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

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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.

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

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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 °C at heating rate of 10 °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 °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 °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 °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):

$$\text{JW} = \frac{Q}{A \cdot t}$$

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

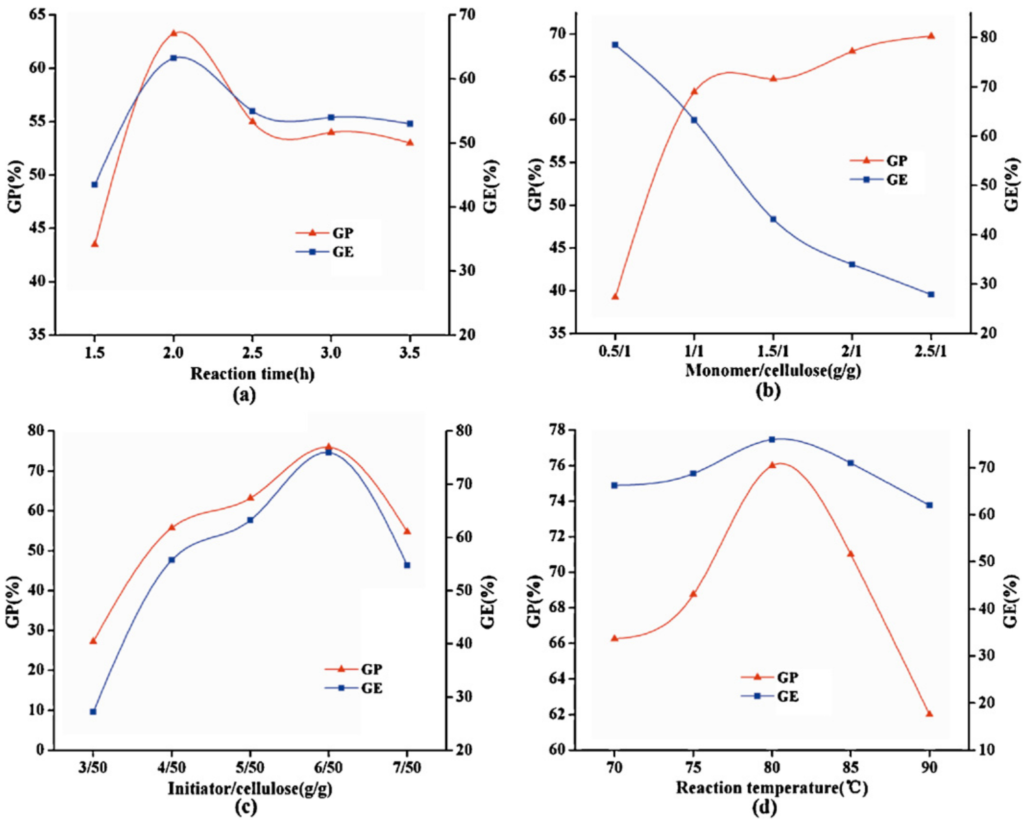

Fig. 1. Effect of reaction time (a), monomer amount (b), initiator dosage (c), and reaction temperature (d) on grafting.

homopolymerization of MMA, which resulted in a decrease in both GP and GE (Holbrey & Seddon, 1999).

3.1.4. *Effect of reaction temperature*

The effect of reaction temperature on graft copolymerization of MMA onto cellulose was investigated by changing the temperature from 70 to 90 °C, while keeping other reaction variables constant. Fig. 1(d) shows that both GP and GE reached a maximum at 80 °C. A higher temperature was helpful in increasing the bimolecular collisions for APS and cellulose, which led to the increase of cellulose macroradicals, and therefore enhanced the graft copolymerization of MMA onto cellulose. On the other hand, GP and GE decreased with a further increase in temperature, probably due to the enhanced possibilities of termination and chain transfer at a relatively higher reaction temperature (Gordon, 2001).

Therefore, the efficient reaction conditions were as follows: reaction time, 2 h; mass ratio of MMA/cellulose, 1/1(g/g); mass ratio of initiator/cellulose, 6/50 (g/g); and reaction temperature, 80 °C. Under these conditions, the GP of homogeneous grafted cellulose reached 76%.

3.2. *Characterization of homogeneous grafted cellulose*

3.2.1. *FTIR spectra analysis*

Fig. 2 shows the FTIR spectra of the native cellulose and its graft copolymer sample. As could be seen from the figure, the spectrum of the native cellulose showed the O—H stretching vibration of hydroxy at 3423.58 cm^{-1} and the characteristic absorption peak of C—O at 1061.78 cm^{-1}. Moreover, the spectrum also showed the β-glycosidic bond characteristic absorption peak at 898.93 cm^{-1} and cellulose characteristic peaks at 2922.79 cm^{-1}, 1629.34 cm^{-1} and 1377.62 cm^{-1}. Different infrared spectrum was observed from Fig. 2. This indicated that the molecular structure of the native cellulose had changed. The new peak at 1734.86 cm^{-1} correspond to the $-\mathrm{C}{=}\mathrm{O}$ group of the MMA, which confirmed the introduction of the MMA side chain into the cellulose backbone by graft copolymerization.

3.2.2. *Scanning electron microscope (SEM) observation*

In this study, the native cellulose membrane and its graft copolymer membrane were prepared via phase inversion method respectively. SEM pictures of the cellulose membrane [Fig. 3(a)] and the graft copolymer membrane [Fig. 3(b)] also confirmed grafting whereby a distinguished change is observed in the surface

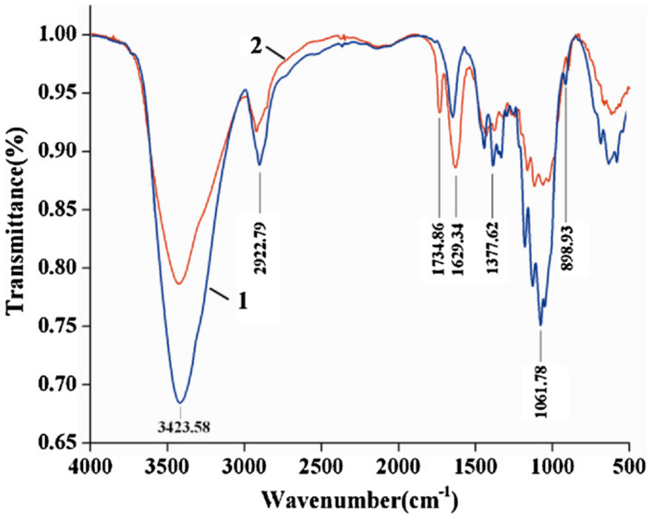

Fig. 2. FTIR spectra of the native cellulose (1) and its graft copolymer (2).

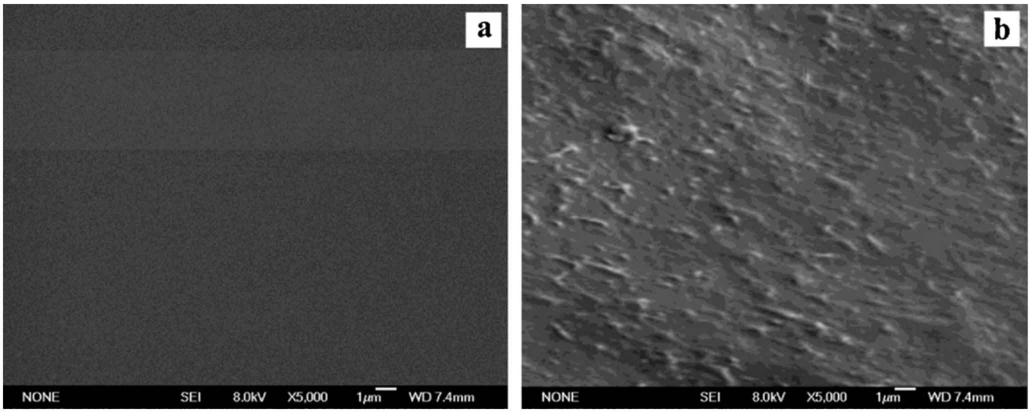

Fig. 3. SEM of the native cellulose membrane (a) and the graft copolymer membrane (b).

morphology after grafting. It could be seen that the smooth surface changed into rough ones with the small clusters. It may arise because of the polar difference between cellulose and MMA and the interruption of intermolecular hydrogen bonds and crystalline regions in cellulose.

3.2.3. *The thermostability of grafted cellulose membranes*

The TG and DTA curves of the native cellulose membrane and grafted cellulose membrane are shown in Fig. 4. As can be seen from the TG curves of cellulose, at the low temperature, 7.06 wt.% in weight loss for cellulose membrane and 8.98 wt.% in weight loss for grafted cellulose membrane were observed owing to slight dehydration. On further heating, there was a sharp weight loss. The decomposition of cellulose membrane occurred at 290 °C with about 66.81 wt.% of weight loss, and the decomposition of grafted cellulose membrane occurred at 300 °C with about 71.63 wt.% of weight loss. The weight loss of grafted cellulose membrane was higher than the weight loss of cellulose membrane at both low temperature and high temperature. Thermopositive peaks of cellulose membrane and grafted cellulose membrane occurred at 601.2 °C and 623 °C, respectively. This thermopositive peak was caused by some reactions with cellulose.

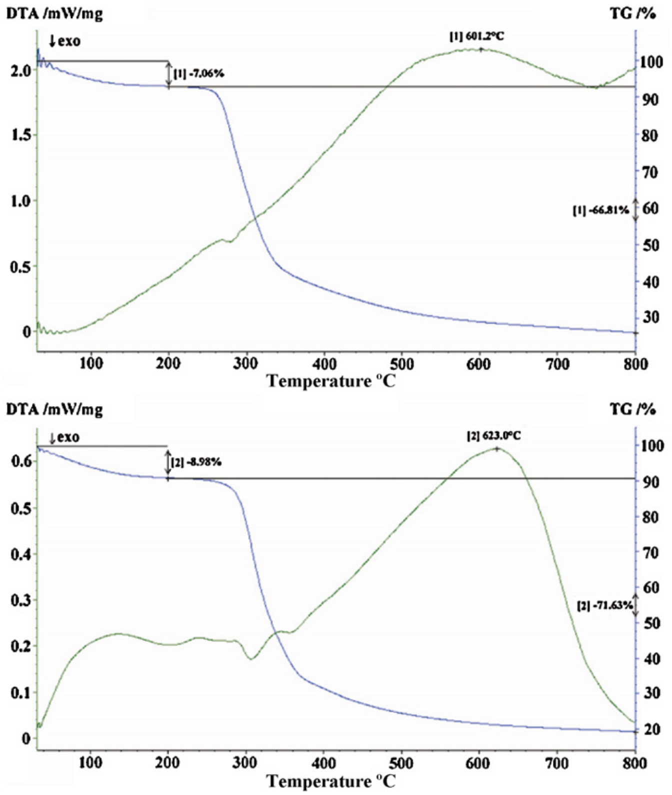

Fig. 4. The thermograms of native cellulose membrane (1) and grafted cellulose membrane (2).

3.3. *Characterization of grafted cellulose/PES blend membranes*

3.3.1. *Mechanical properties of the blend membranes*

The tensile strength and elongation of grafted cellulose/PES blend membranes with varied blend ratios were tested, as shown in Fig. 5. The tensile strength of the blend membranes gradually increased along with the decrease of grafted cellulose. However, the elongation of the blend membranes gradually decreased along with the decrease of grafted cellulose. A reasonable explanation was that grafted cellulose distributed homogenously in PES, which was considered to have a little influence on the mechanical properties. This result suggested that to retain the tensile strength and elongation of the blend membranes, the cellulose/PES blend ratio should be controlled in about 1:16.

3.3.2. *Pure water flux (PWF)*

After compaction, the blend membranes were subjected to PWF at a pressure of 0.1 MPa. Fig. 6 shows the extent of PWF on different blend ratios. It was seen that the increase in the concentration of PES resulted in a decrease of PWF. In other words, the introduction of grafted cellulose in the blend system increased the PWF of

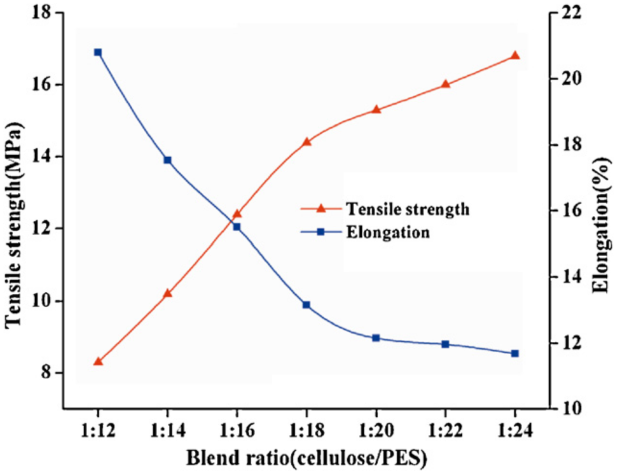

Fig. 5. Mechanical properties of grafted cellulose/PES blend membrane.

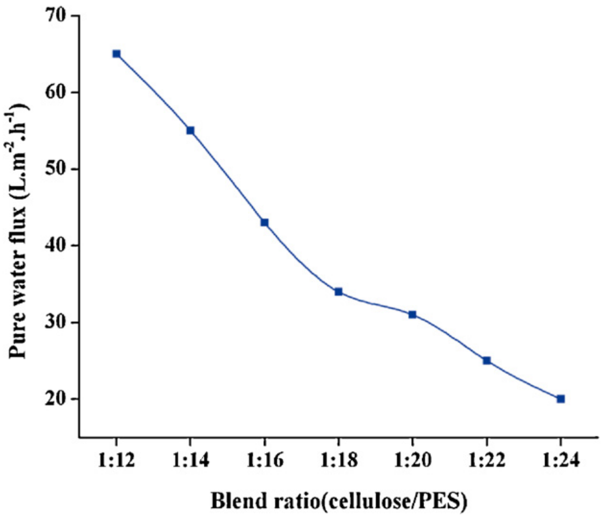

Fig. 6. Change in pure water flux on different blend ratio.

membrane. Put the mechanical properties and PWF of blend membranes with varied blend ratios together a comprehensive consideration, it should be proper to control the blend ratio in about 1:16.

3.3.3. *Morphology of membranes*

The surface morphology is a membrane surface phenomenon, which mainly describes the qualitative nature of the membranes. Moreover, the cross-sectional morphology of membranes may be used to ascertain the type and structure of pores and subsequently would be helpful in identifying the mechanism of the formation of pores (Sivakumar et al., 2000; Han & Bhattacharyya, 1995; Chan, Matsuura, & Sourirajan, 1982; Sivakumar, Mohanasundaram, Mohan, Balu, & Rangarajan, 1998; Zeng & Ruckenstein, 1996). SEM is an important and key tool for the determination of the morphology of the membranes. Therefore, the surface and cross-sectional morphologies of the pure PES membranes (prepared via phase inversion method) and the blend membranes were analyzed by scanning electron microscope (SEM).

The SEM images of the surface and cross section of pure PES membranes and blend membranes are presented in Fig. 7. It could be seen on the micrographs that the introduction of the grafted cellulose in the blend system changed the morphology of the membranes extensively and all membranes had an asymmetrical and finger-like structure. Further, it was also seen that there were plenty of finger-like pores on the surface of blend membranes and the finger-like pores connectivity of blend membranes was better than that of pure PES membranes, which indicated that the introduction of grafted cellulose may result in an increase of the blend membranes pore size and PWF. These above were useful information for the fabrication of grafted cellulose/PES blend membranes.

3.3.4. *Differential scanning calorimetry (DSC)*

The compatibility of blend membrane also was important for its applications, and one of the most commonly used methods to estimate the compatibility of polymer blends was determining the glass transition temperature (T_g) compared to those of the component polymers. DSC thermograms of grafted cellulose, PES and their blends are shown in Fig. 8. Because there was no molecular interaction or repulsion in a compatible system, a miscible polymer blend would exhibit a single glass transition temperature (T_g) between the T_gs of their components. However, the incompatible blends would show two T_gs (Lee & Lai, 1997). Fig. 8 shows the grafted cellulose/PES blends exhibited a single T_g, intermediate between the T_gs of their parent polymers, grafted cellulose and PES, indicating the compatibility of their blends.

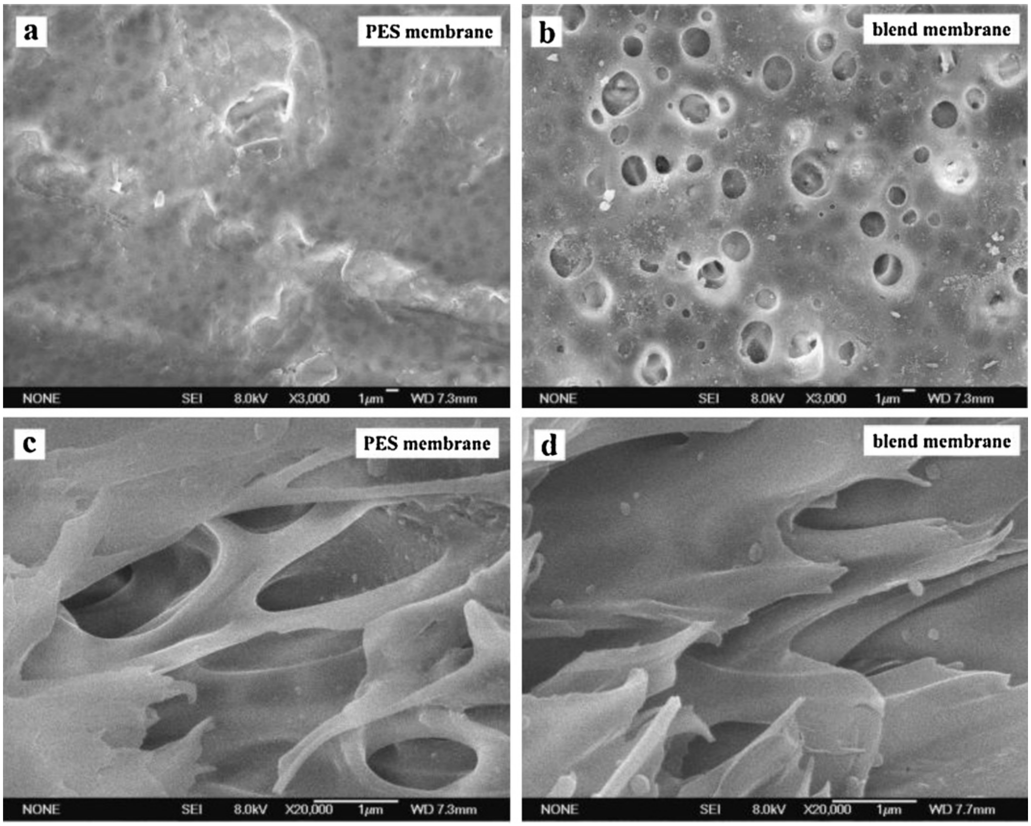

Fig. 7. SEM surface images ((a) and (b)) and cross section images ((c) and (d)) of pure PES membranes and blend membranes.

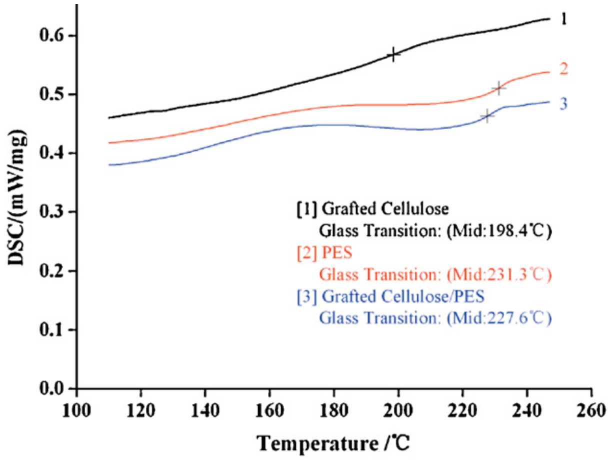

Fig. 8. DSC thermograms of grafted cellulose, PES and their blends.

4. Conclusions

Under the homogeneous conditions of DMAc/LiCl system, MMA was grafted onto cellulose successfully. The efficient reaction conditions were confirmed by weighing methods. The efficient reaction conditions were as follows: reaction time, 2 h; mass ratio of MMA/cellulose, 1/1(g/g); mass ratio of initiator/cellulose, 6/50 (g/g); and reaction temperature, 80 °C. Under these conditions, the GP of homogeneous grafted cellulose reached 76%. The homogeneous grafting of MMA onto cellulose was confirmed by FTIR, SEM and TG-DTA.

Put the mechanical properties and PWF of the blend membranes with varied blend ratios together a comprehensive consideration, the cellulose/PES blend ratio should be controlled in about 1:16. The SEM surface and cross-sectional morphologies of pure PES membranes and blend membranes indicated that all membranes had an asymmetrical and finger-like structure and the introduction of the grafted cellulose in the blend system may result in an increase of the blend membranes pore size and PWF. The DSC results indicated the compatibility of the grafted cellulose/PES blend membranes.

Acknowledgments

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