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The effects of mechanical and chemical modification of TiO_2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes

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ABSTRACT

Recently, TiO_2 nanoparticles blended within polymeric membranes have shown to provide improvements in fouling performance. However, agglomeration of nanoparticles remains as one of the major obstacles for generating a uniform surface, and also the mechanisms for improved fouling performance has yet to be elucidated. In this study, mechanical and chemical modification approaches were adapted using Degussa P25 TiO_2 nanoparticles to improve their dispersion. Afterward, modified TiO_2 nanoparticles were incorporated into polyethersulfone based in-house membranes and their effect on microstructure, surface chemistry, and fouling performance were investigated. Different techniques such as SEM, EDX, TGA, DSC, AFM, FTIR, contact angle goniometry, molecular weight cut-off, static protein absorption and surface free energy measurement were applied to characterize and explore the effect of different factors on fouling performance. The results showed that good dispersion of nanoparticles in the membrane was achieved after both chemical and mechanical modifications of particles, as a result of less agglomeration. The combination of chemical and mechanical modifications was found to have significant effects on surface free energy, roughness, surface pore size and protein absorption resistance as well as hydrophilicity. While previous researchers believe that the increase in hydrophilicity is the most likely reason for improvement in fouling performance, these other parameters such as changes in membrane morphology and local surface modifications may contribute just as much to greater fouling resistance when the effects of unmodified and modified titania were compared.

1. Introduction

In recent years, the incorporation of inorganic additives into polymeric materials has expanded markedly for filtration and gas separation membranes. A variety of nanoparticles have been introduced to modify organic membranes, such as SiO_2, Al_2O_3, Fe_3O_4, ZrO_2 and TiO_2 [1–4]. Among them, TiO_2 has received the most attention because of its good physical and chemical properties, availability as well as its potential antifouling abilities [5–7].

Polyethersulfone (PES) is one of the polymeric materials which commonly used in microfiltration [8–10], ultrafiltration [11,12] as well as nanofiltration membranes [13]. Its wide application is a result of good chemical and thermal resistance, easy processing and environmental endurance. However, its poor antifouling properties affect its application and usage life [14]. Several studies investigated incorporation of TiO_2 into PES membranes. There are two main approaches for making nanocomposite TiO_2 PES membranes: blending the nanoparticles in the membrane [8,15,16] and coating the nanoparticles on the surface of the membrane [14,17,18].

The focus of this paper is on the former approach with the view of improving membrane performance by improving the dispersion of widely available commercial titania powders. Compare to coating approach this method is simpler since the particles are added to the membrane casting solution. Furthermore, coating of membranes can lead to some significant undesirable changes in membrane permeability due to pore narrowing or plugging. The effect is more critical in case of UF membranes due to smaller pore size. There is also potential of delamination of a coating layer.

In this approach, TiO_2 nanoparticles are dispersed in a casting solution and then membranes are cast by phase separation method which was widely used for the preparation of polymeric membranes. Phase separation methods are categorized by four major

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techniques; thermal induced phase separation (solvent evaporation), vapour induced phase separation, control evaporation and immersion-precipitation or non-solvent induced phase separation [19]. In immersion-precipitation which was applied in this study, a solution of polymer and organic solvent is cast on a substrate and immersed in a coagulation bath to form the membrane [20,21].

Although the primary particle size of commercial TiO_2 nanoparticles such as Degussa P25 is about 20 nm, its particle size as powder or in dispersion is in the range of hundreds of nanometres due to agglomeration. This agglomeration leads to not only the uneven distribution in the membrane but also potential reduction in antifouling abilities of TiO_2 particles by changing parameters such as membrane topography and hydrophilicity as well as self cleaning properties of particles [22]. The presence of hills and valleys on the surface of a rough membrane increases the sites which favor the attachment of foulants on the surface of the membrane [23]. It is also evident that membranes with higher hydrophilicity are less prone to fouling than hydrophobic membranes since it absorbs more water molecules than foulant molecules. It was shown that TiO_2 nanoparticles can effectively degrade organic materials under UV light. Agglomeration of particles reduces active sites for degradation of organic materials [24]. All of these deficiencies caused by agglomeration negatively affect the effective utilization of TiO_2 nanoparticles in the nanocomposite membranes. To overcome agglomeration, researchers have tried to use the *in situ* formation of TiO_2 within the PES matrix by sol–gel technology [16]. Using this technique the nanoparticle size can be controlled by varying various parameters including the choice of organic additives [25]. However, agglomeration still exists even for the *in situ* formation of particles due to the poor interfacial interactions between the hydrophilic nanoparticles and hydrophobic polymer and high surface energy of particles [26]. In addition, due to the difficulty and complexity of sol–gel reactions and also cost issues, the potential of using commercial TiO_2 nanoparticles to improve PES membrane properties provides an attractive alternative.

In order to avoid agglomeration, two methods have been generally tried: dispersion of nanoparticles by conventional methods such as sonication and grinding (mechanical modification) and surface pre-treatment approaches for nanoparticles (chemical modification). Most researchers applied the former approach that is based on the shear forces provided by conventional mixers and/or a normal sonicators [6,17]. Since the intra-nanoparticles interaction are very strong, it is hard to break the intra-particle interactions with conventional mixing [27]. Thus, it seems crucial to have a stronger dispersion technique for fabrication of nanocomposite membranes. In general, surface modifications as a complementary approach to mechanical modification of particles has been used for minimizing particle/particle interaction in preparation of polymer composite with microfillers [26]. Recently, with development in nanotechnology, incorporation of chemically modified or functionalized nanoparticles into polymeric materials has become a topic of great interest. In this approach, the inorganic particles are coated with organic coatings by physical and/or chemical interactions between the particles and organic modifiers. In physical treatment, the reaction between organic surfactant or polymer and particles results a weak secondary forces such as van der Waals, hydrogen and electrostatic forces while in the chemical treatment there is a strong covalent attachment. However, the resultant bond is often a combination of chemical and physical reactions. One common method to apply technique for chemical modification of inorganic particles is treatment by silane coupling agents such as 3-methacryloyloxypropyl trimethoxysilane (MAPTMS), methacryloyloxy methylenemethyl diethoxysilane (MMDES), and 3-aminopropyltriethoxysilane (APTES) [28]. Silane coupling agents can effectively reduce the hydrophilic nature and surface energy of the particles consequently reducing agglomerations and increasing matrix interactions [26,28]. Silanization treatment by APTES was targeted in this study for chemical modification of TiO_2 particles.

Li et al. investigated the effect of incorporation of an unmodified Degussa P25 (21 nm particle size, 80% anatase) on the PES microfiltration membrane in terms of surface chemistry and morphology [8]. They found that the addition of TiO_2 could produce membranes with higher hydrophilicity, better thermal and mechanical stability as well as better permeation performance. Although the maximum flux and pore size were obtained when the TiO_2 content was 4–5 wt.%, they recommended 1–2 wt.% TiO_2 nanoparticles in the casting solutions as the optimum level. At higher concentrations agglomeration of particles led to lower stability in membrane performance. Consequently, they had to compromise the higher flux in favor of stability as a result of agglomeration. The fouling performance of the TiO_2 blend membrane was not, however, investigated in their work.

The effect of unmodified Degussa P25 TiO_2 nanoparticles on the performance of PES ultrafiltration membrane for the milk industry was also investigated by Rahimpour et al. [17]. They incorporated the inorganic particles into a PES membrane by two approaches: blending and coating. In their blending approach, contrary to the results presented by Li et al., the initial pure water flux of TiO_2 blend membranes decreased; however, the membrane antifouling property and long term flux stability were enhanced for up to 4% TiO_2 content and a further increased of TiO_2 concentration did not change the antifouling properties of the membranes. The authors believe that during immersion precipitation TiO_2 nanoparticles could plug pores at higher concentrations and consequently hinder the interaction between PES and solvent molecules. The addition of TiO_2 to membranes also increased the hydrophilicity of their membranes, however the effects were not significantly changed by varying the inorganic content. The quality of dispersion and the effect of TiO_2 on the surface chemistry of the membranes were not investigated in their work.

TiO_2 *rutile* nanoparticles (30 nm), modified with γ-aminopropyl triethoxysilane, were used for modification of PES ultrafiltration membrane by Wu et al. [15]. The addition of TiO_2 nanoparticles improved the hydrophilicity, thermal stability, mechanical strength and anti-fouling ability of membrane. The best performance was achieved at 0.5 wt.% TiO_2 content while at higher TiO_2 content, the defective pore structure of the membranes and the decline of the performances were observed. Rahimpour et al. and Li et al. both reported that Degussa P25 with 80% *anatase* phase could change the structure of the membrane significantly, while Wu et al.'s results showed that the 30 nm *rutile* TiO_2 nanoparticles did not affect the structure of the membranes significantly.

In reviewing the previous work it is clear that the adverse effect of particle agglomeration has been overlooked in many studies. In fact, an ideal nanocomposite membrane is a membrane which is free of any agglomerations. The mechanism for improved fouling performance also has yet to be elucidated. In addition, the effect of particle size distribution, mechanical and chemical modification of particles on the membrane structure and surface chemistry (hydrophilicity, roughness and protein absorption) in conjunction with fouling performance has not been investigated. In this study, an effective mechanical modification using different dispersion techniques coupled with a chemical modification of particles (silanization treatment by APTES) was applied to reduce agglomeration of Degussa P25 TiO_2 nanoparticles. The effect of modifications on the surface chemistry, membrane structure and fouling performance of ultrafiltration PES membrane was investigated and the contributing factors which have the most influence on the fouling mitigation were determined.