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Improved antifouling characteristics of acrylonitrile co-polymer membrane by low temperature pulsed ammonia plasma in the treatment of oil–water emulsion

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ABSTRACT

Flat sheet polyacrylonitrile co-polymer membrane was treated by low temperature direct current ammonia plasma to enhance its antifouling characteristics. The surface properties, like, morphology, functional groups and wettability of the membrane were investigated by scanning electron microscopy, fourier transform infrared, X-ray photoelectron spectroscopy and contact angle. Enhancement in membrane hydrophilicity was monitored as function of plasma operating conditions, i.e., duty cycle and treatment time. Nitrogen and oxygen functional groups were identified to be responsible for surface hydrophilicity. The plasma treated membranes were used for separation of oil–water emulsion. It was found that the anti-fouling property of membrane improved remarkably after plasma treatment by enhancement of permeate flux without significant changes in oil rejection.

1. Introduction

One of the widely used materials for ultrafiltration membrane is polyacrylonitrile (PAN) co-polymer owing to its good thermal stability (up to 80 °C) and resistance to many chemicals. Thus, PAN co-polymer membranes have wide application in water treatment, protein purification and juice clarification. Performance of these membranes deteriorates due to fouling associated to the hydrophobic character of PAN. Chemical and physical properties of the surface play an important role in determining the separation and permeation characteristics of membranes [1–3]. Membrane fouling is more pronounced in case of hydrophobic surface due to interactions between the solute and the membrane material [4]. Thus, the surface modification of the membrane to impart more hydrophilicity is an attractive approach to address this issue.

Different methods such as ultra violet irradiation [5], plasma treatment [6,7], gamma irradiation [8], and chemical reaction [9,10] have been employed to modify the membrane surface. Among various surface-modification techniques, low temperature plasma treatment has been regarded as a process with remarkable potential. Plasma treatment is performed to improve wettability, printability, bondability and biocompatibility of the polymer surface [11]. The modification of the top-most surface of the polymer occurs due to hydrogen abstraction and radical formation which in turn leads to the surface activation [12]. Thus it has an advantage of selectively modifying the surface for a specific application while the bulk properties of the polymer remain unaffected [13]. Chemical nature of the plasma gases has strong influence on surface modification reactions. Various gases can be used as plasma, such as argon [14], helium [15], nitrogen [16], ammonia [17], oxygen [11], carbon dioxide [18] and water [19]. The process of ageing or hydrophobic recovery restores the original hydrophobicity of the surface [20–26]. In case of plasma treatment of polymers, this hydrophobic recovery is rapid in the beginning but it gradually slows down with time.

Various studies undertaken for the plasma treatment of different polymeric membranes are summarized in Table 1. A notable improvement in wettability, chemical resistance and water permeability was reported for different polymeric membranes at varied plasma treatment conditions [17,22,27–33]. It can be observed that PAN membranes have been treated with He, N_2, He/H_2O, Ar, He and Air using glow discharge, radio frequency discharge and microwave discharge. Pulsed DC plasma is selected since in this case, the plasma is evenly distributed inside the chamber and it

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Table 1
Surface modification of polymeric membranes using low temperature plasma to reduce their fouling.

Membrane	Plasma medium	Effect of plasma treatment	Performance of modified membranes	Reference
PS	NH_3, NH_3/Ar and 2.45 GHz frequency microwave plasma.	Etching of membrane surface layer and formation of nitrogen and oxygen containing functional groups on the polymer surface	BSA filtration; Performance of NH_3 plasma modified membranes was greatly improved.	[17]
PES	N_2, NH_3, Ar/NH_3, and O_2/NH_3	Degradation of polymer macro-molecules, etching of surface layer	An increase in surface wettability and reduction in protein fouling.	[22]
PP	NH_3 plasma treatment	Formation of nitrogen containing polar groups in the surface layer	An increase in surface wettability and modified membranes exhibited better flux recovery after cleaning than control membranes.	[27]
PP	NH_3, 13.56 MHz RF plasma	Formation of $-NH_2$ groups	An increase in surface wettability and antifouling properties were improved for plasma-treated membranes	[28]
PVC	Air, DC discharge	Etching of surface layer, formation of COOH groups	An increase in surface wettability and water permeability	[29]
PAN, PS	Air, 2.45 GHz microwave discharge	Etching of membrane surface layer and pore surface, formation of oxygen containing groups	An increase in surface wettability and water permeability	[30]
PAN	He, He/H_2O, 20 kHz glow discharge	Cyclization of PAN surface layer	Enhancement of chemical resistance	[31]
PAN	Ar, He, 13.56 MHz RF discharge	Degradation of polymer macro-molecules, etching of surface layer	An increase in surface wettability and water permeability	[32]
PAN co-polymer	N_2, pulsed DC plasma	Etching of surface, formation of nitrogen containing polar groups	An increase in surface wettability and water permeability Ageing effect for 50 days is studied	[33]
PAN co-polymer	NH_3, pulsed DC plasma	Formation of nitrogen containing polar groups	An increase in surface wettability and antifouling properties were improved for plasma-treated membranes Ageing effect for 100 days is studied	This work

Note: PAN: polyacrylonitrile, PVC: polyvinyl chloride, PS: polysulfone, PP: polypropylene polymer and PES: poly ether sulfone.

operates at lower temperature and less gas breakdown voltage providing good functionalization rates [34]. In our previous work, we described the effect of pulsed direct current nitrogen plasma treatment on PAN co-polymer membrane [33]. It was observed that nitrogen plasma treatment leads to significant weight loss due to etching of the top surface causing pore enlargement. As a consequence of this, the plasma treated membranes could not be used for many filtration applications. In the present study we attempt to reduce membrane etching significantly and improve surface wettability by pulsed direct current (DC) ammonia plasma treatment. Pulsed DC instead of continuous discharge was selected due to two reasons. Firstly, pulsed plasma has much higher power during each pulse compared to continuously operated plasma and it provides an off-time during each pulsed wave so that electrical charging or arcing can be avoided. Secondly, pulsed DC prevents charge-induced damage and etch profile distortion as well as it minimizes the average heat load on the substrate surface by using a suitable low duty cycle, which are associated with continuous discharges [35–37]. To the best of our knowledge, no work has been reported for studying the effect of DC ammonia plasma on PAN co-polymer membranes for increasing its hydrophilicity. The membranes were characterized for surface wettability, morphology and surface chemistry. The primary objective of this study is to investigate the effects of low-temperature ammonia plasma on membrane fouling during the filtration of oil water emulsion.

2. Experimental details

2.1. Membrane preparation

The procedure for casting of PAN co-polymer membranes has been described briefly in our previous work [33]. 15% PAN co-polymer (copolymer of acrylonitrile, methyl acrylate and methacrylic acid in ratio 96:3:1, 100 kDa molecular weight, obtained from M/s, Technorbital Advanced Materials Ltd., Kanpur, India) was added in 85% dimethyl formamide (DMF, obtained from M/s, Merck India Ltd.), and dissolved at 60 °C. Complete dissolution of the polymer was obtained by stirring the solution for at least 12 h and then the solution was kept undisturbed for the next 12 h at room temperature to ensure removal of air bubbles from the solution. This solution was then drawn down the fabric attached to glass (non-woven polyester fabric, thickness 118 ± 22.8 μm, product number TNW006013, supplied by M/s, Hollytex Inc., New York, USA) using a casting knife with an adjustable thickness fixed at 200 μm. Final membrane was obtained via non-solvent induced phase separation by immersing the composite in a precipitation bath containing distilled water at room temperature for 10 min followed by immersion in fresh distilled water for 24 h yielding the final membranes which are ready to be tested.

2.2. Plasma treatment

Membranes were cut in 6 cm × 6 cm, cleaned by distilled water for 5 min and then dried in hot air oven for 5 min at 40 °C. Dried samples were fed in the chamber of plasma enhanced chemical vapour deposition reactor (PECVD) (model 1A[S] supplied by Milman Thin Film Systems, Pune, India). A schematic of the PECVD reactor used for the treatment of membrane is shown in Fig. 1. DC ammonia cold plasma was used for this process.

Vacuum (0.1 Pa) was introduced in the reactor chamber and then operated at a constant pressure 12 Pa. Ammonia gas was introduced into the chamber through mass flow controller at a flow