Effect of Poly(vinyl pyrrolidone) Concentration and Coagulation Bath Temperature on the Morphology, Permeability, and Thermal Stability of Asymmetric Cellulose Acetate Membranes

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Received 15 March 2008; accepted 9 August 2008
DOI 10.1002/app.29354
Published online 25 November 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cellulose acetate (CA) is widely used in membrane processes. In this study, CA (weight-average molecular weight = 52,000) was mixed with poly(vinyl pyrrolidone) (PVP; weight-average molecular weight = 15,000) as an additive in 1-methyl-2-pyrrolidone as a solvent. The phase-inversion method was used for the preparation of flat-sheet membranes. The effects of PVP concentration and coagulation bath temperature (CBT) on the morphology, pure water permeation flux, and thermal stability of the prepared membranes were studied and are discussed in this article. The solute rejection of the developed CA membranes was quantified with an insulin protein solution. The results showed that an increase in the CBT levels from 0 to 23°C along with an increase in the PVP concentration in the cast film from 0 to 1.5 wt % resulted in an increase in the macrovoid formation in the membrane sublayer, an increase in the pure water flux (PWF), and a decrease in insulin rejection. Further increases in the PVP concentration from 1.5 to 3, 6, and 9 wt % resulted in gradual suppression of the macrovoid formation, a decrease in PWF, and an increase in insulin rejection. Higher PVP concentrations and lower CBT levels also appeared to result in higher glass-transition temperatures. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2537–2544, 2009

Key words: additives; membranes; phase separation

INTRODUCTION

Membranes have gained an important place in chemical technology and been used in a wide range of applications, such as the production of high-quality water, removal or recovery of toxic or valuable components from various industrial effluents, and applications in the food and pharmaceutical industries. With the advent of membrane technology, separation, concentration, and purification have become industrially viable unit operations because of the high efficiency of separation, low energy of operation, simplicity of operation with modern compact modules, and so on.[1–3]

A wide range of different materials can be used for membrane preparation, such as metals, ceramics, graphite, glass, and powders of polymers. In fact, all polymers can be used as barrier or membrane materials, but their chemical and physical properties differ so much that only a limited number are used in practice.[4] The phase-inversion process induced by immersion precipitation is a well-known technique for preparing asymmetric polymer membranes.[4–9] Through the immersion of a substrate in a coagulation bath, a solvent in the casting solution film is exchanged with a nonsolvent in the precipitation media, and phase separation occurs. This process results in an asymmetric membrane with a dense top layer and a porous sublayer. The sublayer formation is controlled by numerous variables in the polymer dope solutions, such as composition, coagulant temperature, and organic/inorganic additives. To attain the desired membrane morphology and performance, the phase-inversion process must be carefully controlled.[10] Two dominating factors controlling the formation of phase-inversion membranes are thermodynamics and kinetics, the former is related to the phase equilibrium between components in the coagulation bath, and the latter is related to the mutual diffusivities between them. Disturbing the phase equilibrium and increasing the mutual diffusivities result in instantaneous demixing (rapid formation of a membrane in the water bath) and a more open structure.[4,5,9]

Among the different polymeric materials that are used for the preparation of phase-inversion membranes, cellulose acetate (CA) is very common, with

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TABLE I
Compositions of the Casting Solutions, CBTs, and Viscosities of the Casting Solutions

Membrane code	Solution composition			CBT (°C)	Viscosity at 23°C (Pa s)
	CA (wt %)	NMP (wt %)	PVP (wt %)		
M1	15.5	84.5	0	23	37.7
M2	15.5	83	1.5	23	40.5
M3	15.5	81.5	3	23	43
M4	15.5	78.5	6	23	75.7
M5	15.5	75.5	9	23	85.9
M6	15.5	75.5	9	0	85.9

characteristics such as good toughness, high biocompatibility, good desalting, high potential flux, and relatively low cost.[11–14] Thus, it has been widely used for reverse osmosis, microfiltration, and gas separation.[15,16] Also, CA membranes have excellent hydrophilicity, which is very important in the minimization of fouling.[17–19]

Despite the advantages mentioned previously, this material has two major drawbacks: low chemical resistance and low thermal resistance.[2] Because of the low chemical resistance of CA membranes, the usual membrane chemical cleaning with a basic solution cannot be performed (the pH is limited to 9). Costly detergents must be used instead, and they are difficult to treat in the rinsing solution after the chemical cleaning. Also, the feed pH must be neutralized before membrane filtration. On the other hand, the low thermal resistance of CA membranes causes restrictions in

1. Membrane cleaning, which includes flushing the system with hot water and treating with hot detergent solutions.[1]
2. Thermal sterilization, which is essential in medical applications.[1,20]

Any improvement in the thermal and chemical stabilities of CA membranes, along with the many other advantages of these membranes, can extend their applications.

In this study, various combinations of CA and poly(vinyl pyrrolidone) (PVP) concentrations and coagulation bath temperature (CBT) levels were selected, and their effects on the membrane formation mechanism (instantaneous or delayed demixing mechanism), morphology, pure water flux (PWF), and insulin rejection were studied. Also, the effects of PVP and CBT on the thermal stability of the prepared membranes were investigated.

EXPERIMENTAL

Materials

CA with an average molecular weight of 52,000 g/mol (Fluka, Buchs, Switzerland) was used as the membrane-forming polymer. The solvent used was 1-methyl-2-pyrrolidone (NMP) with an analytical purity of 99.5% (Merck), and distilled water was used as the nonsolvent agent. PVP with an average molecular weight of 15,000 g/mol (Fluka) was used as the additive. Solute experiments were performed with insulin with an average molecular weight of 5700 g/mol (Exir Co., Iran).

Preparation process

Various CA/PVP/NMP solutions with a constant concentration of CA (15.5 wt %) were prepared. Their compositions are presented in Table I. The solution was stirred continuously to ensure that the polymers were completely dissolved. When the polymers were dissolved, as indicated by the observation of a clear solution, the solution was subsequently degassed in an ultrasonic bath for about 2 h to remove any air bubbles present and kept away from direct sunlight to slow down its aging process. The casting solution was poured onto a glass plate and spread with a casting knife to a thickness of 180 μm. Then, the glass plate was immediately immersed in a distilled water bath to complete phase separation, where exchange between the solvent and the nonsolvent (water) was induced. Then, membranes were transferred to another container with fresh distilled water to remove the excess NMP and PVP. After 24 h, the membranes were ready to be tested.

Solution viscosity measurements

The viscosities of the prepared casting solutions were measured with a POLYVISC digital rheometer (model VISCO Star L, Luzem, Switzerland) at a constant temperature of 25°C.

Membrane characterization

Scanning electron microscopy (SEM)

The membranes were snapped under liquid nitrogen to give a generally consistent and clean break. The membranes were then sputter-coated with thin film

of gold. The membranes were mounted on brass plates with double-sided adhesive tape in a lateral position. Cross-sectional images of the membranes were obtained with a CamScan SEM model MV2300 microscope.

PWF and solute rejection measurements

The PWF and solute rejection measurements were carried out in a batch mode. A flat-sheet membrane module made from stainless steel was used in the experiments. The effective area of the membrane in the module was 24 cm^2. The schematic representation of setup is shown in Figure 1. PWF experiments were run at a transmembrane pressure of 0.5 bar with the following equation:[21]

$$\mathrm{PWF} = \frac{Q}{A\Delta t} \tag{1}$$

where Q is the quantity of the permeate (L), A is the membrane area (m^2), and Δt is the sampling time (h).

Protein solutions are widely used in membrane characterization.[1] In this study, insulin solutions were prepared at a concentration of 0.01 wt % in aqueous phosphate buffer (0.5*M*, pH 7.2) with distilled water and were used as standard feed solutions and filtered through each membrane sample individually. The permeate protein concentration, collected at certain time intervals, was estimated with a UV–visible spectrophotometer (Shimadzu, model UV2550, Tokyo, Japan) at a wavelength of 280 nm. The solute rejection (R) was calculated as follows:[21]

$$\%R = \left(1 - \frac{C_p}{C_F}\right) \times 100 \tag{2}$$

where C_p and C_F are the concentrations of the permeate and feed solutions, respectively.

Dynamic mechanical thermal analysis (DMTA)

DMTA of the prepared membranes were performed with a Triton DMTA instrument (model Tritic, London, England) operating at a frequency of 1 Hz. DMTA scans were performed between 20 and 160°C at a heating rate of 3°C/min.

RESULTS AND DISCUSSION

Morphological studies of the prepared membranes

SEM images were taken to determine the effects of the PVP concentration and CBT on the membrane morphology. Figure 2 depicts the SEM cross-sectional images of the membranes. According to these images, at a constant CBT (23°C), higher PVP concentrations initially caused greater formation of macrovoids and more porous structures. However, even higher PVP concentrations resulted in macrovoid suppression and denser structures. Explanation of these observations requires an understanding of the membrane formation mechanism.

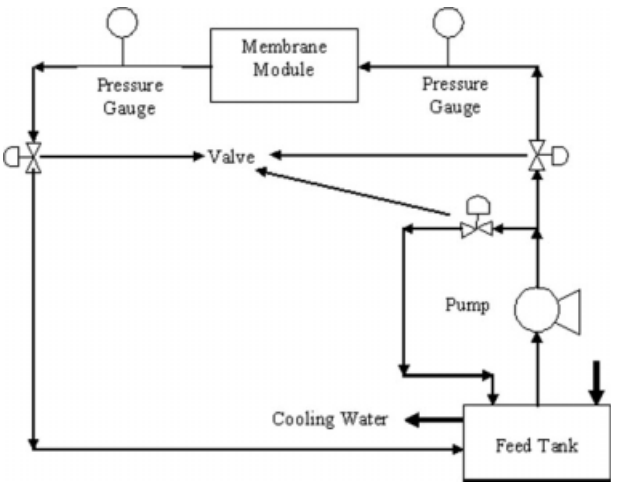

Figure 1 Schematic diagram of the experimental setup.

When the cast film was immersed in the distilled water bath, precipitation started because of the low miscibility between the polymer (CA) and the nonsolvent (water). Simultaneously, the miscibility between the solvent (NMP) and the nonsolvent (water) caused diffusional flow of the solvent and nonsolvent (exchange of solvent and nonsolvent) in several points of the film top layer and the substrate, which subsequently led to the formation of nuclei of the polymer-poor phase. In fact, the low affinity between the CA chains and water molecules at points where the water molecules diffused resulted in the repelling of the CA chains and, consequently, the formation of nuclei of the polymer-poor phase. Because of the continuation of the diffusional flow of solvent from the surrounding cast film, these nuclei continued to grow until the polymer concentration at their boundaries became so high that solidification occurred (the demixing process was completed).[22]

The rate of the demixing process affected the morphology of the membranes. Instantaneous demixing often leads to the formation of macrovoids in membrane structure, whereas slow demixing results in denser structures. In the case of slow demixing, nucleation occurs after a certain period of time, and the polymer concentration increases in the top layer. Then, nucleation starts in the inferior layer at short time intervals successively. Hence, the size and composition of nuclei in the former layer is such that new nuclei are gradually formed in their neighborhood.[4] In other words, in slow demixing, free growth of limited nuclei (on the top layer) is prevented, and a large number of small nuclei is created and distributed throughout the polymer film.

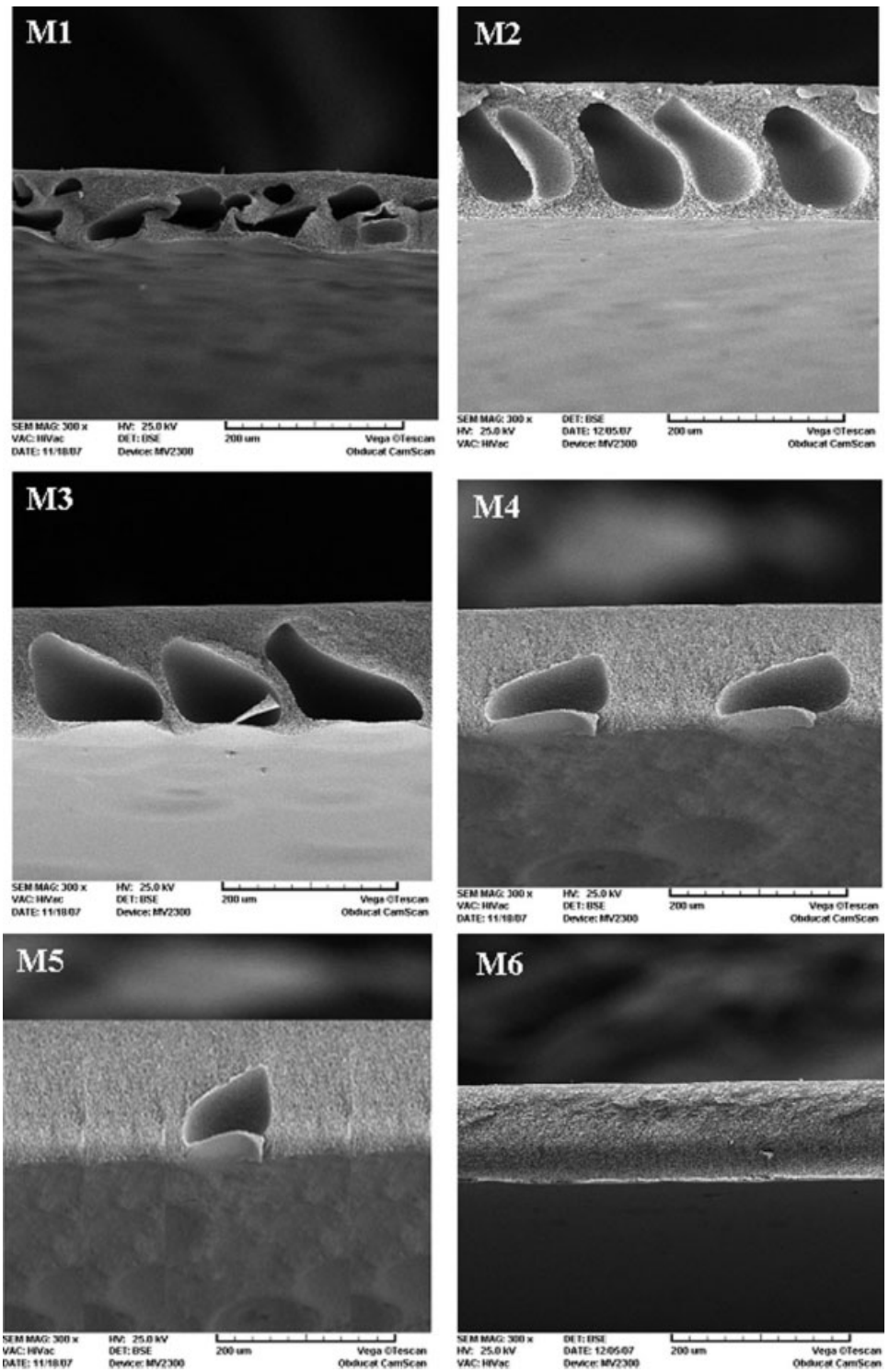

Figure 2 SEM cross-sectional images of the CA membranes.

Consequently, contrary to instantaneous demixing, the formation of macrovoids is suppressed, and denser membranes are synthesized.

In this study, the presence of PVP as a hydrophilic additive with nonsolvent properties [an additive that, similar to nonsolvents, has a high and low affinity to the solvent (NMP) and the polymer (CA), respectively][13,15] increased the thermodynamic instability of the cast film and, consequently, led to instantaneous demixing in the coagulation bath and, thus, to the formation of macrovoids in the membrane structure.[13,23]

From another point of view, the presence of PVP increased the viscosity of the cast film (as shown in

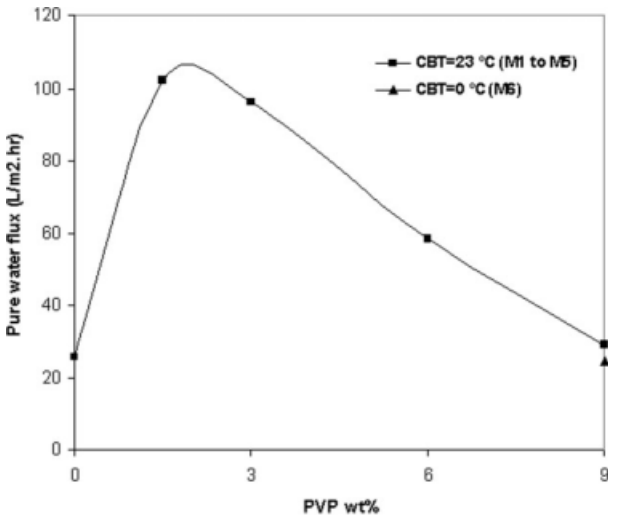

Figure 3 Effect of the PVP concentration and CBT on the PWF of the CA membranes (at a transmembrane pressure of 0.5 bar).

Table I). The viscosity increase of the cast film slowed down the diffusional exchange rate of the solvent (NMP) and nonsolvent (water) during the solidification process and, consequently, hindered instantaneous demixing. This led to delayed demixing and, consequently, the suppression of macrovoids and the formation of denser structures.

Hence, the addition of hydrophilic additives, such as PVP, to the casting solution has a dual effect on membrane morphology. In fact, the final structure depended on the superiority of instantaneous or delayed demixing, which, as mentioned before, both came from the presence of PVP in the cast solution film. In this study and according to the SEM cross-sectional images, an initial increase in the PVP concentration (from 0 to 1.5 wt %) caused a greater formation of macrovoids and more porous structures. However, even higher PVP concentrations resulted in the suppression of macrovoids and denser structures. Thus, it seems that with the initial increase in PVP concentration (from 0 to 1.5 wt %), instantaneous demixing was preferred over delayed demixing. However, with further increases in PVP concentration (from 1.5 to 9 wt %) and because of the importance of viscosity effects, delayed demixing was preferred over instantaneous demixing.

The decrease in CBT levels (particularly to 0°C) intensively reduced the mutual diffusivities between the nonsolvent (water) and the solvent (NMP) in the casting solution during the solidification process. This caused the limited nuclei (formed quickly after immersion of the cast film into the distilled water bath) to grow slowly. This resulted in the formation of a large number of small nuclei in every part of the cast film.[4,22] This caused the production of few and more pores/voids in the membrane top layer and the sublayer, respectively, and this resulted in the suppression of macrovoid formation and an approximately denser structure in M6 in comparison with M5 (Fig. 2). These observations were in agreement with the literature.[24] In general, the formation of macrovoids occurred under quick precipitation conditions, and the precipitation was faster at higher temperatures.

Permeation studies of the prepared membranes

PWF and insulin rejection of the prepared membranes are presented in Figures 3 and 4, respectively. These measurements confirmed the trends observed in the SEM images, where an increase in the PVP concentration from 0 to 1.5 wt % led to increases in the macrovoid formation and film porosity and, therefore, higher PWF values and lower insulin rejection behavior. Further increases in the PVP concentration from 1.5 to 9 wt % reversed these trends.

As mentioned before, a decrease in the CBT levels (particularly to 0°C) intensively reduced the membrane porosity and caused denser structures in the top layer and the sublayer. Thus, a decrease in PWF and an increase in the insulin rejection at lower CBTs were expected, as shown in Figures 3 and 4, respectively.

Thermal stability of the prepared membranes

When an amorphous polymer is heated, a temperature exists at which the polymer changes from the glassy state to rubbery state. This temperature is named the *glass-transition temperature* (T_g) and has a significant effect on the thermal and chemical stabilities of the polymer.[1,4] Up to this temperature, the thermal energy is just sufficient to overcome the restriction in rotation of segments around the main

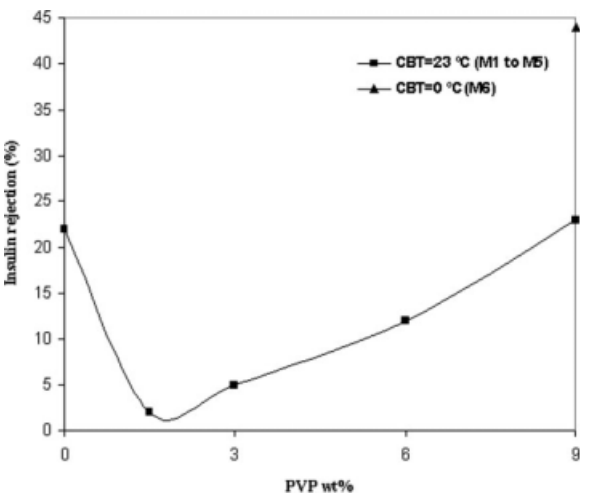

Figure 4 Effect of the PVP concentration and CBT on the insulin rejection of the CA membranes (at a transmembrane pressure of 0.5 bar).

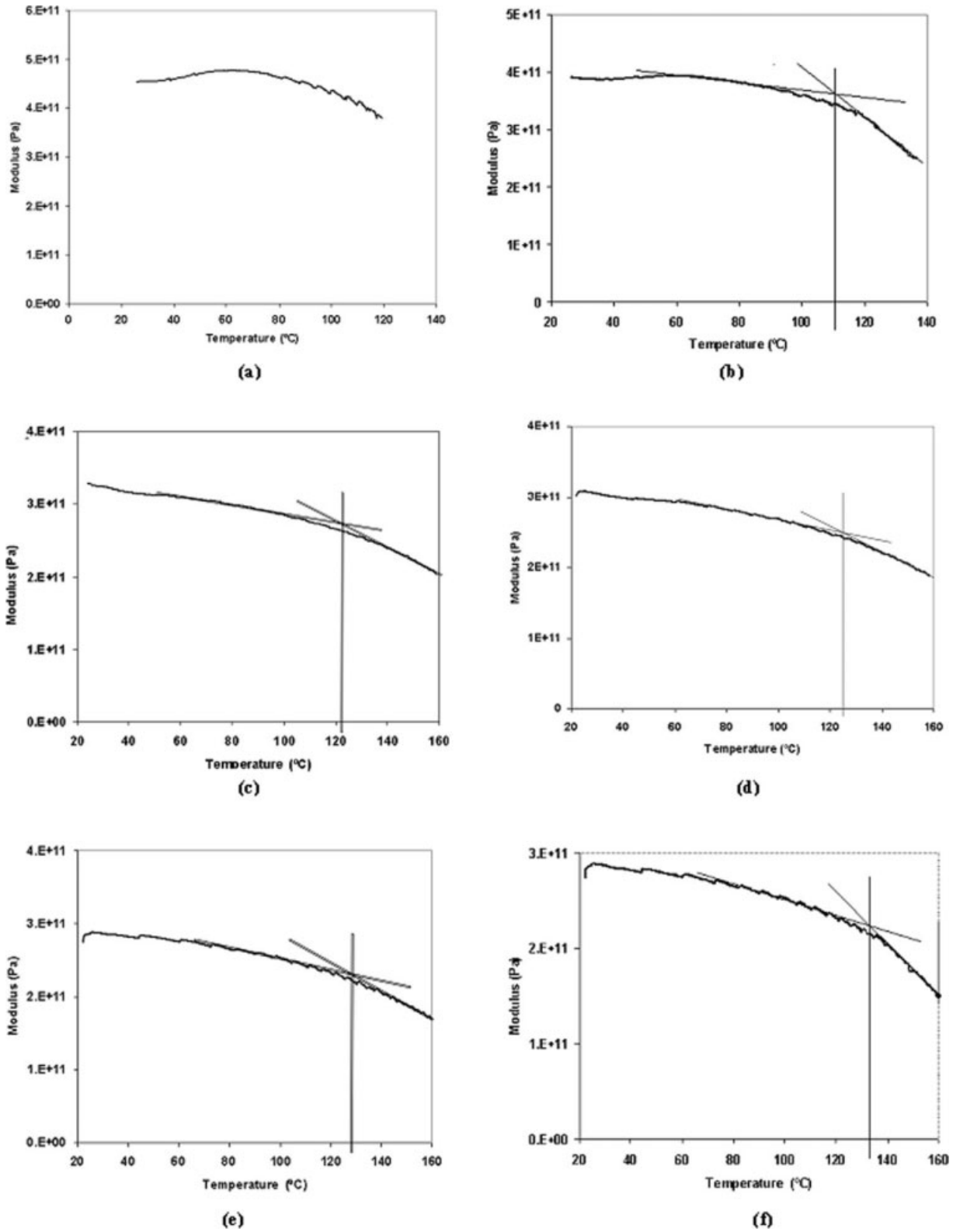

Figure 5 Modulus curves of the CA membranes: (a) M1, (b) M2, (c) M3, (d) M4, (e) M5, and (f) M6.

chain bonds or to overcome the interactions between the chains. For this reason, the important parameters that determine T_g are chain flexibility and chain interactions.[4]

DMTA is a current technique in thermal studies, and exact quantities of T_g values can be obtained from this technique.[25,26] The DMTA results of the prepared membranes were studied in term of

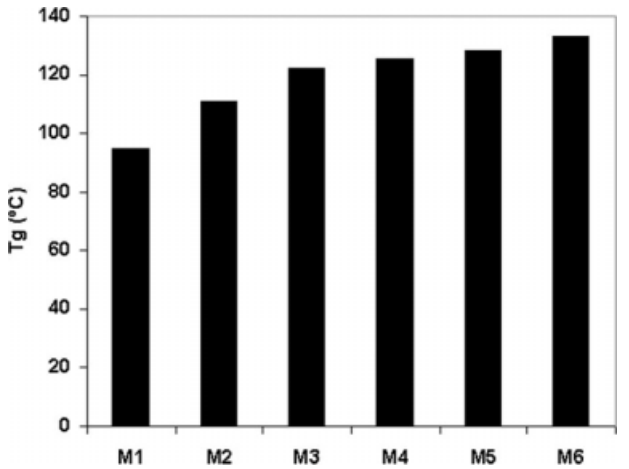

Figure 6 Effect of the PVP concentration and CBT on T_g of the CA membranes.

modulus as a function of temperature. The modulus curves and also T_g values of the prepared membranes are presented in Figures 5 and 6, respectively. According to these figures, an increase in the PVP concentration and a decrease in CBT resulted in higher T_g values, so M6, with the highest PVP concentration and lowest CBT, 9 wt % and 0°C, respectively, had the largest T_g ($\sim$ 133°C) and, thus, the highest thermal/chemical stability. However, M1, with the lowest PVP concentration and highest CBT, 0 wt % and 23°C, respectively, had smallest T_g ($\sim$ 95°C) and, thus, the lowest thermal stability. These could have be due to the following facts:

1. PVP, contrary to NMP, had a relatively low affinity to CA, and consequently, the presence of this additive in the cast solution film resulted in the aggregation and contraction of the polymer chains during membrane formation in the coagulation bath. This resulted in a restriction in the rotation of CA segments around the main chain bonds and, consequently, in higher T_g values in the prepared membranes.
2. A reduction in CBT resulted in the contraction of the polymer chains after immersion of the cast film into the coagulation bath and, consequently, of the prepared membranes. Also, a reduction in CBT resulted in denser structures (as mentioned before). It was evident that the contraction of polymer chains, along with denser structures, led to a restriction in the rotation of CA segments around the main chain bonds and, thus, a higher T_g, which translated into higher thermal and chemical stabilities.

Residual PVP in the CA membranes can affect T_g. However, it seems that low-molecular-weight PVP (in this study, 15,000 g/mol) can be easily and quickly washed out with solvent during the formation and cleaning processes of the membranes. An analysis will be done with NMR or other elemental analysis to evaluate the film composition and/or to determine the probable residual PVP in future studies. It seems that determination of the residual PVP content may support some of the results.

CONCLUSIONS

Various membranes with different PVP concentrations and CBTs were prepared, and their morphology, PWF, insulin rejection, and thermal stability were determined. It was found that

1. Increasing PVP concentration in the cast film from 0 to 1.5 wt % resulted in the facilitation of macrovoid formation in the membrane sublayer, which increased PWF and decreased insulin rejection. However, increasing PVP concentration from 1.5 to 3, 6 and 9 wt % results in a decrease in PWF and an increase in insulin rejection. Also, this trend of PVP variation from 1.5 to 9 caused macrovoid to be gradually suppressed.
2. Increasing PVP concentration, which contrary to NMP had a relatively low affinity to CA, in the cast film resulted in the aggregation and contraction of the polymer chains during membrane formation in the coagulation bath. This resulted in a restriction in the rotation of CA segments around the main chain bonds and, thus, higher T_g values, which translated into higher thermal stability of the membranes.
3. The reduction of CBT resulted in the following:
   a. Suppression of macrovoid formation in the membrane sublayer and the formation of a denser structure.
   b. Reduction of the PWF.
   c. An increase in the insulin rejection and thermal stability of the prepared membranes.

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