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Preparation and characterization of polycarbonate/thermoplastic polyurethane blend membranes for wastewater filtration

Saeed Nazemidashtarjandi, Seyyed Abbas Mousavi*, Dariush Bastani

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Iran

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ABSTRACT

The polycarbonate (PC)/thermoplastic polyurethane (TPU) blend membranes were prepared by phase inversion process applied to membrane bioreactor (MBR) to investigate the fouling characteristics. The impact of TPU and poly (vinylpyrrolidone) PVP concentration in polymer dopes on membrane structure, morphology, and performance were studied. The flat sheet fabricated membranes were characterized by scanning electron microscope (SEM), water contact angle (WCA), membrane surface roughness measurements and mechanical strength. The membrane performance was investigated at subcritical operating conditions. Pure water and critical flux through the fabricated membranes were measured for better understanding of the filtration and antifouling properties in MBR. The results showed that the membrane with polymer composition of 85/15 (PC/TPU) presented better performance in activated sludge throughout critical flux than that of other prepared membranes. Therefore, different dosages of PVP were introduced in this composition to study the effect of the additive in novel blend membranes. Likewise, the results indicated that TPU played the role of pore formation agent during the NIPS process, and the mean pore size of the membranes were increased with the increment in TPU content, which led to higher water flux. Finally, SEM images showed that the sponge-like structure formation was intensified by addition of TPU in casting solution. However, the finger-like structure was found to increase with introduction of 0.5 wt.% PVP content into the casting solution. This study highlights the potential of PC membrane application in wastewater treatment with incorporation of TPU and PVP into PC membrane matrix.

1. Introduction

The membrane bioreactor process has been taken into account as an alternative for conventional activated sludge treatment. However, one of the most significant challenges in membrane bioreactors (MBRs) is the membrane fouling which deteriorates the permeability of membrane; therefore, causes an increment of energy consumption in an MBR [1–4]. Membrane fouling highly depends on the hydrophobicity of the membrane in a MBR [5]. Polycarbonate (PC) is an engineering thermoplastic with good chemical property, good impact strength and dimensionally and thermally stable [6]. Furthermore, the inherent hydrophilicity of Polycarbonate due to its structure leads to improve anti-fouling property of membrane. However, preparing PC membrane with phase inversion process leads to a low membrane flux due to its structure. Some efforts have been done to improve membrane properties such as graft polymerization [8], plasma [9], blending two polymers [10] and so forth. By taking into account all the aforementioned factors, blending two polymers endowed the advantage of two polymers to the blend membrane which attained by casting blend solutions of PC and other polymers [11]. Therefore, blending method has been employed in this study to increase PC membrane flux.

Polycarbonate could be dissolved in halogen derivatives such as chloroform and dichloromethane. However, N-methylpyrrolidinone(NMP), N,Ndimethylacetamide (DMAc), and tetrahydrofuran (THF) are solvents which are appropriate for industrial membrane separation applications. PC exhibits brittleness under sharp impact due to its rigid molecular chains and its high glass transition temperature (T_g). Likewise, it is highly difficult to process polycarbonate as a membrane in wastewater treatment [7]. Bodzek et al. prepared the porous polycarbonate membrane via phase inversion process in which the gelation applied in an atmosphere of air saturated with water vapor. They investigated its application through the separation properties of polycarbonate membrane [6].

In recent years, there has been an increasing amount of literature on blending PC with different polymers. Wang et al.

* Corresponding author.
E-mail address: musavi@sharif.edu (S.A. Mousavi).

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studied the impact property of poly(butylene terephthalate) (PBT)/polycarbonate (PC) blends. They also used the magnesium oxide (MgO) as a trans-esterification catalyst and BPM520 (a commercial acrylic-based core-shell structure impact modifier) as a toughening agent to prepare PBT/PC blends [12]. Their results showed that the impact property of the PBT/PC blends with 5% BPM520was increased almost twice as much as pure PBT/PC. Moreover, they showed that in the presence of MgO and only 5 wt% of BPM520, the PBT/PC blends possess excellent toughness. Huang et al. investigated the morphological, thermal and mechanical properties of poly(methyl methacrylate) (PMMA)/polycarbonate (PC) blends, and used catalyst and hydrophilic silica nanoparticles in compatibilizing the PMMA/PC blends [13]. They found that both catalyst and nanoparticles refined the morphology of PMMA/PC. Also, they showed that with addition of nanoparticles, the mechanical property of blends was increased from 25% to 50% with addition 3 wt% of nanoparticle. Tan et al. studied polycarbonate (PC)/polyurethane elastomer (PUEs) blends in which PUEs have been synthesized and melt blended with polycarbonate [7]. Their results indicated that the PC and PUEs compatibilities were highly influenced by the molecular weight of PUEs. They also found that the PC was completely compatible with PUEs when the NCO/OH ratio for the PUEs prepolymer was 2:1. However, far too little information has been paid to polycarbonate and its blending with other polymers in water and wastewater treatment.

Researches such as that incorporated polymeric blend membranes for modification of filtration membranes have attracted attention significantly. Li et al. investigated the surface hydrophiliciy, anti-fouling properties and mechanical strength of poly(vinylidene fluoride) (PVDF)/poly(*p*-phenylene terephtalamide)PPTA blend membrane via in situ polycondensation of *p*-phenylene diamine (PPD) and terephthaloyl chloride (TPC) in PVDF solution [14]. They showed that the fouling mitigation and hydrophilicity of blend membranes were improved when applied in the MBR. They also studied the thermodynamic and kinetics of membrane solution and observed that PPTA acted as demixing enhancer. Jiang et al. fabricated the ultrafiltration blend membrane poly(vinyl chloride) (PVC)/poly(vinyl formal) (PVF) via phase inversion process [15]. Their results revealed that the PVF played the role of pore former and increased the membrane pore size. However, the hydrophilicity of membrane was greatly increased due to the spontaneous surface segregation. Dan Li et al. prepared asymmetric blend hollow fiber membranes from a casting solution contained poly(vinylidene fluoride) (PVDF), poly(vinylpyrrolidone) (PVP) and thermoplastic polyurethane (TPU). They studied the effect of PVP as an additive on the morphology and crystal structure of PVDF/TPU blend membranes via non-solvent induced phased separation process (NIPS) [16]. The results indicated that PVP worked as demixing enhancer with addition of PVP into PVDF/TPU casting solution. Also, they showed that at high concentrations of PVP in the PVDF/TPU solutions, macro-void formation suppressed and the flux decreased. Mohan et al. studied the performance and the application of cellulose acetate-polyurethane blend membranes [17]. They assessed the effects of polymer composition and additive concentration on membrane compaction. Their results showed that PVP played a key role in controlling of pore size and miscibility of blend membranes. Furthermore, the blend membranes perform well for the separation of proteins and metal ions. Ultrafiltration membranes from poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) were fabricated by Peinemann et al. [18]. They reported that the water permeability highly increased by addition of one percent PMMA and also elevated the size of finger-like cavities.

Polyurethane with physical properties such as high tensile strength, anti-abrasion, and high versatility in chemical structures has been widely used [19]. Furthermore, polyurethane acted as pore former in the CA/PU blends and as the concentration of polyurethane in blending solution increased, the pure water flux increased linearly [17]. Recently, PVP is extensively used for structure control of membranes and improved the permeability and selectivity of ultrafiltration membranes [19,20]. A number of studies have found that not only PVP works as demixing enhancer, but also hinders forming macro-pore size in membrane preparation via the phase inversion process [21–23].

So far, no research has been found that studied preparation of PC/TPU blend membranes for activated sludge according to our realm of knowledge. Therefore, PC/TPU blend membranes were prepared via non-solvent induced phase separation by blending TPU into PC with different ratios. In this study, TPU played the role of pore formation agent during the NIPS process, and the mean pore size of the blend membranes are increased with increased dosage of TPU. Moreover, the PVP was used in PC/TPU solution systems in order to control the pore size and membrane structure. Pure water flux and critical flux were measured for better understanding of membranes filtration applied in a MBR for wastewater treatment. Membranes were characterized by SEM to study their morphology. Membranes surface was studied through contact angle and AFM analysis to investigate anti-fouling properties. Mechanical properties were investigated with incorporation of TPU and PVP in the polycarbonate matrix. Surface compositions were also studied via FTIR-IR analysis. In summary, the aim of this study was to fabricate novel blend membrane in application of activated sludge filtration and develop persistent antifouling properties of fabricated membranes on subcritical condition.

Table 1
Compositions of prepared membranes.

Membrane	Composition (16.5 wt.%)		PVP (wt.%)	NMP (wt.%)
	PC (%)	TPU (%)		
#M_1	100	0	0	83.5
#M_2	95	5	0	83.5
#M_3	90	10	0	83.5
#M_4	85	15	0	83.5
#M_5	80	20	0	83.5
#M_6	75	25	0	83.5
#M_7	85	15	0.25	83.25
#M_8	85	15	0.5	83
#M_9	85	15	1	82.5

2. Experimental

2.1. Materials

Bisphenol-A polycarbonate (PC, M_w = 17 kDa) was procured from Khozestan Petrochemical Co., Iran. Thermoplastics polyurethane (TPU, LPR 7025) was obtained from Coim Group Co., Italy. N-Methyl-2-pyrrolidone and polyvinylpyrrolidone (PVP, M_w 40 kDa) were supplied from Daijung Co., Korea.

2.2. Membrane preparation

2.2.1. Preparation of PC/TPU blend membrane

The blend membranes were prepared by the solution of blend polymers of PC/TPU (16.5 wt.%) with different compositions of polymers at ambient temperature under stirring for 5 h. The blending ratio of PC/TPU varied empirically in the range of 100/0, 95/5, 90/10, 85/15, 80/20 and 75/25. The NMP was used as solvent, and PVP concentration was varied from 0 to 1 wt.%. PVP was used as an additive into casting solution. The phase inversion which is a well-known process was employed to prepare PC/TPU blend asymmetric membranes. The blending ratios of PC/TPU were given in Table 1. The final solutions of the polymer blend were sonicated for 20 min to