Post-treatment of Polymer Membrane through Chemical and Physical Surface Modifications- A Review

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INTRODUCTION

Modern membrane science was first developed in year 1960 and Loed-Souriajan process in particular catches the most attention from other researchers (Zornoza, Casado et al. 2013). Loed-Souriajan process was first applied on synthetic membrane for production of defect free reverse osmosis cellulose acetate membrane with high flux, which consists of ultra-thin selective skin layer and permeable thick micropores structure that support the membrane. Ultra-thin selective dense skin and permeable thick micropores are typical morphology structure for membranes used in various different applications (Baker 2012; Zornoza, Casado et al. 2013). Polymeric hollow fiber membrane, introduced by Mahon in year 1966, was an effort to further improve the stability of membrane produced using the Loed-Souriajan process (Mahon Henry 1966; Wang, Matsuura et al. 2004; Baker 2012).

The introduction of hollow fiber membrane was a major breakthrough in membrane technology and drawn a lot of interest for industrial application. The performance of polymeric hollow fiber was further optimized through variation of spinning parameters and redesigning the spinneret. The separation performance improvement by process optimizations were restricted by the intrinsic property of polymer, leading to the introduction of inorganic materials such as metal, ceramic and carbon for production of hollow fiber with higher separation performance. The introduction of inorganic hollow fiber successfully improved the separation performance of hollow fiber with a tradeoff between high separation performance and production cost. The significantly higher production cost of inorganic hollow fiber has made it not feasible to be industrialized, while polymer hollow fiber is being widely used in industrial application. In order to further improve the performance of polymeric hollow fiber membranes,

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A B S T R A C T

Post-treatment of polymer membrane are studied as an effort in improving the separation performance. Recently, chemical surface modifications of polymer membrane are of great interest focuses in producing a membrane with surface property that is distinct from the bulk of membrane. This distinct property of modified surface can potentially improve the solubility selectivity of the membrane, while the diffusion selectivity of the membrane bulk is maintained, forming a membrane with good physic-chemical property. However, the surface modification methods introduced up to present still fail in producing a polymer membrane that is ideal, without trading between selectivity and permeability. This trade-off trend between selectivity and permeability after surface modification could be a result of restricted accessibility between modified surface and membrane bulk. The surface modification methods through chemical and physical processes previously studied and reported are discussed in this review. The main objective of all these surface modification techniques are to produce a membrane with high chemi-sorption and physic-sorption properties. Surface modification with chemical processes are potentially one of the effective way of post-treating the surface of membrane as it is able to form a surface with high solubility selectivity while retaining the diffusion selectivity of the membrane bulk. Among a few common chemical processes for surface modification such as grafting and cross-linking; chain-end grafting, also named as chain-end enrichment could be an effective way to produce a membrane with distinctly modified surface with highly permeable membrane bulk.

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post-treatment of polymer membranes are being studied as an effort of improving the separation performance of polymer membranes. Post-treatment of polymer membrane is categorized as advanced membrane technology research, which has not been thoroughly studied. The main objective of post-treatment process is to modify and fix defects on membrane surface for separation performance enhancement. Surface modification of polymer is a new field of study focuses in producing a polymer surface with desired properties. These properties are often specific and distinct from the bulk properties of material (Schaub, Kellogg et al. 1996). It is worth mentioning that the chemical modification of bulk membrane material will degrade its desirable mechanical, thermal or even the chemical stability (Yamagishi, Crivello et al. 1995). As a result, a modified surface, which is distinct from the bulk property, is a desired outcome for an ideal separation membrane. Surface modifications of ultrafiltration and desalination polymer membranes in particular, were studied intensively, focus in producing membrane surface that contain different energy and chemical functionalities from those of bulk membrane (Hester and Mayes 2002). Control of surface properties can be achieved through various chemical or physical process such as chain-end enrichment, surface grafting, cross-linking, coating and plasma or heat treatment (Schaub, Kellogg et al. 1996), as shown in Fig. 1.

![Surface modification methods](image)

**Fig. 1:** Methods of chemical and physical surface modification of polymer surface.

1. **Surface Modification with chemical processes:**

   Surface modification with chemical processes involves surface reaction in order to form covalent bonding interaction between modified surface and bulk of polymer membrane. Surface grafting and cross-linking are examples of surface modification with chemical process. Currently, most of the surface modification done focuses in enhancing the hydrophilicity of membrane as well as enhancement of permeability.

   1.1 **Surface grafting:**

   Grafting of complex molecules such as copolymers and metal alkoxide molecules (Wongchitphimon, Wang et al. 2011) are common and it can occur as side chain grafting, or chain-end grafting. Surface grafting is a common method used for surface modification of water filtration membranes made of hydrophobic materials such as polysulfone and polyolefin to improve the hydrophilicity of membrane surface (Yamagishi, Crivello et al. 1995). Researchers had successfully improved the hydrophilicity of membrane surface by co-polymer grafting, which forming additional side chain on the surface of membrane (Hester and Mayes 2002; Weir and Parnell 2011). These additional side chain grafted on the surface of membrane leads to significantly higher pure water permeability as well as fouling resistance towards proteins and oils (Yamagishi, Crivello et al. 1995; Hester and Mayes 2002; Weir and Parnell 2011).

   The concept of polymer surface modification through grafting technique typically results in surface pore channels modification, and reduces the pore size near membrane surface (Nunes, Sforça et al. 1995; Hester and Mayes 2002). Grafting requires an initiator that attracts chain-ends towards the surface. As chain-ends are attracted towards the surface, the density of grafting increases and causes overlapping of polymer chains (Weir and Parnell 2011). These overlapped polymers will start forming repulsive interaction between neighboring chain, and forced the chain to stretching away from the surface, forming brush-like conformation (Weir and Parnell 2011). A few commonly used polymers for polymer brush formation include amphiphilic comb polymer, hydrophilic vinyl monomers and polymer oxides such as polyethylene oxide (PEO) and alkoxide (Hester and Mayes 2002; Park, Acar et al. 2006).

   Park et al. studied the amphiphilic graft copolymers of polysulfone and polyethylene glycol side chains. They suggests that amphiphilic graft copolymer forms and localizes at the membrane surface, forming a dense hydrophilic brush-like
copolymers side chains, while the hydrophobic backbone intermixes with the membrane base component, acting as the anchor (Park, Acar et al. 2006). They found that this grafting has improved the resistance to protein adsorption, and wettability.

In another research work, Hester and group reported that the amphiphilic graft copolymer grafted on the surface have self-organizing character at the surface interface between water and membrane (Hester and Mayes 2002). This self-organizing characteristic has formed a hydrated outer surface that with accessibility to the backbone of the polymer chain in the bulk of polymer which is water-insoluble and entangled with other polymer matrix (Hester and Mayes 2002). It was mentioned that this results is a highly efficient surface modified membrane (Irvine, Mayes et al. 2001; Irvine, Razette et al. 2001). In another review done by Weir and Parnell, they suggested that this self-organizing character of brush-like structure is named as responsive polymer brush, which is an important property that enables the control of interfacial behaviors such as adhesion, wettability, surface adsorption, friction, flow and motility (Weir and Parnell 2011). These are behaviors that characterize the chemical-property of the membrane surface.

Other than grafting of polymers, grafting of organosilanes compounds such as Fluorolink®S 10 and tetraethyl orthometal alkoxides are also common, where grafting initiator are not required. However, a pre-grafting through alkaline treatment was done to introduce hydroxyl groups into the polymer membrane to allow chemical reaction between the organosilanes compound and the surface of most polymeric membranes such as PVDF membrane (Wongchitphimon, Wang et al. 2011). Alkaline treatment is very difficult to control as it could cause the destruction of membrane integrity (Xu, Li et al. 2005; Liu, Lee et al. 2010). However, a careful control of the alkaline treatment process will allow the grafting of Si-O-alkyl groups of organosilanes on the surface of membrane and the carbon dioxide absorption flux was found to improve after the modification (Wongchitphimon, Wang et al. 2011).

It is worth mentioning that grafting can occur as side chain grafting, or chain-end grafting. Surface modification via grafting and segregation of modified polymer chain-end, is also named as chain-end enrichment. This surface chain-end enrichment involves small molecules or oligomeric additives that migrate to the polymer surface, which as reported to be able to compromise the polymer’s bulk properties, however, the bond between these additives and the polymer matrix is weak, which could possibly be removed through evaporation, dissolution or wear (Schaub, Kellogg et al. 1996). It is suggested that the chain-end enrichment process could avoid the formation of micelles that occurs in co-polymer grafting technique, which can adversely affect the physical properties of the bulk (Schaub, Kellogg et al. 1996). There is no research that reports on the use of this technique for membrane separation application. However, it is widely used in polymerization, where the characters of polymer are modified by enriching the chain-end, producing copolymer that can be used for grafting, where aluminum ligand was one of the common initiator used (Nomura, Ishii et al. 2002; Hornrnirut, Marshall et al. 2004). C. A. Fleischer et al. introduced a concept of interpolymer complexation by using acid and base groups as the end-functional termination of homopolymers (Fleischer, Morales et al. 1994). The new concept of polymer complexation with acid and base groups as the chain-end enrichment has shown to successfully promote in situ chain-end enrichment of the immiscible material across the interface (Fleischer, Morales et al. 1994).

Polymer surface chain-end enrichment has been studied as an effort of understanding the impact of different chain-end enrichment molecule on surface property. It was suggested that these surface property is important for the character of polymer surface which includes surface reactivity, electrical contact, adhesion, and fracture (Botelho do Rego, Lopes da Silva et al. 1993; Elman, Johs et al. 1994). The chain-end enrichment end groups that had been studied include deuterium, carboxyl, and fluoroisilane (Botelho do Rego, Lopes da Silva et al. 1993; Elman, Johs et al. 1994; Schaub, Kellogg et al. 1996). Each of the chain-end groups was found to react with the polymer surface differently, where the oscillation of chains depends on the surface energy absorption of the end groups (Elman, Johs et al. 1994). These oscillation of chains stretches from the surface chain-end to the backbone of the polymer chain located in the bulk of polymer membrane (Elman, Johs et al. 1994). This oscillation, the chain mobility, is essential for transportation of gas across the bulk of membrane, which suggests that surface modification through chain-end enrichment process can potentially enhance separation performance of membranes. The improvement of chain mobility as a result of surface chain end enrichment is also reported by other researchers (Han, Han et al. 2012; Jung, Ha et al. 2014).

In one of the study on surface dynamics of poly(methyl methacrylate) (PMMA) done by Zuo Biao et al., they found that the enrichment of chain ends towards film surface increases the excess free volume, therefore substantially suppressing glass transition and enhances the mobility of surface chain (Zuo, Liu et al. 2013). It is worth mentioning that surface chain-end enrichment are studied at recent years for degradable materials (Han, Han et al. 2012; Jung, Ha et al. 2014), where Jung et al. found that poly(dl-lactide) (dl-PLA) and poly (ε-caprolactone) (PCL) blend films showed the enrichment of with poly(vinyldiene fluoride) (PVDF), which allow the control of initial stability of degradable polymers (Jung, Ha et al. 2014).
1.2 Cross-linking:

Other than surface grafting, cross-linking is also a common chemical modification method used. Surface modification through crosslinking was done in two different approaches namely solution-phase modification (Liu, Wang et al. 2001; Tin, Chung et al. 2003; Choi, Jansen et al. 2010) and vapor-phase modification (Wang, Paul et al. 2013). Crosslinking surface modification on glassy polymer was an effort of exploring the method of improving the plasticizaiton effect of polymer membrane that involves carbon dioxide (Tin, Chung et al. 2003; Bakonyi, Neméstőhy et al. 2013). T.S.Chung and group has developed an extremely simple cross-linking modification technology at ambient temperature (Liu, Wang et al. 2001; Tin, Chung et al. 2003) via solution-phase modification approach. The solution-phase approach tends to demonstrate low permeability and brittleness as a result of chain scission In one of the most recent study, H. Wang et al. (Wang, Paul et al. 2013) attempted modifying the surface of membrane by crosslinking diethylenetriamine (DETA) on 6FDA-based polyimides using vapor-phase method (Wang, Paul et al. 2013). When being compared between unmodified and modified membrane, it was found that the temperature for crosslinking condition significantly affect the gas separation performance of modified membrane (Wang, Paul et al. 2013). The pure gas permeability result shows slight hydrogen permeability and hydrogen – carbon dioxide ideal selectivity improvement at the crosslinking temperature of 40 °C for 10 minutes, while higher crosslinking temperature significantly inhibits the permeability of modified membrane. They correlated the permeability reduction to the contribution of the crosslinked portion near membrane surface, suggesting that the intrinsic gas permeability of modified layer dropped drastically with high crosslinked portion (Wang, Paul et al. 2013).

Chemical modification that incorporates both grafting and crosslinking technique were also reported. X. Yang et al. reported a chemical modification on polyvinylidene fluoride (PVDF) membrane by involving hydroxylation of PVDF membrane by an aqueous lithium hydroxide solution and successive reduction with an organic sodium borohydride solution followed by cross-linking with a perfluoropolyether that contains ethoxysilane terminal group (Yang, Wang et al. 2011). Y. Zhuang et al. also reported a similar surface modification method for Polyimide-amide (PAI) membrane, where aminopropyltrimethoxysilane (APTMS) was used for hydroxylation of membrane surface, followed by grafting and cross-linking of the perfluoro-compound containing ethoxysilane terminal groups (Zhang, Wang et al. 2011). Both research finding reported improved wetting resistance, higher hydrophilicity and critical water entry pressure after the chemical modification of surface through grafting and cross-linking (Yang, Wang et al. 2011; Zhang, Wang et al. 2011).

Although chemical surface modification through grafting and cross-linking has shown promising results in separations application, however, the trade-off trend between permeability and selectivity is significant. In one of the research by Low et al. for example reported a trade-off of almost half the hydrogen permeability for a hydrogen – carbon dioxide ideal selectivity improvement of approximately 10 times (Low, Xiao et al. 2008). Similar trend was also reported by other researchers (Shao, Chung et al. 2005; Choi, Jansen et al. 2010). This trade-off trend observed on a modified membrane is related to the stiffness of polymer (Choi, Jansen et al. 2010) and the crystallinity of polymer chain (Lin, Van Wagner et al. 2006), where both factors are inter related. Lin et al. reported a clear relation between the crystallinity of polymer and the gas separation of a membrane (Lin, Van Wagner et al. 2006). In their work, they mentioned that the high crystallinity level will exhibits a very low carbon dioxide permeability, as the crystalline regions will causes a decrease in polymer chain mobility in the amorphous phase, which subsequently increases the size-sieving ability of the polymer membrane (Lin, Van Wagner et al. 2006). The decrease in polymer chain mobility in this context contributes to stiffness of membrane. Low et al. had also reported that the chain tightening as a result of crosslinking reaction has resulted signification lower free volume and diffusion space, leading to significantly lower permeability (Low, Xiao et al. 2008).

From all these research works, we suggest that a membrane should have a modified surface with controlled crystallization in order to maintain the surface high free volume and diffusion space. As reported, crystallinity is essential for size-sieving property enhancement, which contributes to the high selectivity of membrane. However, the position and direction of crystallinity formation on the surface of membrane is important as it contribute to the permeability performance of membrane. In one research work by Hedenqvist and Gedde, they reported that the orientation of crystalline structure will affect the diffusivity (Hedenqvist and Gedde 1996). In their work, they suggested that crystalline structure is impermeable, when the diffusion is perpendicular to the crystalline structure, the diffusivity is zero, while the parallel diffusion depends on the diffusivity of amorphous phase (Hedenqvist and Gedde 1996). This research work shows that a semi-crystalline structure is most ideal for high selectivity and permeability membrane. However, the arrangement of crystalline structure is crucial in order to avoid the tradeoff between permeability and selectivity as a result of impermeable crystal structures.
1.3 Chemical reaction:

Other than grafting and cross-linking, chemical reaction is also another chemical process employed in post-treatment of polymer membrane. Hypochlorite treatment is one of the well-known post-treatment processes through chemical reaction, employed on microfiltration and ultrafiltration hollow fibers (Qin and Wong 2002; Jung, Yoon et al. 2004; Rouaux, Causerand et al. 2006; Figoli, Simone et al. 2014). However, the main objective of this chemical reaction is to leach out the PVP content near the hollow fiber interface, which subsequently leads to a formation of smoother membrane surface as a secondary result. In one of the most recent research work, A. Figoli et al. suggested that the main objective of hypochlorite treatment was to leach out the hydrophilic additive from the bulk of hollow fiber to ensure the hydrophobicity of membrane (Figoli, Simone et al. 2014). Jung et al. and Rouaux et al. reported that smoother membrane surface was observed as PVP decomposed by sodium hypochlorite (Jung, Yoon et al. 2004; Rouaux, Causerand et al. 2006).

2. Surface Modification with physical processes:

Surface modification of membrane with physical processes is widely applied and mainly focuses in fixing defects on surface. It is especially common for polymer hollow fiber membranes for gas separation application as presence of defect surface will significantly reduce the selectivity of membrane (Wang, Li et al. 2000; Cao, Chung et al. 2004; Qin and Chung 2004; Peng, Widjojo et al. 2012; Feng, Khulbe et al. 2013). Hollow fiber spinning is complex process that depends on various parameters simultaneously. Many times, the extruded hollow fibers have minor defects on the surface (Dong, Li et al. 2010) such as cracks and pores. The complication of producing a defect-free hollow fiber has led to introduction of physical surface modification as an effort of improving the separation performance of hollow fiber.

2.1 Heat treatment:

Heat treatment and plasma treatment are examples of physical process that modifies both the surface and bulk property of membranes. Heat and plasma treatment fixes the surface defects and controls the pore size and removing residual solvent from the bulk of polymer membrane (Drioli and Giorno 2010; Liu, Xiao et al. 2011; Peng, Widjojo et al. 2012). Liu et al. did a full study on the effect of heat treatment on morphology and performance of polyurethane-based (PU) hollow fiber extruded through melt-spinning method (Liu, Xiao et al. 2011). During the experiment, hollow fiber was stretched and post-treated in a water bath with various different temperatures followed by a drying process at 20°C in dry air oven for 48hours (Liu, Xiao et al. 2011). They concluded that PU hollow fiber post-treated in 50°C water bath for a minimum of 50 minutes under stretched condition is optimum, where the pore size of membrane decreased and polymer chains mobility improved, forming narrowed, long surface pores and some even closed (Liu, Xiao et al. 2011). In a review reported by Peng et al., it was summarized that about six researchers agreed that heat treatment is one of the common methods to enhance carbon dioxide gas selectivity and improve anti-plasticization properties of hollow fiber (Peng, Widjojo et al. 2012). However that would need to be trade off with carbon dioxide permeability (Peng, Widjojo et al. 2012).

2.2 Coating:

Other than heat and plasma treatment, coating is another physical process of surface modification. most common post-treatment process used by researcher to improve gas separation properties of hollow fiber, but many times cause undesired extra resistance towards gas flow and subsequently reduces the permeability (Chung, Teoh et al. 1997; Cao, Chung et al. 2004; Dong, Li et al. 2010; Feng, Khulbe et al. 2013). This technique was known to be invented by Henis and Tripodi to restore the selectivity of a defective ultrathin dense-selective layer (Peng, Widjojo et al. 2012). This technique is widely used until present where hollow fiber will be dip coated in a solution with composition of 3wt% polymethylsiloxane and 97wt% n-hexane for 2 minutes followed by 2 days curing is a common mixture used for dip coating (Cao, Chung et al. 2004; Qin and Chung 2004). Wang and Teo also used a similar technique but coated hollow fiber with solution composition of 3wt% polydimethylsiloxane in n-pentane for 5 minutes, followed by curing for 1 day (Wang, Li et al. 1996). Other than that, other solution such as mixture of silicone elastomer and curing agent (Sylgard-184) in n-pentane is also reported (Wang, Teo et al. 2002). Silicon coating was known to be able to seal defects, and improve selectivity but it may also hinder permeability due to flux resistance (Chung, Teoh et al. 1997; Wang, Li et al. 2000; Wang, Teo et al. 2002; Cao, Chung et al. 2004; Qin and Chung 2004; Peng, Widjojo et al. 2012).

It is worth mentioning that Hester and Mayes had suggested that an ideal strategy for surface modification of polymer membranes should have the following attributes: 1) a high degrees of surface coverage with good long-term stability, 2) high membrane permeability, 3) coverage of the internal pore channels as well as the separation surface, 4) low materials and processing costs, 5) minimal impact on bulk membrane properties, and 6) flexibility in the section of surface chemistry (Hester and Mayes 2002). In these physical processes introduced for surface modification of polymer membranes, heat and plasma treatment has impact the bulk membrane property by causing pore sizes...
decreases after the treatment process. This has resulted in permeability reduction in conjunction to the improved selectivity contributed by the modified defect-free surface. Silicon dip coating process on the other hand does not impact the bulk membrane property. However, the coating layer has affected the coverage of internal pore channels as well as the separation surface. This causes a poor accessibility between two phases, and subsequently causes a trade-off between selectivity and permeability.

3. Conclusion:
This review reports different types of polymer post-treatment techniques and they are all related to surface modification. It is clearly shown that chemical process is a better approach for an ideal strategy for surface modification of polymer membrane as compared to physical process. It is clearly shown that chemical process is a better approach for an ideal strategy for surface modification of polymer membrane as compared to physical process. However, the present chemical processes, especially surface grafting methods are mostly done for water filtration membranes, focuses in enhancing the hydrophilic property of membrane. The introduction of chemical cross-linking method on the other hand focuses in reducing the plasticization effect in gas separation application. Other than chemical cross-linking, surface modification through physical processes are also widely used for membrane in gas separation application. However, these methods result in non-ideal surface modification of polymer membrane, which causes a significant trade-off between permeability and selectivity which is highly due to the low accessibility between modified surface and membrane bulk. From this review, it can be concluded that the solution of producing an ideal membrane with high selectivity and enhanced permeability is through chemical surface modification. The chemical surface modification should be able to control the crystalline structure arrangement, which is parallel to the direction of diffusion. This would allow a higher accessibility between surface and bulk of membrane, minimizing or eliminating the potential trade-off between selectivity improvement and permeability. In addition to that, incorporation of additives on surface of membrane could potentially enhance the chemisorption property of membrane surface, which further improve the permeability of membrane.

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