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A new method for cellulose membrane fabrication and the determination of its characteristics

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Abstract

A novel method to fabricate semipermeable cellulose membranes based on cellulose regeneration of a dry membrane cast by the neutralization reaction is presented in this paper. In this method, an environmentally acceptable cellulose dissolution procedure is employed to prepare the membrane casting solution comprised of microcrystalline cellulose dissolved in aqueous NaOH. Moreover, a new cast drying/cellulose regeneration technique is proposed and successfully applied to prepare membranes after the exploitation of the conventional immersion precipitation method, which results in the formation of granular cellulose particles rather than membranes due to the low cellulose concentration (<5 wt%) in the cast. In the present technique, the cellulose concentration in the membrane cast is dramatically increased through water evaporation, and glycerin is utilized in the cellulose regeneration process to achieve a gentle neutralization reaction. As a result, defect-free membranes with a uniform structure are developed. A detailed investigation is also presented concerning the effects of membrane forming parameters, i.e., the concentrations of cellulose, solvent, and acid, and the membrane thickness, on membrane properties. In addition, by coordinating the molecular separation experiments via the ultrafiltration process against a number of macromolecules with various molecular weights, the fabricated membranes are demonstrated to be capable of sieving molecules with a MW above 50,000.

Keywords: Cellulose membrane; Membrane fabrication; Microcrystalline cellulose; Cellulose regeneration; Water flux; Solute rejection

1. Introduction

Cellulose is one of the richest natural polymers in the world and is applied vastly by manufactures to produce various useful products such as clothing, drug dressing, packing materials, and membranes. Currently, many commercial membranes are made of cellulose due to its unique hydrophilic characteristics, relatively high chemical stability, and remarkable environmental protecting capability. Cellulose can be conjugated with other polymers to form blend or composite membranes [1–4] for different separation purposes. However, cellulose cannot be easily dissolved in ordinary solvents because of the strong hydrogen bonds between cellulose chains. The viscose and cuprammonium [5–7] processes are currently applied by most of the regenerated cellulose industries to dissolve cellulose due to its unique abilities, such as chemical derivatization and modification in cellulose dissolution. However, the environmentally hazardous problem has been proved inevitable in these processes. Therefore, there has been an intensive search of various methods for cellulose dissolution to solve this problem, and a wide variety of aqueous, nonaqueous and complex solvent systems have therefore been proposed [8–12]. Among these methods, the one reported by Isogai [12], in which the dissolution of various cellulose samples in aqueous NaOH has been investigated, is distinctive for its simplicity and low-energy cost characteristics. In this method, a certain concentration of completely dissolved microcrystalline cellulose can be obtained by using this solvent with a freeze–thaw process. The cellulose is swelled in aqueous NaOH and dissolved in the freezing procedure. This

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method is proved to be effective in dissolving low DP (degree of polymerization) cellulose regardless of its crystallinity indices without chemical modification and derivatization. Therefore, the regenerated cellulose products may be manufactured mainly by extensively reducing the solvent concentration or by using HCl to neutralize the cellulose solvent, i.e., NaOH, which yields no harmful by-products. However, no attempt has been made to bring this particular method into practical fabrication.

In the present paper, the method mentioned above is successfully applied to fabricate the regenerated cellulose membranes. First of all, a standard immersion precipitation technique [13,14] is exploited, in which a cast of thin-film cellulose solution is immersed into an acid bath and the cellulose is regenerated and precipitated. However, no membrane but granular cellulose particles can be obtained due to the low cellulose concentration (<5 wt%) in the casting solution by utilizing Isogai's cellulose dissolution method. Based on this experience, a new cast drying/cellulose regeneration method is proposed, in which the cellulose concentration is increased prior to the cellulose regeneration process by slowly evaporating water off the casting solution to the air at room temperature. By the subsequent addition of HCl solution to the dry cast with the use of glycerin for achieving a gentle neutralization reaction during the cellulose regeneration, the defect-free semipermeable cellulose membranes with homogeneous pore morphology and steady sieving properties can be formed. Moreover, a detailed investigation is made into the effects of the concentrations of cellulose, NaOH, and HCl, and the membrane thickness, which are the critical membrane forming parameters, on membrane properties, i.e., the water permeation rate and the solute rejection. The resulting membranes are proved to be capable of sieving molecules with a MW above 50,000 according to the molecular rejection results obtained via the ultrafiltration experiment.

2. Experiment details

2.1. Materials and reagents

In this experiment, the microcrystalline cellulose (Avicel Type 102, DP 250), which is a purified and partially depolymerized alpha cellulose derived from fibrous plants, is provided by FMC. The aqueous NaOH solutions with various concentrations from 1.6 to 2.6 M are used as the solvents for preparing the cellulose solution, namely the membrane casting solution. The aqueous HCl solutions with different concentrations from 0 to 8.4 M are utilized during the cellulose regeneration. The isopropyl alcohol with a concentration of 99.9 wt% is used as the contraction agent of the cellulose polymer after the membrane formation. The glycerin with a concentration of 99.7 wt% is used as a medium for the HCl solution to diffuse and spread homogeneously inside before reaching the membrane cast. The NaCl and sucrose are used as the model solutes in the ultrafiltration experiments. The later six chemicals mentioned above are obtained from Fisher Co. The protease, cellulase, albumin from egg, and albumin from human with molecular weights of 20, 31, 45 and 67 kDa, respectively, are provided by Sigma–Aldrich Co. and used as the model solutes in the ultrafiltration experiments to investigate the membrane separation properties.

2.2. Membrane preparation

Various cellulose solutions with different concentrations of cellulose and solvent are prepared for the membrane fabrication. During the cellulose dissolution process, a predetermined amount of microcrystalline cellulose is dissolved in the aqueous NaOH through a freeze–thaw process proposed by Isogai [12]. The cellulose should be completely dissolved before the membrane fabrication to avoid membrane structural defects. The resulting cellulose dissolution is measured by using the turbidity measurement technique, in which a UV–vis spectroscopy (Shimadzu TCC-260) with the wavelength at 600 nm is utilized. It can be seen in Fig. 1 that the cellulose solubility decreases as the cellulose concentration increases. It is also evident that the cellulose concentration should be lower than 5 wt% so that the high solubility larger than 90% can be ensured.

First of all, the standard immersion precipitation [13, 14], in which the cellulose solution with a volume of 5 ml is cast on a glass plate and immersed into a 500 ml HCl bath with a acid concentration of 2.1 M, is exploited to develop membranes. However, flakes and granular particles instead of intact thin membrane are obtained during the cellulose regeneration, indicating that, in our case, this method is incapable of fabricating membrane. The fact is due to the low cellulose concentration in the casting solution. To solve this problem, a new cast drying/cellulose regeneration process is developed based on increasing the cellulose

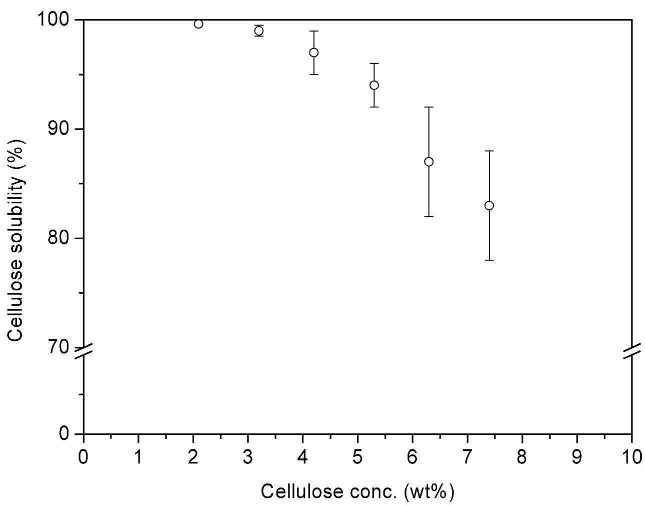

Fig. 1. Solubility of cellulose vs cellulose concentration in the casting solution.