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Al_2O_3 and TiO_2 entrapped ABS membranes: Preparation, characterization and study of irradiation effect

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ABSTRACT

The present study focuses on the aluminum oxide (Al_2O_3) and titanium oxide (TiO_2) entrapped acrylonitrile–butadiene–styrene (ABS) membranes prepared from phase inversion method. The effect of Al_2O_3 and TiO_2 nanoparticles on the hydrophilicity, tensile strength, thermal stability, permeate flux, and rejection of wastewater pollution indices was investigated. Some of the membranes were exposed to ultraviolet (UV) irradiation. Al_2O_3 and TiO_2 nanoparticles generally improved performance of the membranes. Thermal stability and tensile strength of the membranes were also enhanced in the presence of the nanoparticles. Increasing the nanoparticles concentration increased viscosity of the casting solutions. The UV irradiated membranes had better performance than the non-irradiated ones.

1. Introduction

ABS copolymer is widely used owing to its good mechanical properties, chemical resistance and processing characteristics and also relatively low cost [1]. Unfortunately, some inappropriate features may impose the restrictions on application of ABS copolymer, such as the acrylonitrile migration to water coagulation bath during phase inversion process. In our previous work, heptane (C7) coagulation bath was used to get over this negative point [2]. In addition, light-induced degradation of polybutadiene is the cause of weathering-related ABS problems [3]. Rodriguez-Tobias et al. [4] studied the effect of zinc oxide (ZnO) nanoparticle as a UV shield in the ABS based nanocomposite produced by in situ mass-suspension polymerization. Moreover, one of the special requirements for ABS is improvement of thermal stability property according to its intrinsic flammability. Hence, other researchers surveyed the improvement of ABS thermal stability by using lead sulfide (PbS) and tin sulfide (SnS) [1,5].

TiO_2 nanoparticles have many advantages such as UV resistance, super hydrophilicity, good chemical stability, as well as antifouling, antibacterial and photocatalytic properties [6–10]. Generally, TiO_2 is highly noticed among inorganic oxide nanoparticles according to its special features such as antifouling and antibacterial properties and also good chemical stability [9]. Furthermore, the photocatalysis and hydrophilicity for TiO_2 can take place on the same surface simultaneously [10]. In the present study, Al_2O_3 was also added to the casting solution as a secondary metal oxide nanoparticle in order to investigate its impact on performance of the entrapped membranes. Al_2O_3 is inexpensive, nontoxic, available, stable, hydrophilic, and resistant [11,12]. Arsuaga et al. [13] showed that Al_2O_3 particles were distributed with the highest number in the vicinity of polyethersulfone (PES)-Al_2O_3 membrane surface due to low density of Al_2O_3. However, metal oxide particles with higher density, i.e. TiO_2 and ZrO_2, were found more in the intermediate and bottom zones of the membrane, respectively. Therefore, Al_2O_3-entrapped membrane had more hydrophilic centers (metal oxide particles) in the vicinity of its surface.

Regarding the aforementioned useful explanations, the present research was proposed with the aim of preparing Al_2O_3 and TiO_2 entrapped ABS membranes by phase inversion method. Variations of hydrophilicity, tensile strength, thermal stability and membrane performance were investigated in terms of the concentrations of TiO_2 and Al_2O_3 in the casting solution. The effects of UV irradiation in the presence and absence of Al_2O_3 and TiO_2 nanoparticles were also studied.

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Table 1
Composition and tensile strength of the prepared membranes.

Membrane	ABS (wt.%)	TiO_2 (wt.%)	Al_2O_3 (wt.%)	Solvent (wt.%)	UV time (min)	Tensile strength (MPa)
M1	19	0	0	81	0	9.06 ± 0.02
M2	19	1	0	80	0	9.78 ± 0.09
M3	19	2	0	79	0	10.08 ± 0.05
M4	19	3	0	78	0	11.38 ± 0.05
M5	19	3	0	78	5	11.38 ± 0.02
M6	19	3	0	78	10	11.38 ± 0.06
M7	19	3	0	78	15	11.38 ± 0.01
M8	19	0	0	81	15	9.06 ± 0.07
M9	19	3	0.5	77.5	0	12.81 ± 0.04
M10	19	3	1	77	0	13.96 ± 0.02
M11	19	3	1.5	76.5	0	14.28 ± 0.08
M12	19	3	1	77	15	13.96 ± 0.04

2. Materials and methods

2.1. Materials

ABS was supplied from Tabriz Petrochemical Company. TiO_2 nanoparticles with size of 25 nm were purchased from Degussa. Al_2O_3 nanoparticles with size of 20 nm were provided by Iranian Nanomaterials Pioneers Company. 1-Methyl-2-pyrrolidone (NMP) was supplied from Merck as solvent. Car wash wastewater was obtained from a local car wash and was used as treatment test feed.

2.2. Membrane preparation

Neat ABS membranes and Al_2O_3 and TiO_2 entrapped membranes were prepared via phase inversion induced by immersion precipitation technique. The homogeneous solutions of ABS in NMP were prepared in different concentrations of Al_2O_3 and TiO_2 using a magnetic stirrer at 200 rpm and room temperature. The composition of different casting solutions for the prepared membranes is listed in Table 1. The solutions were cast on a glass plate by using a film applicator. The glass plate was immediately moved to the coagulation bath containing C7 as nonsolvent for immersion precipitation. Some of the membranes were exposed to the UV irradiation with UV light lamp for 5, 10, and 15 min. This lamp with the power of 15 W (TUV15WSLV) was purchased from Philips. The absorbance of UV light irradiated to the membrane surface was measured at the wavelength of 254 nm.

2.3. Membrane characterization

2.3.1. Thermogravimetric analysis (TGA)

Thermal degradation was conducted by a thermalgravimetric analyzer (TGA/DSC 1, Mettler Toledo). 1 g of sample was heated from 25 to 800 °C at a heating rate of 5 °C/min under N_2 atmosphere with a flow rate of 20 ml/min.

2.3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the virgin ABS membranes prepared in C7 coagulation bath were recorded by using a Thermo Nicolet Avatar 370 FTIR. All samples were scanned with a 4 cm^{-1} resolution between 4000 and 500 cm^{-1}.

2.3.3. Viscosity measurement

The rheological properties and viscosities of the casting solutions with different concentrations of TiO_2 and Al_2O_3 nanoparticles were investigated by using a Brookfield LVDV-III Ultra rheometer at 25 °C. The relationship of viscosity and shear rate for each casting solution was obtained in the shear rate range of 5–50 s^{-1}.

2.3.4. Contact angle measurement

In order to examine surface hydrophilicity of the prepared membranes, water contact angle was measured by OCA 15 plus, Dataphysics, Germany. Deionized water was used in all the measurements. To minimize the experimental error, the contact angles were measured at four random locations for each sample and the arithmetic average value was reported.

2.3.5. Scanning electron microscopy (SEM)

SEM was used to prepare cross-sectional and surface images of the prepared membranes. To have a better view of the cross section, the membranes were cooled in liquid nitrogen and then fractured. Prior to preparing the images, all membranes were sputter coated with gold for providing good electric conductivity. The images were obtained by KYKY-EM3200 microscope.

2.3.6. Tensile strength test

In order to prepare the sample for tensile strength test, all the membranes were cut out in same shapes. The samples were stretched to the breaking point with Zwick tensile test machine at a speed of 1 mm/min. For each test, four samples were used and the arithmetic average value of tensile strength was reported.

2.3.7. Flux and retention

The treatment performance of the prepared membranes was evaluated by means of an experimental setup. The flat sheet membranes with 38 cm^2 effective area were used in a stainless steel membrane module. The permeate flux and also the rejection of pollution indices of car wash wastewater were evaluated at the transmembrane pressure (TMP) of 2 bars and room temperature. The pollution indices of turbidity, total dissolved solids (TDS) and chemical oxygen demand (COD) were determined for the feed and permeate in order to calculate the rejections. Each of the experiments was repeated four times.

3. Results and discussion

3.1. Thermal stability of the membranes

The trends of the membranes thermal stability by addition of the nanoparticles are followed in Fig. 1. M1, M4 and M10 samples were selected for thermal analysis with a heating rate of 5 °C/min. The results demonstrated that the membrane thermal decomposition temperature increased from 427.8 °C to 431.5 °C by addition of 3 wt.% TiO_2 (M4). It also increased to 435.7 °C by addition of 3 wt.% TiO_2 and 1 wt.% Al_2O_3 (M10). Similarly, TiO_2 delayed thermal decomposition temperature of the cellulose acetate membrane [14]. TiO_2 and Al_2O_3 increased thermal decomposition temperature of the PES membrane as well [13]. Furthermore, Yousefi et al. [5] reported the thermal decomposition temperature of 416 °C for the ABS which is near to the number reported in the present