



Preparation of homogeneous grafting cellulose and partial substitution for polyethersulfone membrane material



Fushan Chen, Zhonghua Sun*

Qingdao University of Science and Technology, Qingdao 266042, China

ARTICLE INFO

Article history:

Received 23 November 2012

Accepted 26 February 2013

Available online 5 March 2013

Keywords:

Grafting

Cellulose

Membrane

Substitution

Polyethersulfone

ABSTRACT

The homogeneous grafting was carried out by using N,N-dimethylacetamide/lithium chloride as the solvent of cellulose. The results showed that the efficient reaction conditions were as follows: reaction time, 2 h; mass ratio of monomer/cellulose, 1/1(g/g); mass ratio of initiator/cellulose, 6/50 (g/g); and reaction temperature, 80 °C. Under these conditions, the grafting percentage could reach 76%. The grafted polymer was characterized by Fourier transform infrared spectroscopy, scanning electron microscope and thermogravimetric analysis. An exploration about the partial substitution of grafted cellulose for polyethersulfone membrane material was carried out by preparing blend membranes. The blend membranes were characterized by tensile testing, pure water flux, scanning electron microscope and differential scanning calorimetry. The results showed that the blend membrane was a compatible system and the blend ratio should be controlled in about 1:16. The introduction of the grafted cellulose may result in the increase of pores size and pure water flux.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Cellulose is cheap, renewable, biodegradable, and is the most abundant organic raw material in the world, which has been widely used in industries and daily lives (El-Khouly et al., 2010). It is very likely that they will be a major chemical resource for the future (Schurz, 1999). To further expand the industrial applications of the cellulose, modification methods of physical and chemical properties of the cellulose have been continuously studied to investigate the required properties (Dessarki, Toher, & El-Arnauty, 1998; Gawish, Kantouch, El-Naggar, & Mosleh, 1995; Gosh & Dev, 1996; Gupta & Sujata, 2000; Okieimen & Ogbeifun, 1996). Graft copolymerization of vinyl polymers onto cellulose is one of the most extensively studied procedures. According to the nature of the vinyl monomer grafted on the cellulose, some desired properties such as strength (Biermann, 1996), hydrophobicity (Yang & Deng, 2008), and thermal resistance (Jain, Xiao, & Ni, 2007) can be improved. In this study, the purpose of homogeneous grafting of methyl methacrylate (MMA, hard monomer) onto cellulose was to improve strength, hydrophobicity, and thermal resistance that may meet potential application needs.

To achieve homogeneous cellulose reactions, suitable solvent systems that can both dissolve cellulose and provide a feasible reaction environment are prerequisites. The discovery of new solvents of cellulose in the past decades opened the possibility

of performing derivatization and/or grafting reactions in homogeneous conditions, thus assuring important advantages, such as better control of the substitution degree, a more uniform distribution of substituents along the polymer chain, and a higher conversion yield (Lin, Zhan, Liu, Fu, & Lucia, 2009). N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) is one of the most efficient solvent systems for cellulose. Its dissolving capacity could reach 13 wt.% (Potthast, Rosenau, Buchner, Thomas, & Gerald, 2002). In this study, cellulose was dissolved in 8 wt.% DMAc/LiCl solution and the efficient reaction conditions of the grafting reaction were examined by weighing methods.

Polyethersulfone (PES) is an attractive membrane material because it possesses excellent membrane-forming properties and high thermal/chemical stability if regardless of its high cost. This study is an exploration about the partial substitution of low-cost cellulose for high-cost polyethersulfone membrane material. In this study, the asymmetric membranes were prepared from blends of homogeneous grafted cellulose and polyethersulfone via phase inversion method induced by immersion precipitation. The surface/cross-sectional morphology, compatibility and physical properties of blend membranes were investigated by scanning electron microscope (SEM), differential scanning calorimetry (DSC) and tensile testing.

2. Experimental

2.1. Materials and equipment

Cotton linter (cellulose) was used as the cellulose material. Polyethersulfone (PES) was supplied by Changchun Jilin University

* Corresponding author. Tel.: +86 13863308157.

E-mail address: zhonghuasun@yahoo.com (Z. Sun).

Special Plastic Engineering Co., Ltd (China). All the other reagents were of analytical grade and used as received. Infrared (IR) spectra were recorded using a TENSOR27 FTIR spectrometer in the range of 4500–400 cm^{-1} . SEM images were taken on a JSM-6700F scanning microscope. The sample was coated with a thin layer of gold in a vacuum before examination. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the samples were carried out on a Pyris Diamond TG-DTA analyzer (STA449C/3/F, German). DSC was carried out with a NETZSCH DSC204F1 differential scanning calorimeter in the temperature range 110–250 $^{\circ}\text{C}$ at heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen.

2.2. Preswell and dissolution of cellulose

The following preswell procedures of cellulose were carried out to increase the reactivity of its crystalline regions before the grafting. Cellulose was preswelled in DMAc at 160 $^{\circ}\text{C}$ for 0.5 h. Then the mixture was filtered to obtain the preswelled cellulose. The dissolution of cellulose was carried out according to the literature (Lin, Cheng, Kang, Chen, & Young, 1998). The preswelled cellulose was added to DMAc/LiCl in a three-neck flask. The mixture was stirred at 100 $^{\circ}\text{C}$ for 2 h to guarantee the complete dissolution of the cellulose. The flask was continuously purged with gaseous N_2 .

2.3. Grafting of cellulose with MMA in homogeneous conditions

Following complete dissolution of the cellulose, the temperature was lowered to 70–90 $^{\circ}\text{C}$, then a solution of ammonium persulfate (APS) in DMSO, the initiator, was added; after stirring for 15 min, a predetermined volume of MMA were added to the reaction. As the reaction was complete, the product was isolated by precipitation into excess deionized water, filtered, and washed several times. Finally, the grafted sample was extracted with acetone in a Soxhlet apparatus for 48 h to dissolve all the homopolymer and dried to constant weight. The efficient reaction conditions were confirmed by weighing methods.

2.4. Preparation of blend membranes

Blend membranes were prepared by mixing two separate homogeneous solutions. Firstly, the solution of grafted cellulose was obtained under the confirmed efficient reaction conditions above. Secondly, the homogeneous solution of PES was prepared by using DMAc as the solvent. The casting solution was prepared by uniformly mixing together the two solutions with a given ratio and then stirred at room temperature for further 30 min. The blend membranes were prepared by the phase inversion technique (Sivakumar et al., 2000; Machado, Habert, & Borges, 1999; Munari, Bottino, Camera Roda, & Capannelli, 1990). The casting solution was cast on a glass plate using a doctor blade. The glass plate was quickly immersed in the gelation bath. Membrane sheets were subsequently stored in deionized water for 24 h to remove the residual DMAc/LiCl completely to obtain the membrane. These casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions would largely affect the performance of the resulting membranes (Barth, Goncalves, Pires, Roeder, & Wolf, 2000). The membrane was kept in deionized water before tests.

2.5. Grafting percentage and grafting efficiency

Grafting percentage (GP) and grafting efficiency (GE) were calculated by the following equations:

$$\text{GP} = \frac{W_2 - W_0}{W_0} \times 100$$

$$\text{GE} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_0 , W_1 , and W_2 are the weight of the raw cellulose, the monomer, and the graft copolymer, respectively.

2.6. Tensile testing

Tensile tests of the blend membranes were performed on a TTM computer tensile testing machine equipped with a 500 N cell, and the rate used in the test was 25 mm/min. Five replicates were performed to obtain an average value.

2.7. Pure water flux (PWF)

Membranes after compaction were subjected to a transmembrane pressure of 0.1 MPa to measure PWF. The flux was measured under steady state conditions. From the observed flux, the PWF was estimated from the expression (Yu, Qiu, & Tian, 2010; Zhang, Shao, & Wu, 2001):

$$J_w = \frac{Q}{A \cdot t}$$

where, J_w is the water flux ($\text{L m}^{-2} \text{h}^{-1}$), Q the permeate volume (L), t the sampling time (h), and A the membrane area (m^2).

3. Results and discussion

3.1. Homogeneous grafting of cellulose in DMAc/LiCl

3.1.1. Effect of reaction time

The effect of reaction time on the graft copolymerization is shown in Fig. 1(a). As shown in Fig. 1(a), both GP and GE showed a gradual increase with time during the time period of 1.5–2 h and leveled off 2 h later, reaching a saturated grafting value. The reduced monomer and free radicals in the reaction system with an increase in reaction time led to the leveling off effect (Earle & Seddon, 2002). Therefore, the optimal reaction time was 2 h for the homogeneous grafting of MMA onto cellulose.

3.1.2. Effect of monomer amount

The grafting percentage (GP) was found to increase with an increase in the mass ratio of monomer to cellulose [Fig. 1(b)], which could be due to the greater availability of the monomer molecules in the proximity of the cellulose increasing the chance of the molecular collision and hence grafting. The continuous decrease of GE (grafting efficiency) with an increase in monomer amount may be associated with the fact that increasing numbers of monomer molecules led to an increase of the likelihood of homopolymerization versus graft copolymerization (Welton, 1999). When the mass ratio of MMA to cellulose was 1/1 (g/g), both GP and GE were more higher relatively.

3.1.3. Effect of initiator dosage

Fig. 1(c) shows the effect of only the mass ratio of APS to cellulose on the graft copolymerization of MMA onto the cellulose backbone as other reaction variables were maintained constant. Both GP and GE showed an increase at first, followed by a decrease with an increase in the initiator dosage. The increase of GP may be ascribed to the increase of macroradicals generated by increasing levels of APS (radical initiator) on the glucose unit of cellulose, and therefore, more available sites of cellulose to react with MMA. When the mass ratio of APS to cellulose was increased by more than 6/50 (g/g), the concentration of persulfate radicals increased and consequently initiated more of the

Download English Version:

<https://daneshyari.com/en/article/10603558>

Download Persian Version:

<https://daneshyari.com/article/10603558>

[Daneshyari.com](https://daneshyari.com)