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Modification methods of polyethersulfone membranes for minimizing fouling – Review

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Abstract. Membrane Fouling was considered as major drawback in various industrial applications. Thus, this paper reviews the surface modification of polyethersulfone (PES) membranes for antifouling performance. Various modification techniques clearly indicate that hydrophilicity has to improve on the PES membrane surface. Moreover, the mechanism of fouling reduction with corresponds to various modification methods is widely discussed. Incorporation of hydrophilic functional groups on PES membrane surface enhances the surface free energy thereby which reduces the fouling. Characterization techniques adopted for the surface modified membranes was also discussed. These studies might be useful for the other researchers to utilize the modification technique for the applications of waste water treatment, chemical process industry and food industry.

Keywords: surface modifications; fouling; hydrophilic modifiers; polymer additives; flux decline

1. Introduction

Membrane technology is a novel separation technique. In recent days lot of research is going on to develop new polymeric synthetic membranes. Based on very specific properties, originating from structural factors and the final application of the membrane, the membrane material has to be chosen. Normally, organic or inorganic polymer materials are used for fabrication of ultrafiltration membranes. Commonly, PES is used as a membrane material for various industrial applications as given below.

- Dairy industry for protein separation and whey protein recovery
- Pharmaceuticals
- Beverage filtration and concentration
- Haemodialysis
- wastewater treatment (Maximous *et al*. 2010)
- Gas separation
- Bacteria and particulate removal (Yadav 2009)

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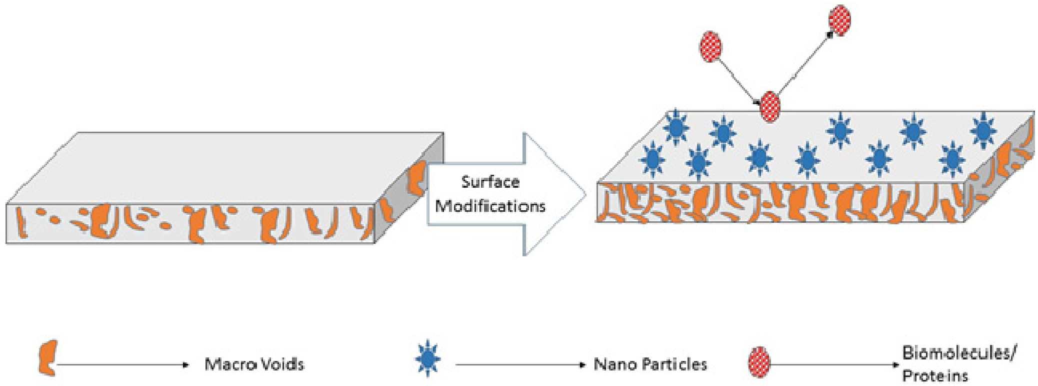

Fig. 1 Schematic diagram of surface modification methods

PES polymer is widely used as ultrafiltration membrane material because of its very good chemical, film forming property (Lin *et al*. 2009), low protein binding (Wang *et al*. 2006a), mechanical and thermal stability. However, PES membrane usage is limited because of fouling problem. Fouling refers to the accumulation of suspended or dissolved solids on the external membrane surface, on the membrane pores, or within the membrane pores. The fouling material can consist of either living organisms (biofouling) or non-living substances (inorganic or organic). Fouling causes flux decline which leads to decrease in performance of a membrane and may alter separation characteristics. Lifetime of the membrane might be shortened due to fouling (Ramesh *et al*. 2006, Wang *et al*. 2006b). Surface morphology of modified membrane is illustrated in Fig. 1.

To improve the antifouling property of the membrane, various surface modification methods have been suggested. For example, coating, blending, composite, chemical, grafting, surface physical treatment, grafting, or a combination of these methods (Van der Bruggen 2009). The results of the modification will yield different membrane responses to chemical resistance, fouling and absorption.

2. Membrane modification techniques

2.1 Surface functionalization

Attachment of functional groups on the surface of the membrane is referred as surface functionalization. This can be achieved by plasma treatment, sulfonation, etc. Various researches have been conducted to functionalize surface of membrane by plasma treatment. Surface functionalization also has been carried out by the photochemical methods. Photochemical surface functionalization of polysulfone ultrafiltration membranes for the purpose of covalent immobilization of biomolecules was reported by Ulbricht *et al*. (1996). Surface functionalization can be achieved by introducing polar groups on membrane surfaces to improve their wetting, adhesion properties which is reported by Goddard and Hotchkiss (2007).

Fang *et al*. (2010) studied on the protein adsorption, platelet adhesion property of terpolymer blended PES membrane. Blending a synthesized functional terpolymer Poly (acrylonitrile-co-vinyl pyrrolidone-co-acrylic acid) (P(AN-VP-AA)) with PES followed by grafting bovine serum albumin (BSA) on to the surface of the membrane. The antithrombogenicity of the modified membranes had been investigated. From the results, it could be concluded that antithrombogenicity of the membranes, the prothrombin time (PT) and activated partial thromboplastintime (APTT) increased. They also reported BSA modified PES membranes had a good biocompatibility and hydrophilic property of the membrane is increased.

Zhao *et al*. (2011b) studied about surface functionalization of membrane done by free radical polymerization and then followed by wet phase inversion method. Fluorine-containing segments prepared by free radical polymerization method. Copolymer poly (butyl methacrylate)-b-poly (methacrylic acid)-b poly(hexafluorobutyl methacrylate) (PBMA-b-PMAA-b-PHFBM) with hydrophobic segments, hydrophilic segments and fluorine-containing segments incorporated into PES ultrafiltration membrane by wet phase inversion method. Due to the presence of fluorine-containing PHFBM segments, the membranes exhibited desirable fouling release property with the highest and stable cleaning efficiency above 57%, whereas the blank membranes PES/PBMA5-b-PMAA exhibited drastic protein fouling.

Zhu *et al*. (2007) studied about the surface modification of porous PES membranes which were prepared by corona induced graft polymerization of acrylic acid (AA). The hydrophilic characterization of grafted PES membrane studied by the contact angle analysis. Porosity and protein permeability of the modified membranes were studied. Modified membrane surfaces characterized by ATR-FTIR and X-ray photoelectron spectroscopy (XPS) analysis. The above experiments results showed that the porosity of modified reduces with increase in grafting yield. The permeability studies of the modified membranes had shown that enhanced flux and antifouling properties compared to neat PES.

2.2 Grafting

It is a versatile method to modify the polymer membrane. Grafting is technique where is monomers are covalently bonded onto the polymer chain. Grafting is achieved by chemical treatment, photo-irradiation, high-energy radiation technique, etc. (Bhattacharya and Misra 2004).

A common strategy is to graft a layer of hydrophilic polymer on the membrane. Hydrophilic surfaces have proven to be less susceptible for fouling and are often reversible (Marshall *et al*. 1993). Belfer *et al*. (2000) studied about the surface characterization of unmodified, modified and protein fouled PES membranes which are modified by radical grafting with the aid of redox initiators to create new functional groups of methacrylate-based monomers on the surface. The modified membrane surfaces were characterized by FTIR-ATR spectroscopy to detect chemical changes during modification. The results of their study showed that redox initiation grafting could be successfully applied to PES.

Wavhal and Fisher (2002) studied the effect of plasma-induced graft polymerization on PES membranes for the purpose of improving the hydrophilicity. In this study, permanent hydrophilic modification of PES membranes is achieved by argon plasma treatment followed by polyacrylic acid (PAA) grafting in vapor phase. This has been confirmed by high energy resolution XPS and it shows PAA grafted over the membrane surface. Because of plasma treatment, the modified membranes are less susceptible to protein fouling than the unmodified membranes and the pure water flux for the modified membranes was massively increased for modified membranes.

Susanto *et al*. (2007) had done surface modification of PES UF membranes via photo graft polymerization of the hydrophilic monomer PEGMA onto the membrane surface to minimize the fouling. Pure water flux studies and static adsorption experiments by using BSA and sugar cane juice were conducted. The membranes were characterized with FTIR-ATR and contact angle. FTIR – ATR shows that there is a significant change in a chemical structure. Static adsorption studies results revealed that functionalized membranes had improved fouling resistance compared to unmodified membrane. This study provides the novel membrane for sugarcane juice clarification with better antifouling property.

Peeva *et al*. (2010) studied about modification of the commercial PES ultrafiltration membranes. They had performed the modification of membranes using photo-initiated "grafting-from" technique. In this study, polyethylene glycol methacrylate (PEGMA) (40 g/l) used as a surface modifying agent to modify commercial PES ultrafiltration membrane and N,N-methylene bisacrylamide (MBAA) and pentaerythritoltriallyl ether (PETAE) are crosslinkers which are added to improve the performance of modified membrane. Commercial membrane was kept inside the petridish which having 2 ml PEGMA and cross linker solution in different composition and it was irradiated by the UV irradiation system. After the grafting process, the membrane was treated with ultrapure water to remove the excess crosslinkers. Degree of functionalization, hydrophilicity, surface characteristics, and surface charge of the modified membrane studied. Flux and filtration measurements were conducted. The results showed that crosslinking with the "two-armed" MBAA yielded denser hydrogel layers and hydrogel layers cross-linked with the "three-armed" PETAE yielded a more open barrier structure. Modified membranes are much more hydrophilic than commercial membrane.

2.3 Cross-linking

Among the available techniques asymmetric polymer membranes are often prepared from soluble polymers by phase inversion method. Their solvent resistance is usually low and can be improved by cross-linking. Schematic diagram of surface modification by cross linking is shown in Fig. 2.

Oh *et al*. (2009) studied about the heat-induced crosslinking of the allyl-terminated telechelicsulfone polymers using a bisazide to prepare sulfonated PES with a network structure. In this study, the blend solution is prepared by sodium hydride was added in a DMF solution of the hydroxyl terminated PES at 0°C under nitrogen. This was left to stir for 1 h at this temperature before allyl bromide was added. The reaction mixture was stirred at room temperature for 12 h under nitrogen and then precipitated into of methanol. The membrane is prepared by immersion – precipitation method and film thickness is controlled by a doctor blade. Cross linkable sites were synthesized on the membrane and their structure was analyzed by NMR.

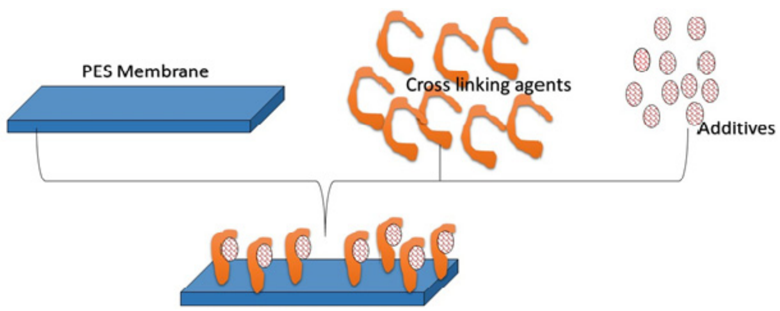

Fig. 2 Schematic diagram of surface modification by cross linking

Mu and Zhao (2009), investigated about the thermal-induced surface crosslinking approach to achieve the hydrophilic surface modification of PES membrane. PES porous membrane was prepared via a dual-bath coagulation method. Difunctional polyethylene glycol diacrylate (PEGDA) was used as the main crosslinking modifier. The addition of trifunctional trimethylol-propanetrimethylacrylate (TMPTMA) into the reaction solutions accelerated the crosslinking progress of PEGDA on PES membranes. Cross linking process is done with the application of heat. Characterizations of surface modified membrane were studied by Fourier transform infrared spectroscope with an attenuated total reflectance unit, contact angle goniometer and scanning electron microscope. The hydrophilicity of PES membranes was improved significantly by the surface crosslinking process. Antifouling ability of PES membrane could be optimized nicely.

Qin *et al*. (2014) have done in situ cross-linking, copolymerization of 2-hydroxyethl methacrylate (HEMA) and acrylic acid (AA) in PES solutions to synthesis blood compatible membrane. Modified PES membranes had characterized by water contact angle, protein adsorption, platelet adhesion, and clotting time. The results of above studies revealed that the modified membranes show improved hydrophilicity, good blood anticoagulant and antifouling properties after introducing HEMA and AA.

Peeva *et al*. (2012) fabricated hydrogel composite membranes based on PES ultrafiltration (UF) membranes by the addition of the crosslinking agents N,N-methylene bisacrylamide (MBAA) and pentaerythritol triallyl ether (PETAE) to the modifier solution of poly(ethylene glycol)400 methacrylate (PEGMA) in water under variation of the UV irradiation intensity and dose. The modified membrane properties were studied by water permeability, degree of grafting (DG), modification depth and cross-section structure by SEM. The results showed that the modified membranes exhibited better flux with antifouling property.

2.4 Modifications by nanoparticles

Nowadays, the various nanoparticles introduced on the PES polymer surface to improve their hydrophilicity. Incorporation of nanomaterial in/ on the membrane structure showed more porous membrane structure which may results in higher water flux compared to neat PES membrane (Daraei *et al*. 2013, Mierzwa *et al*. 2013, Huang *et al*. 2014). Nanocomposite membrane can reduce the organic fouling and biofouling. This can be achieved by following methods.

(a) Blending of PES with the hydrophilic nanoparticles like SiO_2, ZrO_2, and TiO_2
(b) Grafting with hydrophilic polymers
(c) Coating with hydrophilic polymers

Mingliang *et al*. (2011) reported that various nanoparticles used to modify organic membranes among which TiO_2 receives most attention because of its stability, availability, and hydrophilicity. In his research he fabricated sulfonated PES with nano-TiO_2 ultrafiltration membrane and he studied about anti fouling mechanism of it. He reported that the hydrophilicity of the membrane surface is improved remarkably.

Celik *et al*. (2011) studied the protein fouling behavior of composite membrane during water filtration. Composite membrane had been fabricated by phase inversion method from multi-walled carbon nano- tube/PES (C/P). Bovine serum albumin (BSA) and ovalbumin (OVA) used as the model protein for investigating the protein fouling behavior. The results revealed that BSA adsorption on C/P composite membranes was 58% less at pH 3 and 72% less at pH 7 compared to the bare PES membrane. Based on these results, C/P composite membranes had the potential to curtail the protein fouling.

Zhao *et al*. (2011a) conducted experiments to modify the PES membrane surfaces by blending the polymeric nanoparticles with the PES. In this study, polyvinyl pyrrolidinone employed as a polymeric nano particle. PES/PVP membranes were fabricated by solution polymerization. Morphology, hydrophilicity, surface characterization, permeation studies were conducted. Scanning electron Microscope and TEM were used for the study the morphological characteristics of membrane and their results showed that significant agglomerations were not observed. Moreover, the size distribution was broad. Ultrafiltration experiments were conducted to study the permeability and performance of the modified membrane compared to unmodified membrane. The results of various experiments showed that the hydrophilicity and flux of the modified membranes increased obviously, while the protein adsorption decreased.

Daraei *et al*. (2012) had conducted the experiments for removal of CU (II) from water. In this study they had fabricated the mixed matrix membranes (MMMs) from (PES) and polyaniline/ iron (II, III) oxide (PANI/Fe_3O_4) nanoparticles by phase inversion method. The fabricated membrane potential for copper ion removal and adsorption mechanism had been assessed by dead end cell. The performance test exhibited that the membrane with 0.1wt% nanoparticles had the highest Cu (II) ion removal capability but the lowest pure water flux.

Liu *et al*. (2012) studied about the preparation of organic-inorganic PES-SiO_2 composite UF membranes by conventional immersion precipitation phase inversion method for the application of H_2/Cl_2 fuel cell and for the alternative for ion exchange membranes. The prepared membrane comprised of nano size SiO_2, PES and aqueous acid. The composite membrane has high hydrophilicity and high porosity.

Arthanareeswaran and Thakur (2012) studied about the effect of inorganic particle on the performance of PES-Cellulose Acetate (CA) UF membranes. In this study, they have investigated the effect of Al_2O_3. Blend solution prepared by dissolving the PES and CA in DMF and followed by adding Al_2O_3 particles. The top surface and cross section of membrane were studied Scanning Electron Microscope (SEM). The results showed that macrovoids formed due to the addition of Al_2O_3. Pure water flux increased from 33.87 to 103.22 $L/m^2/h$ when the 30% of Al_2O_3 was added with the blend.

Zhang *et al*. (2012) blended modified halloysite nanotubes (HNTs) loaded with silver nanoparticles (Ag NPs) with PES and ultrafiltration membranes were prepared via phase inversion. The membrane performance studies showed that pure water flux of modified membrane was 396.5 $L \cdot m^{-2} \cdot h^{-1}$ which was about 251.5% higher than that of the neat PES membrane, and the rejection was slightly affected by the addition of the modified HNTs. The contact angle data supported that the hydrophilicity of the membranes was enhanced by the addition of modified HNTs. The microstructure of modified membrane was studied by SEM. SEM results reveal that modified membrane had porous sublayer, and fully developed macropores at the bottom.

Li *et al*. (2009) studied the effect of TiO_2 on surface morphology of PES membrane. PES–TiO_2 composite membranes were prepared via phase inversion by dispersing TiO_2 nanoparticles in PES casting solution. Surface characteristics of membrane studied by XRD, DSC and TGA. The results showed that the interaction existed between TiO_2 nanoparticles and PES and the thermal stability of the composite membrane had been improved by the addition of TiO_2 nanoparticles. Mechanical test also revealed that the mechanical strength of composite membranes enhanced as the addition of TiO_2 nanoparticles. Hydrophilicity of the composite membranes was enhanced by the addition of TiO_2 nanoparticles.

Jamshidi Gohari *et al*. (2013) synthesized a novel PES/hydrous manganese dioxide UF mixed matrix membrane (MMM) for adsorptive removal of Pb(II). The characteristics of MMMs were studied by FTIR, AFM and SEM. In addition, membrane pure water flux, hydrophilicity, porosity and Pb(II) adsorption capacity were also studied. The membrane pure water flux increased because of increased porosity, more hydrophilicity and better surface roughness. The results of adsorption studies showed that PES/HMO had capable to remove the Pb(II).

Jamshidi Gohari *et al*. (2014) fabricated the mixed matrix membranes (MMMs) by introducing nano material hydrous manganese dioxide (HMO) via the immersion precipitation method to improve the antifouling property of the PES membrane. Synthesized membranes had been characterized by SEM, AFM, FTIR, contact angle and ultrafiltration experiments of oily wastewater. The result of the study shows that hydrophilic HMO improves the hydrophilicity of PES/HMO membrane which has been proved by lower contact angle (16.4). PES/HMO membrane (573.2 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) has more water flux than virgin PES membrane (39 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). MMMs revealed tremendous oil rejection (almost 100%) when they were performed experiments for synthetic wastewater containing 1000 ppm of oil.

2.5 Surface modification by UV irradiation

To modify the membrane surfaces, membrane surfaces may be exposed to UV irradiation. It will lead to increase the hydrophilicity of the membrane (Kilduft *et al*. 2000). Much of the research conducted on PES ultrafiltration (UF) membrane surfaces were modified by applying UV light for the purpose of decreasing biofouling. Pieracci *et al*. (1999) conducted their research on PES 10 kDa ultrafiltration membrane surface modification is done by UV photolysis which results graft polymerization of monomer on the membrane surface. Modified PES membranes have more hydrophilic nature in other words decreased protein fouling relative to the neat PES membrane.

Susanto *et al*. (2008) reported that PES-based thin layer hydrogel composite (TLHC) membrane synthesized by UV initiated graft copolymerization of Polyethylene glycol methacrylate (PEGMA) which yields best performance of protein and humic acid ultrafiltration. TLHC membrane higher fouling resistance compared to the neat PES membrane.

Rahimpour *et al*. (2008) studied a comparison between UV-irradiated TiO_2-entrapped and deposited membranes. In this study they prepared PES/TiO_2 membrane by phase inversion induced by immersion precipitation technique and also prepared TiO_2 coated PES membrane. Synthesized membranes were exposed to UV irradiation for various time intervals. Characteristics of membranes were studied by contact angle, SEM, FTIR, pure water flux and fouling studies by milk. Results showed that TiO_2 deposited membrane have antifouling characteristics and flux compared to TiO_2 entrapped membrane.

Liu and Kim (2012) studied surface modification of commercial PES membranes were achieved by UV / ozone pretreatment with sub-sequent grafting and interfacial polymerization to improve antifouling property of the modified membranes. In this study, hydrophilic polymers like poly (vinyl alcohol) (PVA), poly(ethylene glycol) (PEG) and chitosan were grafted on UV/ozone pretreated virgin commercial PES membrane. The modified membranes had been examined by contact angle, static protein adsorption test and XPS. Contact angle results shows that contact angle value of modified membranes were 19 to 58% lesser than virgin membrane. XPS spectra revealed that commercial membranes were modified successfully. The UV / ozone pretreatment followed by grafting and interfacial polymerization improves the anti-fouling property of the modified membrane which had been shown by static protein adsorption test.

2.6 Surface modification by adding additives

During the membrane fabrication process the additives mixed with the casting solution. Additives may be organic or inorganic material. The major functions of additives are given below.

- To avoid the formation of macro voids
- To improve the hydrophilicity
- To enhance or reduce the pore formation

Anand *et al*. (2012) investigated the effect of organic and inorganic additives in the PES membranes, to maximize the efficiency of the ultrafiltration process. In this study, they have blended tetraethylorthosilicate (TEOS) and polyetheleneimine (PEI) with the PES casting solution which results viscosity and hydrophilicity were increased. Surface of the membrane studied by SEM and AFM analysis and the results showed that surface of the membrane changed from dense like structure to finger like face.

Huang *et al*. (2011) investigated that surface modifications of PES membrane by blending PES with triblock copolymers of methoxylpoly (ethylene glycol)-polyurethane-methoxyl poly(ethylene glycol) (mPEG-PU-mPEG), which were synthesized through solution polymerization with mPEGMns of 500 and 2000, respectively. After blending the copolymers, the hydrophilicity and protein antifouling property increased.

Rahimpour *et al*. (2010a) reported during the fabrication process of PES membrane, potassium perchlorate ($KClO_4$) as an additive in the casting solution which results viscosity of the PES casting blend solution increase with the concentration of $KClO_4$ and hydrophilicity of the membrane also increased. Accordingly, the water flux of membranes prepared with $KClO_4$ must be high compared to pristine membrane. Membrane performance studies demonstrated that the pure water flux is reduced at presence of modifier $KClO_4$ in the casting solution. When KClO4 is added in the casting solution, membrane morphology was altered with dense top surface, thick skin layer and small finger-like pores. In addition, the milk water permeation of PES membrane increased from 27 L/m^2 h to 39 L/m^2 h by addition of 5 wt.% $KClO_4$ in the casting solution.

Rahimpour *et al*. (2010b) studied effect of hydrophilic monomers like acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA) introduced in the gelation media, during the membrane preparation by phase inversion method by using PES and pore former polyvinylpyrrolidone (PVP) which leads to the hydroxyl hydrophilic groups of AA and HEMA present in the membrane, surface porosity, increased, the pure water flux, milk water permeation of the membrane were improved increases with the AA and HEMA concentrations.

Borneman, *et al*. (1997) removal of polyphenols and brown colour in apple juices using PES/PVP membranes in a single-ultrafiltration process. Wang *et al*. (2011) demonstrated the concentration of food product “gelatin” by modified PES ultrafiltration membranes. They had done the modification by adding the additives like PVP and acetone in casting solution. In addition to that they had done membrane performance measurements. The results for modified membrane reveal that pure water flux 373 L/m^2 h at 0.1 MPa, and the rejection to BSA was 91%. Compared to neat PES membrane, pure water flux of modified membrane slightly low but rejection was high.

Rahimpour *et al*. (2012) reported that amine functionalized Multi-walled carbon nanotubes (F-MWCNTs) mixed with the dope solution containing PES, PVP and dimethylacetamide (DMAC). From the dope solution membranes was fabricated by phase inversion induced by immersion precipitation. Due to the addition of F-MWCNTs, pore size, porosity, surface roughness and hydrophilicity of the membrane was significantly increased.

Lithium bromide used as an additive for the preparation of flat sheet PES membrane by microwave technique, which results good increase in the rejection and permeation rates and it is reported by Ahmed *et al*. (2011).

Pieracciz *et al*. (1999) reported that PES 10 kDa UF membranes were surface modified by UV irradiation-induced grafting and polymerization of hydrophilic monomers like N-vinyl-2-pyrrolidinone (NVP), N-vinylformamide (NVF), and N-vinylcaprolactam (NVC) onto the surface to form covalently bound polymer chains. The characteristics of modified membranes are increased hydrophilicity which has translated into decreased protein fouling relative to the unmodified PES membrane.

Susanto and Ulbricht (2009) studied about the characteristics, performance and stability of PES ultrafiltration membranes. In this research, they prepared PES membrane by phase separation method using different macromolecular additives like polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG) and poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (Pluronic, Plu). Surface hydrophilicity (by contact angle), surface charge (by zeta potential), surface chemistry (by FTIR spectroscopy) of the prepared membrane was analyzed. They had also investigated about water flux and rejection of macromolecular test substances. The contact analysis studies showed that modified PES-PEG membrane had hydrophilic in nature.

Zhao *et al*. (2008) studied the antifouling PES ultrafiltration membranes were prepared by phase inversion technique. During this study, multifunctional additive pluronic F127 added with blend solution in different wt.%. Contact angle, surface morphology by XPS and protein rejection studies had been conducted. The results were compared with PES/PEG membrane. Contact angle and surface morphology results confirmed that hydrophilic modification of the PES membrane. The protein rejection studies showed that pore size of the modified membranes was improved because of adding pluronic F127.

Zhao *et al*. (2013) demonstrated 0 to 2wt.%. sulfonated polyethersulfone (SPES) was directly blended with PES at any ratios to prepare modified membranes. Surface morphology study was conducted by SEM which indicated that the structure of the PES membranes had an obvious change after the modification. The water contact angles of the modified PES membranes decreased from 84° to 68°, and the water fluxes had a dramatic increase from 162 to 1912 mL/m^2 mmHg h for various ratios of SPES. The blood platelet adhesion on the PES membrane was largely suppressed after the modification. These results indicated that the modified membranes had a potential to be used in blood purification fields.

Sakinah *et al*. (2007) described fouling during separation of cyclodextrins from starch and CGTase. The additive polymer of polyethylene glycol (PEG 400) was added with PES polymer to synthesis the modified membrane. The performance of the modified membrane showed maximum achievable flux recovery of cyclodextrins (CDs) separation was found to be 95%.

Shi *et al*. (2007) studied about preparation of antifouling ultrafiltration membrane by pegylated PES membrane by phase inversion method. In this study, pegylated PES was prepared by facile method. Pegylated PES added with blend solution in DMF. PEG 2000 added as pore forming agent. The blend solution was casted for fabrication of modified membrane. Various kinds of experiments like liquid porosimetry experiments, protein rejection and ultrafiltration experiments were conducted to study the characterization of modified membrane. The modified membranes showed higher hydrophilicity and superior resistance to protein adsorption compared with neat PES membrane. Liquid porosimetry and protein rejection experiments showed that the incorporation of pegylated PES to the casting solution resulted in an increase of membrane pore sizes. From these results showed that pegylated PES approved as a desirable modifier for PES membrane.

2.7 Surface modifications by coating methods

Coating means formation of layer on the membrane. This can be achieved by dip coating, Coating method is one of the cheapest methods in surface modification because it does not require any costliest equipment.

Prihandana *et al*. (2013) studied about the antithrombogenicity of nano porous PES Membrane which is coated by fluorinated diamond-like carbon films (F-DLC). F-DLC deposited onto the PES using radio frequency (RF) plasma enhanced chemical vapor deposition (CVD) method. Antithrombogenicity of PES/ F-DLC membrane was examined by microfluidic device. From the results, they concluded F-DLC films improve the antithrombogenic characteristics of the membrane surfaces in hemodialysis systems which indirectly means F-DLC drastically reduced the amount of blood cells attached to the surface.

Li *et al*. (2014) have employed to surface modification of commercial PES ultrafiltration membrane by polydopamine coating and further poly(ethylene glycol) grafting to minimize the fouling. The fouling studies had been conducted by using BSA model foulant. Moreover, SEM and stability analysis also performed for modified membrane. The SEM results revealed that pore size of the modified membrane had been reduced. Stability analysis shows that modified membrane had reliable mechanical stability and better chemical stability. Furthermore, the membrane modification improved the hydrophilicity of the membrane.

Atiyeh and Duvnjak (2005) demonstrated purification of fructose syrups produced from cane molasses media using ultrafiltration membranes followed by activated carbon. They had done modification on commercially available PES membrane (PES-HO51) (Osmonics Inc., USA). They coated brominated sulfonated poly (2,6-dimethyl-1,4- phenylene oxide) (SPPOBr) selective coating layer over PES-HO51 that served as a support. The total fructose recovered after the carbon treatments of permeates of the PES-HO51 and coated PES-HO51 membranes were 74 and 85%, respectively.

Ali and Tari (2012) were also done membrane modification via the coating. Myoglobin was used as coating agent on the PES membrane. Protein separation performance of membrane was conducted by using lysozyme (model protein) at different rpm and feed concentration. At 1500 rpm speed, greater rejection (99%) and better flux (80 L/m^2 h) was attained.

Nady *et al*. (2012) studied enzyme-catalyzed modification of PES surfaces. After plasma cleaning, model PES surfaces was spin coated with 0.25% w/w PES solution in dichloromethane for 10 s at 2500 rpm. The spin-coated PES model surfaces were incubated in 20 ml 0.1 M sodium acetate buffer containing different concentrations of phenolic acids (substrates or monomers) and laccase enzyme. The modified surfaces are evaluated for model protein adsorption (BSA, dextrin and tannin) using in-situ reflectometry and AFM imaging. The results revealed that enzyme-catalyzed coated PES surfaces show a reduction in the adsorption of BSA, dextrin and tannin.

Pourjafar *et al*. (2012) synthesized and characterized PES/PVA/TiO_2 composite membrane. PES/PVA fabricated by phase inversion induced by immersion precipitation. The PES/PVA composite membrane dipped in a cross-linking solution (glutaraldehyde) in order to reduce the membrane swelling by chemical cross-linking. For the modification, PES/PVA membranes were then immersed in to various concentration of TiO_2 solution. The surface morphological characteristics were investigated by AFM, SEM, contact angle and X-ray diffraction (XRD). The membranes performances were also evaluated in terms of permeate flux, salt rejection. The contact angle measurement and XRD studies indicated that the TiO_2 nanoparticles successfully were coated on the surface of PVA/PES composite membranes. However, rougher surface was obtained for membranes by TiO_2 coating. The filtration performance studies revealed that the 0.1wt.% TiO_2-modified membrane has higher performance in terms of flux and NaCl salt rejection.

Susanto *et al*. (2012) studied about the preparation of low fouling ultrafiltration membranes for biomolecules separation. In this study, post-modification with hydrophilic polymer and blending of hydrophilic agent during either conventional or reactive phase separation (PS) were conducted. The post-modification was done by photo graft copolymerization of water-soluble monomer, poly (ethylene glycol) methacrylate (PEGMA), onto a commercial PES UF membrane. In non-solvent induced phase separation (NIPS), PEG (hydrophilic additive) blended with the PES in N-methyl-2-pyrrolidone (NMP). In reactive phase separation, PES is dissolved in NMP and polymer additive also added with polymer blend. The blend solution was casted on glass plate and subjected UV irradiation for the purpose of covalently linking the polymeric additive with membrane in one step. The modified membrane had been analyzed by surface morphological studies and performance studies. FTIR studies proved that membrane has been modified because there was an observable changes in IR spectra. Performance studies results shows that all modified membranes had much higher flux ratio than neat membranes.

3. Conclusions

Modification of PES membrane using various techniques was extensively reviewed. The salient features of the review were discussed as follows.

Hydrophilicity is an important parameter to enhance on PES membrane surface to minimize the fouling. Hydrophilicity improvement can achieve by using various modification techniques such as grafting, coating, cross linking and blending.

Among the various methods, blending techniques was the cheapest and effective method to improve the PES membrane by incorporation material. Under this method, hydrophilic polymer, biopolymer and nanomaterial can used to enhance the hydrophilicity.

Characterization techniques shows FTIR would be an effective tool to confirm the surface functionality. Membrane morphology also can visualize using SEM to formation of the structure. Contact angle measurement is the prerequisite tool to determine hydrophilicity.

Combined modification methods would be a promising and versatile tool to improve the super hydrophilicity property. These methods obtained membranes results to lesser binding with solutes due to the presence of ionizable functional groups.

Overall, these review would reveals the advantages and disadvantages of each modification methods. The study concludes that fouling is a natural phenomenon which can control by modified membranes.

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