

EFFECTS OF COAGULATION-BATH TEMPERATURE AND MONTMORILLONITE NANOCLAY CONTENT ON ASYMMETRIC CELLULOSE ACETATE BUTYRATE MEMBRANES

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Abstract—A major problem with polymeric membranes is low hydrophilicity and consequently a tendency to fouling. Preparing composite membranes is one way to improve the properties and performance of the neat membrane. In the present study, the effects of coagulation-bath temperature (CBT) and the hydrophilic nanoclay concentration of montmorillonite (MMT) on the morphology and performance of asymmetric cellulose acetate butyrate (CAB) membranes were investigated. The membranes were prepared *via* phase inversion induced by immersion precipitation in a water-coagulation bath. The morphology of the membranes prepared was studied by scanning electron microscopy (SEM). The permeation performance of the membranes prepared was studied by experiments using pure water and bovine serum albumin (BSA) solutions as feeds. The results showed that the membrane thickness and pure water flux (PWF) were increased by adding up to 2 wt.% MMT nanoclay to the casting solution. These two parameters decreased with further addition of MMT, however. In addition, the results obtained in the case of filtration of BSA solution indicated that the addition of MMT in the casting solution increased permeate flux and reduced BSA rejection slightly. Furthermore, increasing the MMT nanoclay concentration in the casting solution increased pure water flux recovery and consequently decreased the fouling. Decreasing the CBT in the presence of MMT during membrane preparation resulted in the formation of a more porous structure and consequently increased the flux and simultaneously decreased the BSA rejection.

Key Words—Cellulose Acetate Butyrate, Coagulation Bath Temperature, Flux Recovery, Membrane Preparation, MMT Nanoclay.

INTRODUCTION

Clay polymer nanocomposites represent a new class of materials that serve as alternatives to conventionally filled polymers in which nano-sized inorganic fillers are dispersed in the polymer matrix, offering tremendous improvement in the properties of the polymers (Soundararajah *et al.*, 2010; Nguyen and Baird, 2006; Ray and Okamoto, 2003). The interest in production of clay polymer nanocomposites stems from the large spectrum of possible applications. Features such as greater thermal, mechanical, and chemical resistances, barrier properties, low expansibility, and ease of processing can be achieved through use of this type of nanocomposite (Soundararajah *et al.*, 2010; Huang *et al.*, 2011; Anadão *et al.*, 2010, 2013; Wang *et al.*, 2011; Vora and Vora, 2006).

One of the most widely used nanoclays is MMT, a common clay mineral from the smectite family. A rich intercalation chemistry allows MMT to be modified chemically and to become compatible with various polymers (Adoor *et al.*, 2006). Montmorillonite can be introduced into polymer nanocomposites because of its large surface area, unique two-dimensional nanostructure, and programmable layered response (Xing *et al.*,

2011). Because MMT is a hydrophilic clay (Anadão *et al.*, 2010; Hashemifard *et al.*, 2011; Yoon *et al.*, 2007), addition to polymers can be used not only to produce the nanomaterials with known improved properties, but also to enhance the hydrophilicity and consequently to reduce the tendency to fouling. The fouling phenomenon is undesirable because it results in reduction in flux and in the life of the membrane as well as increases in the operating costs. Therefore, the modification of the membranes is necessary for reducing the membrane fouling (Shekarian *et al.*, 2013).

Cellulose acetate butyrate membranes are frequently employed in membrane separation processes due to their tolerance of chlorine and chemical stability (Fu *et al.*, 2008; Sabde *et al.*, 1997). Their low hydrophilicity (Shibutani *et al.*, 2011) can cause fouling on the membrane surface, however, and can reduce separation productivity.

Published research articles on the modification of CAB membranes are rare (Hajasgarkhani *et al.*, 2013). To the best of the authors' knowledge, no previous articles have been published on the effects of addition of nanoclays as hydrophilic additives or on the variation of CBT to improve the permeation and reduce the fouling tendency of CAB membranes.

The purpose of the present study was to prepare modified CAB membranes with greater hydrophilicity which can show greater resistance to the fouling phenomenon. In the present study, MMT nanoclay was

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selected as a hydrophilic additive to blend with CAB in the membrane-preparation process. The effects of MMT concentration and variation of CBT on the morphology, PWF values, BSA rejection, and pure water flux recovery of the CAB membranes were investigated in detail.

MATERIALS AND METHODS

Materials

Cellulose acetate butyrate with $M_n \approx 65,000$ and MMT nanoclay with molecular weight of 180.1 g/mol were supplied by Sigma Aldrich (Saint Louis, USA). Dimethylformamide (DMF) was purchased from Akkim Company (Istanbul, Turkey) and used as a solvent. Polyethylene glycol (PEG) with a molecular weight of 25,000 g/mol was obtained from Merck (Frankfurt, Germany). Bovine serum albumin was obtained from Equitech-Bio Inc. (Texas, USA). Distilled water was used as the non-solvent in all experiments.

PREPARATION OF MEMBRANE

Two types of membranes, neat cellulose acetate butyrate and cellulose acetate butyrate/montmorillonite, were prepared here *via* phase inversion using the immersion precipitation method.

The different concentrations of MMT nanoclay, *i.e.* 2, 4, and 6 wt.% were added to the DMF solution with 2 wt.% of PEG additive as a pore former. Cellulose acetate butyrate (18 wt.%) was dissolved in the aforementioned suspension at room temperature along with stirring (mechanical stirring for 10 h at 200 rpm) to obtain a uniform and homogeneous casting solution. After formation, the homogeneous solutions were held at ambient temperature for 6 h to remove air bubbles. Afterward, the prepared homogeneous solutions were cast using a film applicator with 200 μm clearance gap on a glass plate substrate at room temperature. After 5 s of exposure to air, the glass was immersed immediately in the bath of non-solvent.

The percent of CAB, solvent, MMT nanoclay, and PEG and also the preparation conditions are summarized in Table 1.

Membrane characterization

Scanning electron microscopy. The membrane surfaces and cross sections were examined using a KYKY-EM3200 scanning electron microscope (SEM) (Beijing, China). All specimens were freeze-dried and coated with a thin layer of gold before examination. Each cross section was prepared by the fracturing of the membranes in liquid nitrogen. The coated samples were then fixed on plates with adhesive, and photomicrographs were taken in very high-vacuum conditions at 25 kV.

Flux and rejection measurements. The flux and rejection of all membranes were determined under the 5 bar transmembrane pressure at $14 \pm 1^\circ\text{C}$ in a cross-flow filtration cell. The effective area of the membrane in the module was 10 cm^2 . In order to calculate the rejection of BSA, its concentrations in the permeate and feed were measured by UV spectrophotometry (using a Unico UV-2100 instrument, Midsci, St. Louis, Missouri, USA) at 280 nm.

Initially the PWF value was measured and used as a reference for the membrane flux (J_{wi}). Subsequently, in order to investigate the fouling, the membrane was tested and fouled for 2 h with freshly prepared BSA solution (1 g/L) and the flux was obtained. After that, the filtration was stopped and the membrane was taken out and rinsed with distilled water for ~ 15 min. After rinsing, the PWF of membranes was measured again (J_{wc}). This fouling process was repeated twice. In order to assess the fouling-resistant capability of the membranes, the flux recovery (*FR*) was calculated using the following equation (Mousavi *et al.*, 2012a):

$$FR(\%) = \left(\frac{J_{wc}}{J_{wi}} \right) \times 100 \quad (1)$$

Porosity measurement. The ‘soaking’ method (Saljoughi *et al.*, 2009b) was used to determine the membrane porosity. In order to evaluate porosity of the membranes, the membranes were initially impregnated with distilled water and then weighed after wiping away superficial water using filter papers. Next, the wet membranes were placed in an air-circulating oven at 80°C for 24 h to be

Table 1. Compositions of casting solutions and CBTs.

Membrane code	Solution compositions				CBT ($^\circ\text{C}$)
	CAB (wt.%)	PEG (wt.%)	MMT (wt.%)	DMF (wt.%)	
M1	18	2	0	80	25
M2	18	2	2	78	25
M3	18	2	4	76	25
M4	18	2	6	74	25
M5	18	2	0	80	0
M6	18	2	2	78	0
M7	18	2	4	76	0
M8	18	2	6	74	0

dried completely, and, finally, the dry membranes were weighed. The porosity of each membrane was calculated using the equation (Saljoughi *et al.*, 2009b):

$$P(\%) = \frac{Q_0 - Q_1}{Ah} \times 100 \quad (2)$$

where P is the membrane porosity; Q_0 and Q_1 are the weights of wet and dry membranes (g), respectively; A is the membrane surface area (cm²); and h is the membrane thickness (mm).

RESULTS AND DISCUSSION

Morphology of the prepared membranes

Effect of MMT concentration. The morphology of the membrane surfaces was examined using SEM (Figure 1). The distribution of nanosized filler particles in the matrix is clearly observed in the filled membranes. Clearly the inorganic filler particles agglomerated together even at low loading ratios. This phenomenon was similar to the results reported by Liang *et al.* (2012), Samanta *et al.* (2012), Picard *et al.* (2007), and Lin *et al.* (2009). As the amount of inorganic filler content increased, aggregation of the filler particles became more significant and larger agglomerates were formed (Liang *et al.*, 2012; Samanta *et al.*, 2012; Lin *et al.*, 2009).

According to the cross-sectional images (Figure 2), the presence of MMT particles within the membrane led to the formation of elongated pores which may be explained by the presence of inorganic nanoclay in the casting solution. The inorganic nanoclay may reduce the interaction between polymer and solvent and consequently enlarge the spacing of the network within the polymer congeries. This phenomenon may accelerate the diffusion of the solvent molecules and pervasion of the coagulant (Lin *et al.*, 2009). In the absence of nanoclays, the CAB membrane was more dense. The formation of pores can be explained by the means of membrane formation using the phase-inversion method. Phase separation occurs by the nucleation and growth of the polymer poor phase. As growth of the nucleated phases occurs, clay particles are excluded from the polymer-rich phase and are imprisoned in the polymer poor phase, which originates in the pores (Anadão *et al.*, 2013).

During formation of the membrane in the coagulation bath, the rate of the demixing process affects the structure of the membranes prepared. Instantaneous demixing often terminates the formation of the more porous structure, whereas slow demixing leads to the

formation of a denser structure (Saljoughi *et al.*, 2013). The formation of a more porous structure with greater permeability after the addition of MMT nanoclay may also be related to the increase in the thermodynamic instability of the polymeric solution. Montmorillonite seems to be a hydrophilic additive with non-solvent properties [an additive which, like other non-solvents, has a strong affinity for the solvent (DMF) and a weak affinity for the polymer (CAB)]. Thus, MMT increases the thermodynamic instability of the polymeric solution. Intensification of the thermodynamic instability of the casting solution can facilitate instantaneous demixing during membrane formation in the coagulation bath and consequently the formation of a more porous structure.

The big holes seen in the SEM images of the membranes without MMT represent a structure defect which disappeared when nanoclay was added to the polymeric solutions. The addition of nanoclays regulated the structure of the membranes by facilitating the formation of the afore-mentioned elongated pores throughout the polymeric membrane. In other words, addition of MMT to the CAB solution modified and organized the structure of the final membrane.

By increasing the MMT concentration from 0 to 2 wt.%, the number of pores in the structure increased but those pores were closed to the membrane surface (Figure 2). A greater increase in the MMT concentration (up to 6 wt.%) resulted in a reduction in the membrane porosity (Table 2) due to the viscosity of the casting solution. Increasing the MMT concentration in the casting solution resulted in increased viscosity and consequently prevented entry by non-solvent molecules into the casting solution during the formation of the membrane in the coagulation bath (kinetic hindrance phenomenon). Hence, the diffusion of the non-solvent was reduced and delayed local phase separation occurred (Anadão *et al.*, 2013). The result is the formation of a denser structure at greater concentrations of MMT >2 wt.%. A similar trend was seen in relation to the thickness of the membranes prepared in the SEM images (Figure 3). In other words, the initial increase in the MMT concentration from 0 to 2 wt.% resulted in the formation of a thicker membrane; further increase in the MMT concentration (up to 6 wt.%) led to a reduction in the membrane thickness.

Effect of CBT. According to the top-surface images of the prepared membranes (Figure 1), the probability of the nanofiller aggregation was increased by decreasing

Table 2. Porosity of the prepared membrane.

Membrane code	M8	M7	M6	M5	M4	M3	M2	M1
Porosity (%)	71	73	81	55	70	71	77	59

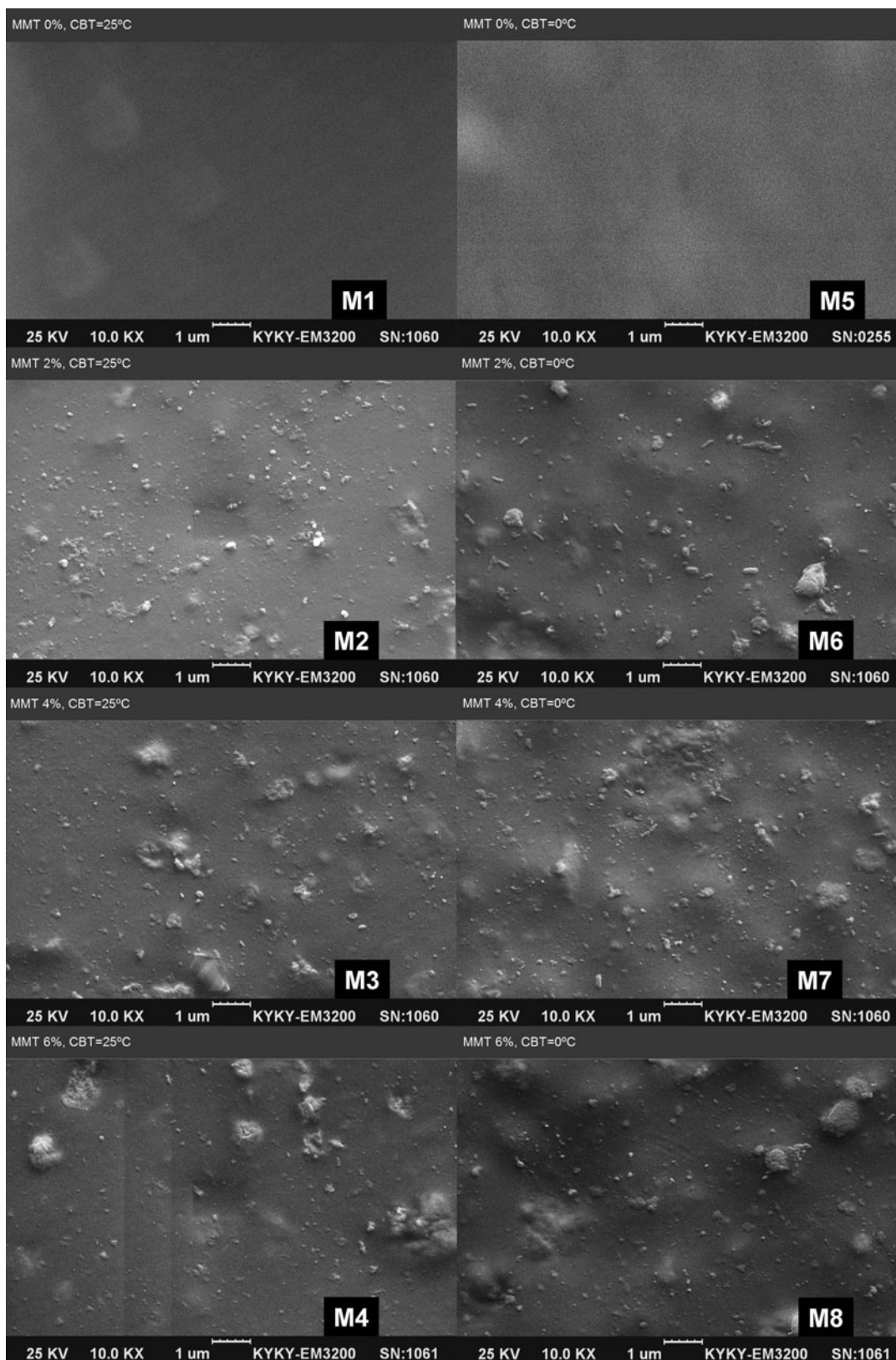


Figure 1. Top-surface images of the prepared membranes (CAB wt.% = 18, PEG wt.% = 2).

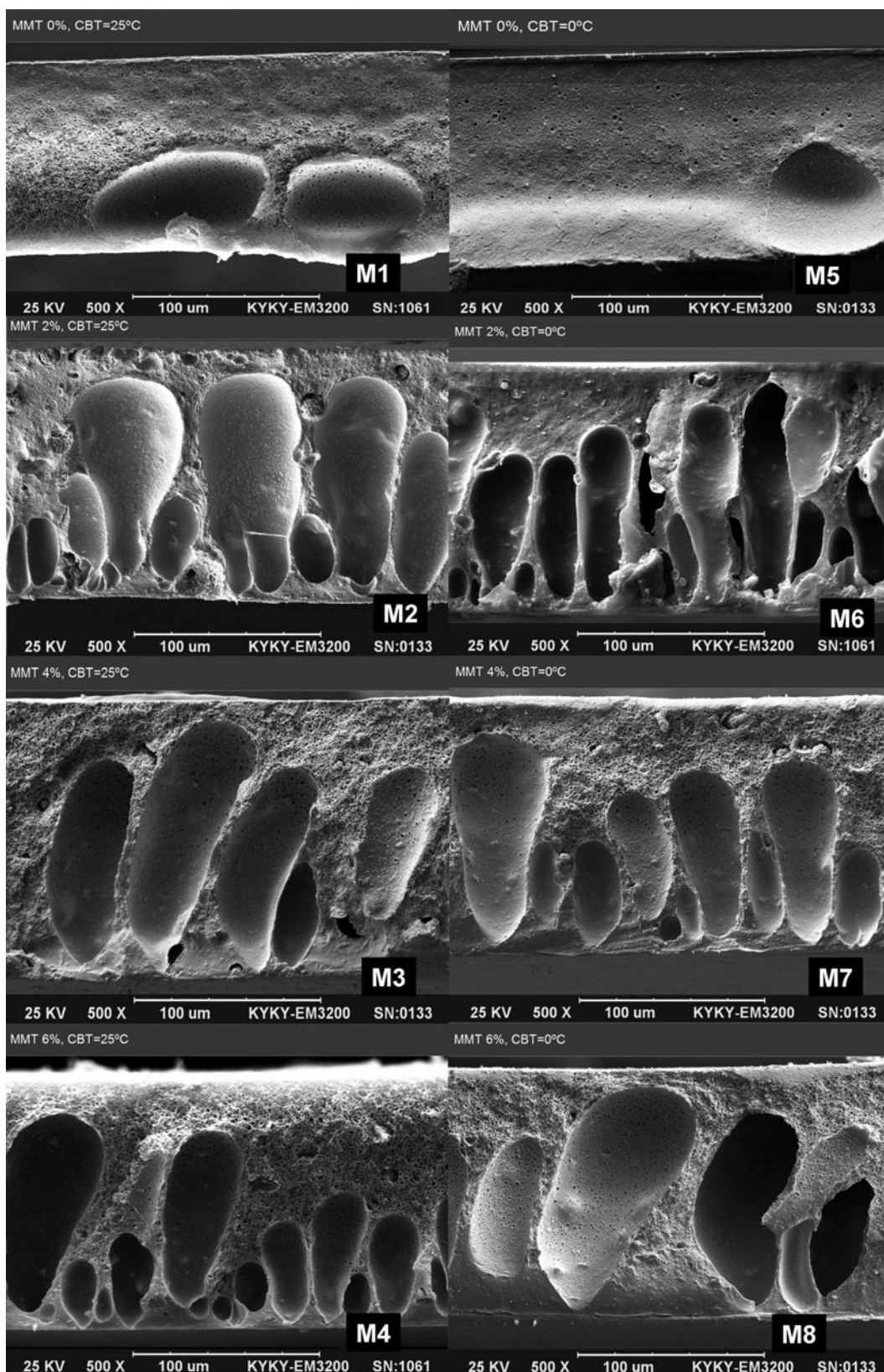


Figure 2. SEM cross-sectional images of the prepared membranes (CAB wt.% = 18, PEG wt.% = 2).

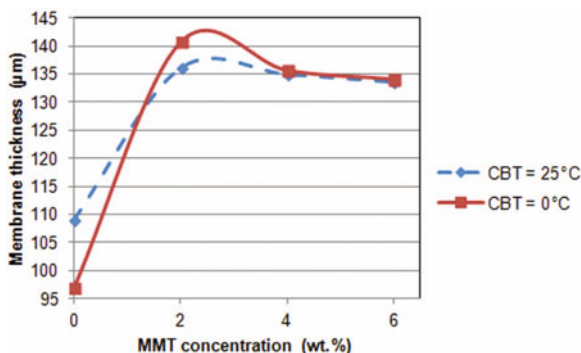


Figure 3. Effect of MMT concentration and CBT variation on the thickness of the prepared membrane.

the CBT. The decrease in CBT level reduced the mutual diffusivities between the non-solvent (water) and solvent (DMF) in the casting solution during the solidification process (Saljoughi *et al.*, 2009a, 2010; Mousavi *et al.*, 2012b, 2013; Yang *et al.*, 2006). Thus, delayed local phase separation occurs. In the membranes containing MMT, nanofillers move to the top surface of the casting solution during the phase-separation process; slower membrane formation allowed the MMT nanofillers to find an opportunity to aggregate during their movement to the surface.

According to the SEM cross-sectional images (Figure 2), in the membrane without MMT nanoclay, the reduction of CBT results in the formation of a denser structure. In fact, the reduction of CBT slowed the growth of limited nuclei formed after the immersion of the cast film into the coagulation bath. This retarded growth of primary nuclei resulted in the formation of numerous nuclei in the cast film. A greater number of nuclei, along with intensive reduction in the growth rate of the nuclei resulted in the suppression of macrovoids and the formation of denser structures (Saljoughi *et al.*, 2009a, 2010; Mousavi *et al.*, 2012b, 2013; Yang *et al.*, 2006). Furthermore with the decrease in CBT from 25 to 0°C (Figure 3), the thickness of the membrane prepared without MMT nanoclay was reduced (Mousavi *et al.*, 2013). However, for membranes which did contain MMT nanoclay, decreases in CBT resulted in the formation of thicker membranes with greater porosity (Figure 3). This difference can be attributed to and explained by the MMT aggregation enhancement following decrease of the CBT. The increase in the aggregation of hydrophilic MMT on the surface of the casting solution during the formation of the membrane in the coagulation bath can result in the acceleration of water permeation into the casting solution and consequently can facilitate the phase separation process and the formation of membrane with greater thickness and porosity.

Permeation experiments

Effect of MMT concentration. The initial increase in the MMT concentration up to 2 wt.% resulted in larger PWF

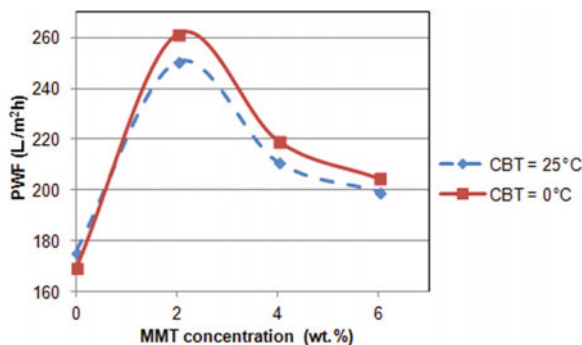


Figure 4. Effect of MMT concentration and CBT variation on PWF.

values (Figure 4). Further increase in the MMT concentration, up to 6 wt.%, however, led to a decrease in the PWF value of the membranes prepared. The PWF value of membranes containing MMT was greater than that for membranes without MMT. This result can be explained by the hydrophilic property of MMT nanofiller that increases the preferential water–membrane interaction (Samanta *et al.*, 2012). So the improved hydrophilicity of the membrane can attract the water molecules inside the membrane matrix and promote the transmission of water molecules through the membrane. Furthermore, according to Figure 2, the membranes containing MMT are more porous than those without. Membranes containing MMT are better at conducting water than membranes which do not contain MMT.

The increase in the porosity of the membrane containing 2 wt.% of MMT greatly enhanced the PWF value. Adding more than 2 wt.% MMT, however, resulted in a highly viscous casting solution, which slowed the formation process of MMT/CAB membranes and consequently reduced the porosity, which had a negative effect on the permeability (Yang and Wang, 2006; Yang *et al.*, 2006). The addition of a high concentration of MMT nanoclay to the initial casting solution resulted in the formation of a sublayer containing considerable MMT particles which could block the membrane pores and thereby produce a negative effect on the PWF value (Yang and Wang, 2006; Rahimpour *et al.*, 2008).

The results of the flux behavior of membranes in the filtration of the BSA solution showed that, at greater MMT concentrations, due to higher hydrophilicity, the flux reduction decreased (Figure 5). The reduction in BSA rejection due to the initial increase in the MMT concentration can be explained by the increase in porosity and the formation of the more open structure (Table 3). Note, however, that the aforementioned reduction in BSA rejection was significant and, therefore, the general performance of membranes was improved by the addition of MMT nanoclay. A further increase in the MMT concentration in the casting solutions from 2 to 6 wt.% resulted in the formation of

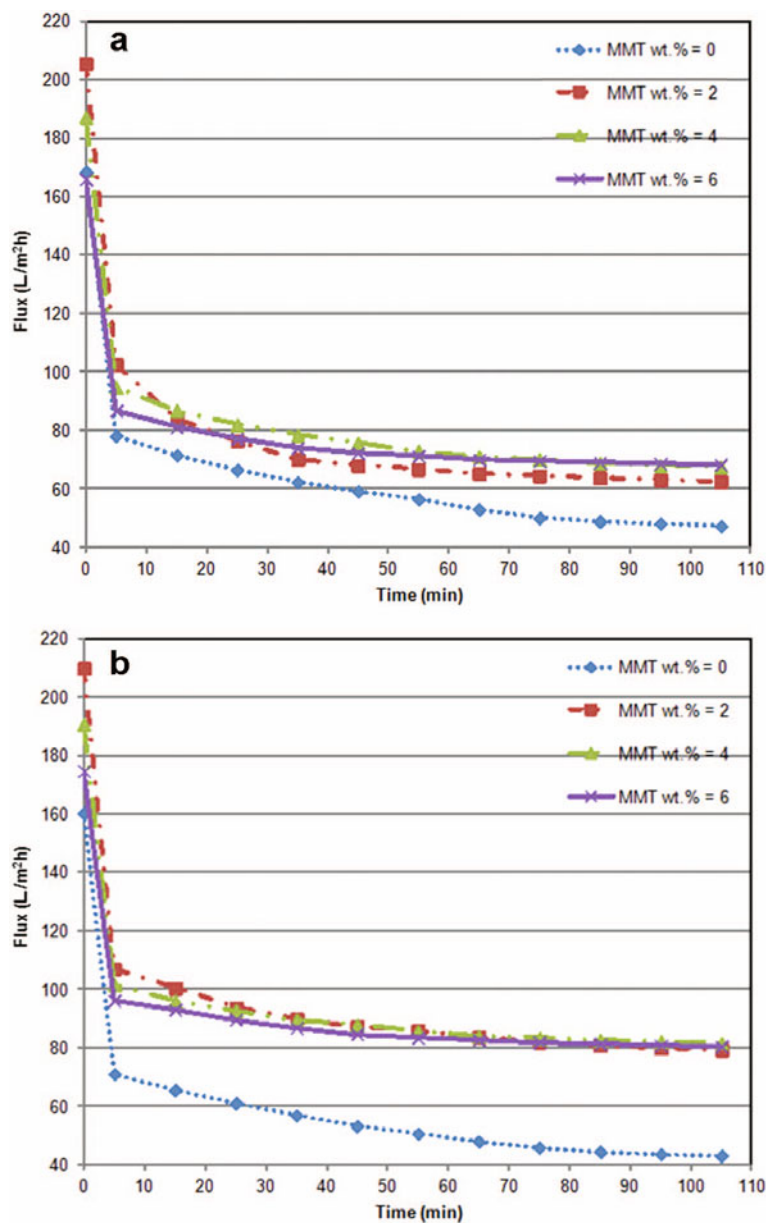


Figure 5. Flux behavior of the prepared membranes during filtration of BSA solution for: (a) CBT at 25°C; (b) CBT at 0°C.

membranes with greater hydrophilicity and less porosity. Clearly, the variations listed had a positive effect on the rejection value. Therefore, in the membranes containing MMT nanoclay, the increase in MMT concentration enhanced BSA rejection.

Effect of CBT. According to Figure 4, the PWF value for the membrane without nanoclay was reduced by the decrease in CBT. In addition, in membranes which did contain MMT nanoclay, the PWF was increased by the CBT decreased. The PWF measurements confirmed the

Table 3. BSA rejection of the prepared membrane.

Membrane code	M8	M7	M6	M5	M4	M3	M2	M1
Rejection (%)	93.64	93.48	92.15	95.81	94.02	93.83	92.69	95.27

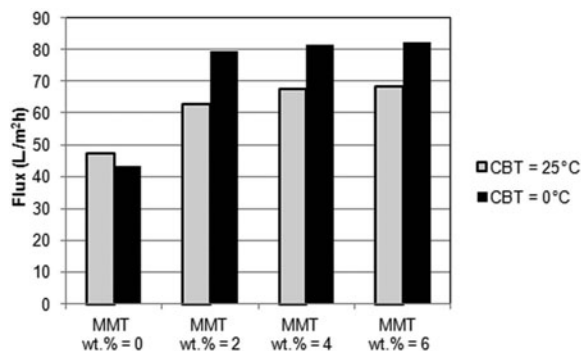


Figure 6. The effect of CBT on the steady-state flux of BSA solution.

trends observed in the SEM images. In fact, comparison between Figure 4 and the SEM images showed a direct relationship between the porosity and the PWF values of the prepared membranes. Clearly, the increase in porosity reduced the resistance to the permeation of water molecules and consequently resulted in larger PWF values. These observations are in agreement with others in the literature (Saljoughi *et al.*, 2009a, 2010; Mousavi *et al.*, 2012b, 2013; Amirilargani *et al.*, 2010).

Because of the formation of a more porous structure, according to the flux behavior in the filtration of BSA solution of the prepared membranes containing MMT (Figure 6), the steady-state fluxes of the membranes prepared in the cold coagulation bath (CBT 0°C) were greater than those of the membranes prepared in the normal coagulation bath (CBT 25°C). Furthermore, the aforementioned higher porosity resulted in a lower rejection rate of BSA for the membranes prepared in the cold coagulation bath (Table 3). For membranes without MMT, all the results for PWF and rejection were reversed, this because of the formation of a denser structure after use of the cold coagulation bath (Saljoughi *et al.*, 2009a, 2010; Amirilargani *et al.*, 2010).

Flux recovery. According to the results of analysis of membrane fouling with respect to the *FR* parameter (Figure 7), the *FR* value of the membranes containing MMT was greater than that of the membrane without MMT. The antifouling property of the CAB membranes is improved by addition of MMT nanoclay to the casting solution (Mousavi *et al.*, 2012a; Rahimpour *et al.*, 2008, and Mansourpanah *et al.*, 2009). Moreover, the CBT variation caused no significant change in the *FR* values.

As the MMT concentration in the casting solution increased, the recovery increased due to the accumulation of more nanoclay on the membrane surface and led, consequently, to the formation of membranes with higher hydrophilicity.

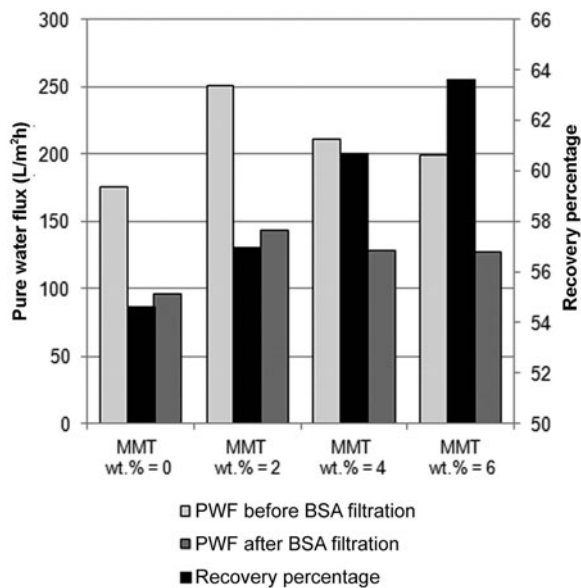


Figure 7. PWF before and after BSA solution filtration and the pure-water-flux recovery percentage for the prepared membranes in constant CBT at 25°C.

CONCLUSIONS

The effects of the presence of hydrophilic MMT nanoclay in CAB/DMF/PEG casting solutions and the variation of CBT on the fundamental characteristics of membranes such as morphology, PWF values, permeate flux, rejection, and tendency to fouling were investigated. The following conclusions were made:

(1) With respect to the SEM images, the membrane thickness was increased by increasing the MMT concentration in the casting solution from 0 to 2 wt.%; but, the addition of further MMT nanoclay to the casting solution increased the compaction of the structure and simultaneously decreased the membrane thickness.

(2) The decrease in CBT for the membranes without MMT and with MMT resulted in the formation of membranes with less and more porosity, respectively.

(3) The membranes with high porosity containing larger pores showed higher PWF values. These membranes were prepared by the addition of MMT to the casting solution.

(4) The PWF value was increased with increasing MMT concentration up to 2 wt.% in the casting solution and then decreased with further addition of MMT.

(5) The results showed that, as the MMT concentration in the casting solution increased, the flux reduction of BSA solution decreased due to greater hydrophilicity of the membrane. Therefore, the *FR* value was increased by increasing the MMT value in the casting solution.

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