder used for membrane manufacturing was kindly supplied by Arkema Group (France). Graphene nanoplatelets (GNPs) have been provided by Haydale Ltd (UK) and used as membrane enhancing additives. N-methyl-2-pyrrolidone (NMP) 99% pure Arcos Organics was purchased from Fisher Scientific (UK). The humic acid technical grade was purchased from Sigma Aldrich (UK). For membrane support non-woven fabric have been used and purchased from CraneMat CU632 Neenah Technical Materials (USA).

2.2. Membrane preparation

The membrane preparation method was chosen to be phase inversion because of its simplicity and low production cost [3]. Firstly, lose PVDF powder was dried for 24hr in an oven at 105°C in order to remove any moisture trapped within the polymer. For manufacturing of pure PVDF membranes the dry PVDF powder was dissolved in N-Methyl-2-pyrrolidone (NMP) without any additives. In case of graphene modified membranes the graphene nanoplatelets were first dispersed in NMP and sonicated in an ultrasonic bath FB15047 Fisherbrand (UK) with ice for 3hr to break down graphene agglomerates and improve dispersion in the solvent. The PVDF-NMP (G-NMP) mixture is then stirred for 3 hours using mechanical stirrer while maintaining mixture temperature at 60°C in a water bath. After 3 hours the dissolved polymer solution was sonicated in an ultrasonic bath to remove any bubbles within the mixture and cooled to 20 ±1°C using an ice bath. The membrane was then cast using casting blade with controlled casting thickness on a sheet of glass. The glass sheet containing the cast membrane was immersed in 20L deionised water bath at room temperature for 2 hours to ensure complete solvent-non-solvent displacement. The percentage of graphene was set in this study to 2 wt %.

2.3. Membrane Characterisation

Scanning electron microscopy is often used for structural characterisation of membranes using high resolution imaging of near atomic scale dimensions. JEOL 7800F Field Emission Gun Scanning Electron Microscope (FEG SEM) (USA) was used to provide close up images of the surface and cross section of the membranes. For surface analysis the membranes were dried, and sputter coated with Au/Pd layer (nm) to reduce surface charging during the imaging. The samples cross section images of the membranes were prepared via freeze fracture method using liquid nitrogen and coated with Au/Pd using the same sputter coating technique as for SEM surface analysis.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to produce detailed analysis of types of bonding present within the samples. Perkin Elmer UATR Two ATR-FTIR (UK) was used to obtain spectra from the dried membrane and graphene samples.

Hydrophilicity of the membranes can be evaluated by measuring contact angles using sessile drop method. VCA optima contact angle instrument (USA) was used, where a single drop of deionised water was placed on membrane surface and captured by a

camera. VCA optima software analyses the image and determines the value of the contact angle.

Tensile strength and elongation at the break have been measured for the pure and modified membranes using the HT Hounsfield test equipment (UK). The mechanical testing was performed on dry membrane samples 50mm in length at room temperature with strain rate of 10mm/min.

2.4. Membrane Performance

2.4.1. Pure water flux

Membrane performance was tested by measuring permeation of deionised water through the membrane using a cross flow filtration unit (CFU). The CFU operation conditions were set at room temperature, water flow 1L/min and transmembrane pressure 4.0 bar. Prior to testing, the membrane unit was assembled using a non-woven fabric support and a circular 36 mm in diameter (active area of 10 cm²) membrane. The permeate was collected over 20 minutes and recorded every 10 seconds using an electronic balance interfaced with a PC. The pure water fluxes of the membranes were calculated using following equation:

$$(1) \quad J_w = \frac{V}{A \times \Delta t}$$

Where J_w is the pure water flux, V is the permeate volume (L), A is the membrane area (m²), and Δt is the experiment length (h). The pure water permeation was calculated by dividing J_w pure water flux by the transmembrane pressure.

2.5. Membrane fouling

Dead end filtration set up was used to investigate the anti-fouling efficiency of the membranes. The fouling medium was chosen to be the humic acid solution at 1 g/L concentration and pH 6. The tests were performed at set pressure 3.5 bar, room temperature and experiment length of 120 minutes. The permeate was collected and mass recorded using an electronic balance interfaced with a PC.

3. RESULTS

3.1. Membrane morphology

Membrane surface and cross section images can be seen in Figures 2 and 3 respectively. All of the membranes are of typical asymmetric porous structure with a thin top skin layer and a finger like porous sublayer. This can be supported by the data presented in Figure 3 where it can be suggested that the pores are enlarged with addition of graphene. This rise in pore size can be explained by the interactions between the PVDF polymer and the graphene nanoplatelets.

The oxygen containing groups on the graphene surface give rise to improved hydrophilicity. Thus increases the mass transfer rate of solvent-non solvent displacement during membrane manufacturing which in turn directly affects the membrane microstructure and formation of the pores [11]. It can be noted that the effect is even greater with the GNP-O PVDF membranes, where the pores appear to be further enlarged. By introducing a larger number of oxygen containing groups the dispersion stability of the graphene in NMP increased and therefore improved the

dispersion stability in the polymer mixture prior membrane casting [12]. This in turn enhances the interactions between the polymer and graphene producing more porous membrane structure with larger size pores.

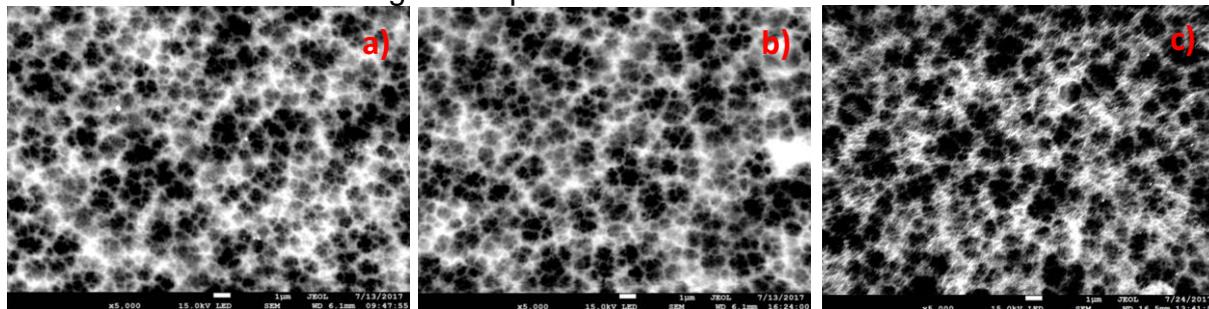


Figure 1. Surface images a) Pure PVDF, b) GNP-R PVDF c) GNP-O PVDF (5,000X magnification, WD 6.1, voltage 15kV)

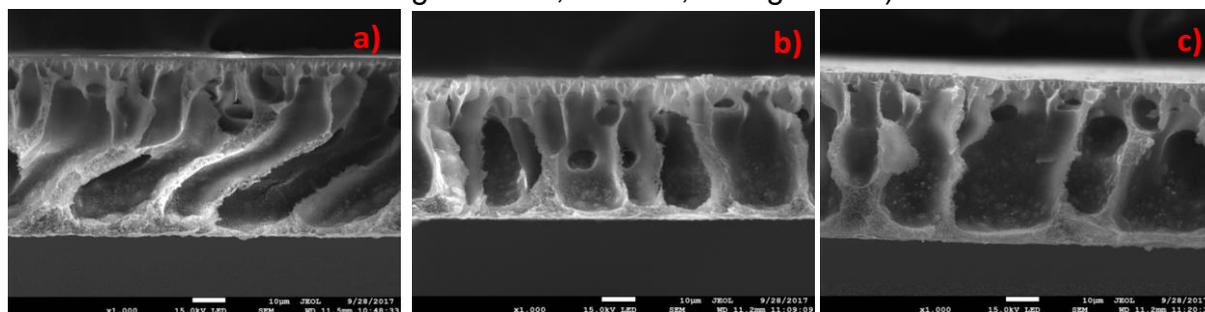


Figure 2. Cross section a) Pure PVDF, b) GNP-R PVDF c) GNP-O PVDF (1,000X magnification, WD 11.2-11.5, voltage 15.0 kV).

3.2. FTIR

Figure 6 shows FTIR spectra of pure and graphene modified membranes. The membranes have a number of peaks in common such as C-O stretching at 1076 cm^{-1} , while the $1120\text{-}1280\text{ cm}^{-1}$ and 1400 cm^{-1} can be attributed to the -CF₂- and C-F vibrational stretching within the PVDF polymer molecule. Apart from these peaks the graphene enhanced membranes also contain an additional absorption peak at 1670 cm^{-1} which corresponds to C=C bond of graphene.

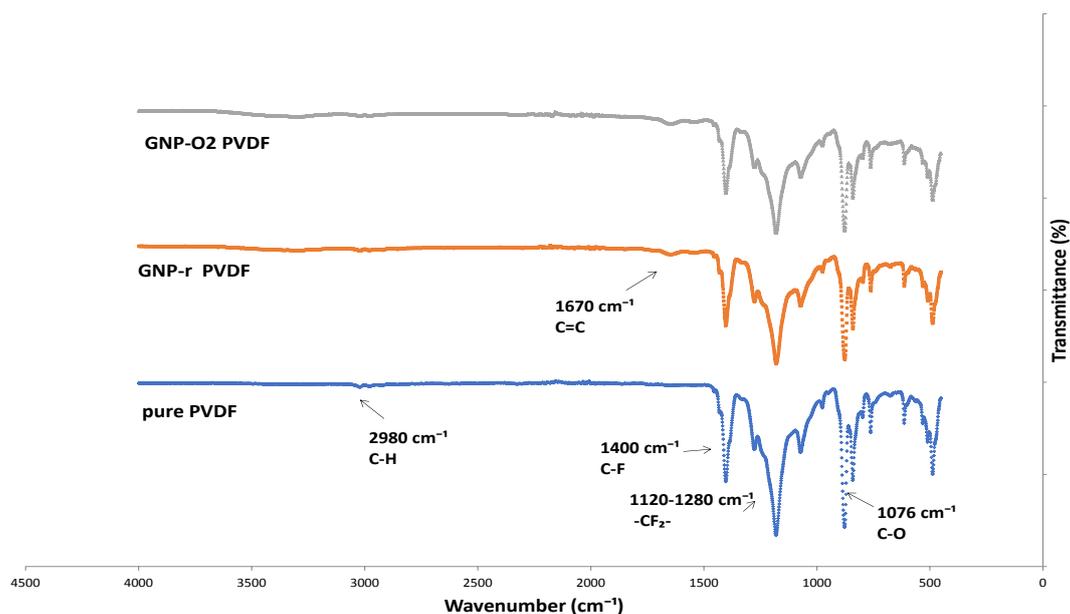


Figure 3. FTIR spectra of pure and graphene modified membranes

3.3. Contact angle

Membrane surface hydrophilicity was measured by the means of contact angle. It is generally accepted that the higher the contact angle the lower is the surface hydrophilicity [9]. From Figure 7 it can be seen that pure PVDF membrane exhibits the highest contact angle and therefore highest hydrophobicity out of the three membranes tested. With addition of graphene, the contact angle drops from $75.6 \pm 1.6^\circ$ for pure PVDF to $71.3 \pm 1.4^\circ$ for raw graphene and to $68.6 \pm 1.3^\circ$ for oxygen functionalised graphene membranes. This indicates that addition of graphene dramatically increases the membrane hydrophilicity due to the oxygen containing groups on the surface of the graphene sheets. Higher hydrophilicity benefits the membranes in many different ways such as resulting in improved water permeation and reduced fouling.

3.4. Mechanical strength

Membrane mechanical strength was evaluated via measurement of Young's modulus. The data shows that the Young' modulus of the membranes changed from 98.3 ± 2.6 MPa to 141.7 ± 12.7 MPa and then 159.5 ± 3.5 MPa for pure PVDF, GNP-R PVDF and GNP-O PVDF membranes. This indicates that the strength of the membranes increases with incorporation of graphene in the membrane matrix. The effect improved further with oxygen functionalised graphene enhanced membrane which could be due to the improved dispersion stability originating from the oxygen containing groups on graphene surface. This improved the graphene-polymer interaction during membrane preparation.

3.5. Membrane performance

3.5.1. Pure water permeation and flux.

Membrane performance was investigated using pure water permeation and flux testing. Figure 8 shows typical water permeation curves for the manufactured membranes. More data on flux and permeation is included in Table 3.

The permeation data shows substantial improvement in pure water permeability of membranes enhanced with graphene compared to pure PVDF membrane. Where the improvement is 51.3% and 91.3% for GNP-R PVDF and GNP-O PVDF membranes respectively. This improvement can be attributed to the increased porosity, enlargement of pores and fall in contact angle caused by graphene addition to the polymer matrix.

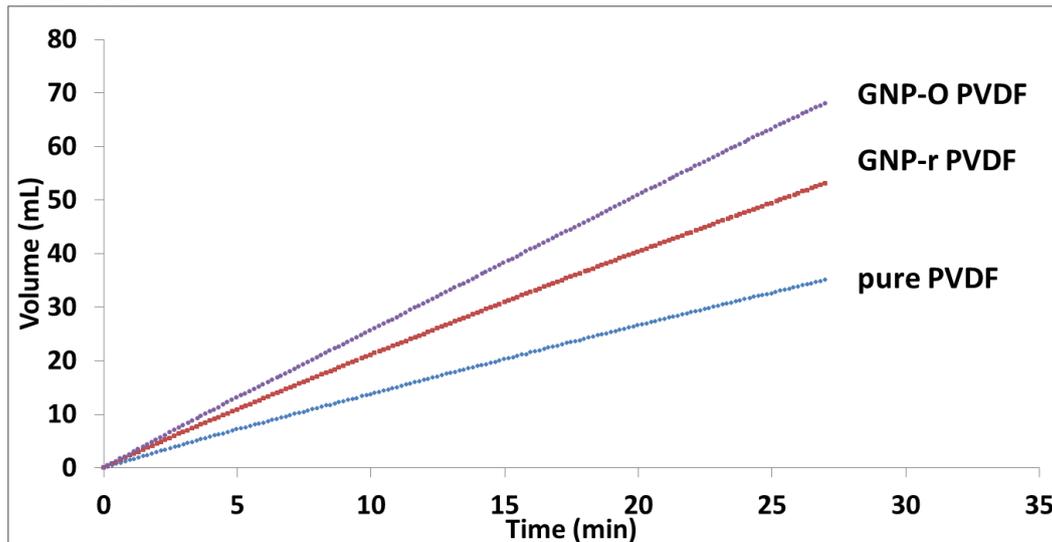


Figure 4. Pure water permeation curves for the pure and graphene modified membranes

Membrane	Flux (L/h.m ²)	Permeation (L/h.m ² /bar)	% increase compared to pure PVDF
Pure PVDF	78.3	19.6	-
GNP-R PVDF	118.5	29.5	51.3
GNP-O PVDF	149.8	37.5	91.3

Table 1. Pure water permeation and flux testing.

3.5.2. Membrane fouling

The ability to accumulate material on membrane surface and in the pores is directly related to anti-fouling efficiency of the membrane. According to Figure 9 the fouling of pure PVDF membrane occurs more rapidly compared to the graphene enhanced membranes. In comparison, GNP-O PVDF membrane has a smoother less rapid fouling with decreased reduction in flux. This data suggest that the degree of fouling of the graphene enhanced membranes is much smaller than of pure PVDF due to improved hydrophilicity of the membrane.

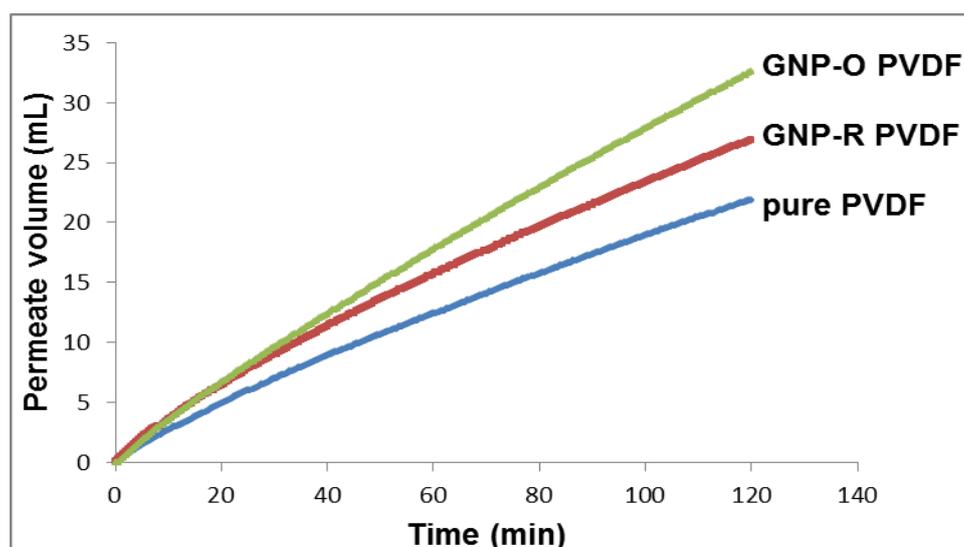


Figure 5. Membrane fouling comparison.

4. CONCLUSION

In this paper, three types of membranes have been successfully prepared: pure PVDF, raw graphene PVDF and oxygen functionalised graphene PVDF via phase inversion method. A number of characterisation techniques were used to investigate membrane morphology, composition and properties.

Addition of graphene nanoplatelets have affected the membrane morphology producing more porous membrane structure with larger pores compared to the pristine PVDF membrane. It was shown that this change could be attributed to the increase in oxygen containing groups on graphene surface. Oxygen containing groups improve dispersion and its stability in membrane mixture which enhances and strengthens the interactions between the graphene and PVDF polymer. As well as dispersion, oxygen containing groups were also suggested to be responsible for the increase in membrane hydrophilicity, dropping from 75.6 ° to 71.3 ° and then to 68.6 ° for pure PVDF, GNP-R PVDF and GNP-O PVDF membranes respectively. This decrease in contact angle was connected to improved anti-fouling ability of the graphene enhanced membranes. The resulting membranes also showed improvement in mechanical strength, where young's modulus increased from 98.4 (± 2.6) MPa to 141.7 (± 12.7) MPa and then to 159.5 (± 3.5) MPa for the pure, GNP-R and GNP-O PVDF membranes respectively.

Enhancement of membrane with graphene materials gave rise to better pure water permeation and flux compared to pristine PVDF membrane, which increased 51.3% for the raw graphene and 91.3% for the oxygen functionalised graphene PVDF membranes. This improvement was suggested to be due to the increase in porosity, pore size and hydrophilicity which originated from the graphene and its interaction with the polymer within the membrane matrix.

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