

Characterization and Pervaporation Properties of Modified PU Membranes

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ABSTRACT: Pervaporation will have broad application prospects in the treatment of phenolic wastewater. Polyurethane (PU) membrane is promising but needs to be further modified. In this study, both β -CD and CNT were used to modify the PU membrane. The structure and property of these membranes were characterized by FTIR, DSC and TGA. The pervaporation performances were investigated, and the effects of β -CD and CNT on membrane separation were discussed. TGA shows that three kinds of modified membranes have enough thermal stability to afford pervaporation test and start weight loss at about 200 °C. In pervaporation, the total flux, separation factor and PSI value all increase with increased feed temperature. That is anti-trade-off phenomenon. Among these membranes, HTPB+ β -CD-PU shows the best comprehensive performance at 80°C and has great potential for further application.

Keywords: carbon nanotube; polyurethane; cyclodextrin; pervaporation

1 INTRODUCTION

Pervaporation (PV) is one of the new membrane separation technologies, and has many advantages such as high efficiency, energy saving and so on. It has broad application prospects in the chemical industry, environmental protection and some other energy-consuming fields [1]. Membrane material is the most important key factor in membrane separation, and it decides membrane performances directly. Polyurethane (PU) is synthesized with oligomeric polyols (such as polyether or polyester) as soft segment, along with diisocyanate and chain extender (diamine and glycol) as hard segment block. PU has been developed as pervaporation membrane material recently, and it has great importance in the research of this field for its good permeability, versatile structure and easy preparation. Many researches have used PU membrane to separate phenolic compounds from water and found the very high selectivity of PU to phenol. Gupta [2, 3] used PU membranes to separate phenol from water and adjusted different NCO/OH ratio to obtain crosslinked material. As a result, the high separation factor over 1000 was obtained at 60 °C, but the total flux was very limited (less than 10g/m²h). Das [4] intended to prepare porous structure of PU. LiCl was used as pore-forming agent. The results showed that the porous PU membrane had 44.3% higher flux than PU with totally dense structure. But in general, the

flux of these membranes was less than 80 g/m²h, which was far away from the industrial application. Thus more modification work of PU should be developed.

Usually, there are two types of modifiers which are organic and inorganic additives to polymer.

β -Cyclodextrin (β -CD) is a kind of organic modifier and verified to have good affinity to phenol. Shi [5] and Zhou [6] used β -CD to adsorb phenol in water; the maximum adsorption reached 94.1%. Carbon nanotube (CNT) is a kind of inorganic modifier and strengthen the polymer [7], and that is good for membrane separation. There are many researches focused on organic or inorganic modifier into polymer, but less study is concerned about the discussion to the combination modification effect of organic and inorganic additives.

In this study, both β -CD and CNT were used to modify the PU membrane. The structure and property were characterized. The pervaporation performances were investigated and the effects of β -CD and CNT on membrane separation were discussed.

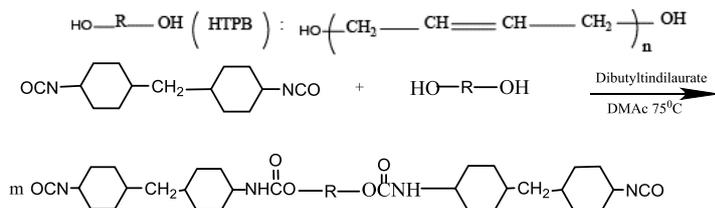
2 EXPERIMENT

2.1 Materials

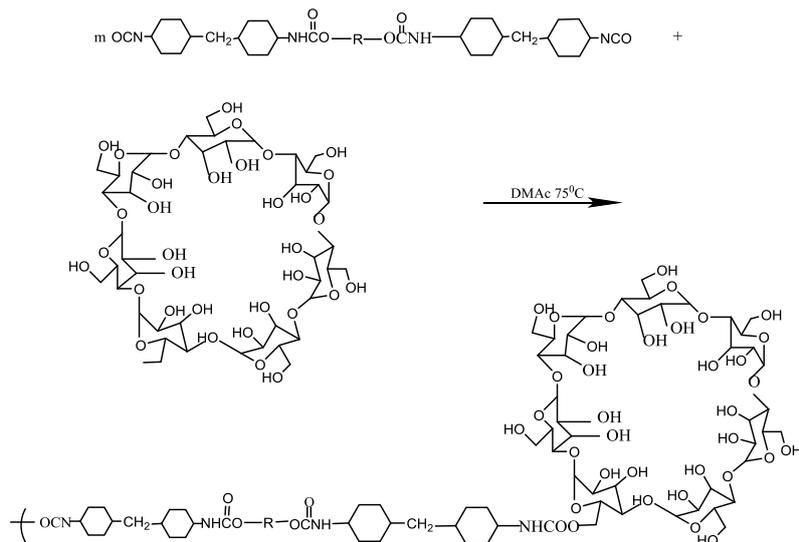
Toluene diisocyanate (TDI, a mixture of 80% 2,

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Step 1: preparation of prepolymer of PU



Step 2: chain extension of CD-modified PU

Figure 1. Preparation of CD-modified PU

4-TDI and 20% 2, 6-TDI) was supplied by Tianjin Damao Chemical Reagents Factory and used as received. HTPB ($M_n=2500$ g/mol) was obtained from Qilong Chemical Co., Ltd and dehydrated under vacuum at 110°C with constant stirring for 1h before used. 1, 4-butanediol (BDO), Dibutyltindilaurate (DBTDL), N,N' -dimethyl acetylamine (DMAc) and β -cyclodextrin (CD) were purchased from Huihaikeyi Co., Ltd. MDA and CD were dried at 110°C under vacuum for 12 h before used. DMAc was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4Å). Carbon nanotube (OD>50nm Length: 10–30 μm , dispersed in n-Butyl acetate, 70.0wt%) was purchased from Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China) and used as received.

2.2 Preparation and characterization of CD-modified PU membrane and CD-CNT-modified PU membrane

The CD-modified PU (PUCD) membrane was synthesized via a two-step method including prepolymerization and chain extension reaction as shown in Figure 1. As shown by Figure 1 (Step 1), the solution of HTPB in DMAc was placed into a three-necked flask

equipped with a reflux condenser and N_2 inlet and then added dropwise with TDI at 30°C in the presence of 0.05 wt% DBTDL as catalyst. The reaction mixture was stirred intensively for 1 h for the synthesis of NCO-terminated PU prepolymer. Then in following Step 2 in Figure 1, the solution with MDA and CD in DMAc was added under mechanical stirring for 15mins, and the solid content of solution was adjusted to about 30% by adding solvent. Thus the membrane solution to prepare PUCD was obtained. When carbon nanotube which was added to the above solution was also added, the membrane solution to prepare PU membrane with CD and CNT (CD-CNT-PU) was obtained.

The above two kinds of solutions were cast on a Teflon® plate and left under room temperature for 30 minutes followed by thermal curing at 80°C for 10h to remove the residual solvent. The thickness of these PU membranes was 80–130 μm . The molar ratio of HTPB, TDI and MDA+CD in PUCD was 1:2: (0.5+0.071).

2.3 Characterization of membranes

FTIR measurement (Nicolet IR560) was used to characterize the chemical structures of PU membranes. The samples for that were obtained by spreading a thin

film of their solutions in DMAc.

Thermogravimetric analysis (TGA) was performed on a TGA-2050 thermal analyzer using a heating rate of 20°C/min in N₂ within the temperature range of 30–700°C to examine the thermal stability.

The morphology of PU membrane was characterized by a high-resolution scanning electron microscope (SEM, FEI Company, XL 30).

The Differential Scanning Calorimetry (DSC) curves of the membranes were obtained through DSC (Seiko DSC6200) under nitrogen (N₂) atmosphere at a heating rate of 10°C/min from -100°C to 180°C. The heat history was removed before testing, and the data of DSC was from the second thermal scan.

The dried PU membranes were weighed and then immersed into aqueous solution of 1–5wt% phenol in sealed vessels at 30°C for 48h. The membranes were carefully wiped by tissue papers to remove surface solvent, and then weighted to measure the weight of the swollen membrane obtained. The degree of swelling (DS) of the membranes was then determined from following equation:

$$DS = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

Where: m_0 and m were respectively the weights of dry and swollen membranes.

The thicknesses of the membranes were determined by using a micro screw gauge.

2.4 Pervaporation experiments

The pervaporation performances of the membranes were tested by using an apparatus developed in our laboratory as shown in Figure 2. The feed was heated and circulated from the feed tank (volume of $1.5 \times 10^{-3} \text{ m}^3$) through the upstream side of the membrane cell by a pump with adjustable function of flow rate. A membrane supported by a porous sintered stainless steel in the permeated side was mounted in the pervaporation cell. The measurements were carried out for phenol/water mixtures, in which the content of phenol was 0.5 wt%. The feed mixture was maintained at temperature between 60°C and 80°C using a thermostat. The effective area of the membrane was $2.2 \times 10^{-3} \text{ m}^2$. Vacuum on the permeate side was maintained below 700 Pa. Two cold traps were set in parallel allowing the collection of permeate without rupture of the vacuum. The concentrations of the permeated and feed mixture were analyzed by gas chromatography. The permeability was evaluated by the normalized flux (J , $\text{kg} \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) as defined in formula (2) to compare pervaporation performances of membranes with different thickness.

$$J = \frac{Q}{A \cdot T} \cdot l \quad (2)$$

Where Q (kg) is the total mass of permeation collected through the effective area of membrane (A , m^2) during time T (h), l is the membrane thickness (μm).

The selectivity of membrane was demonstrated by

separation factor and defined as:

$$\alpha = \frac{Y_A \cdot X_B}{X_A \cdot Y_B} \quad (3)$$

Where Y_A and Y_B represent the weight fractions of phenol and water in the downstream permeation, and X_A and X_B respectively represent those in the feed mixture.

The pervaporation separation index (PSI) was defined as shown in Formula (4). Because PSI was an important guide for the design of new membrane materials in PV separation with an optimal integration of permeation flux and selectivity, it was introduced here for easy comparison of performances of different membranes.

$$PSI = J \cdot (\alpha - 1) \quad (4)$$

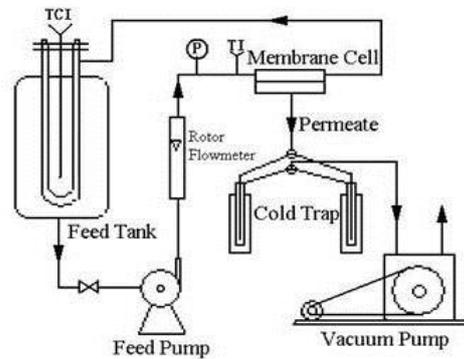


Figure 2. Pervaporation performances test apparatus

3 RESULT AND DISCUSSION

3.1 FTIR

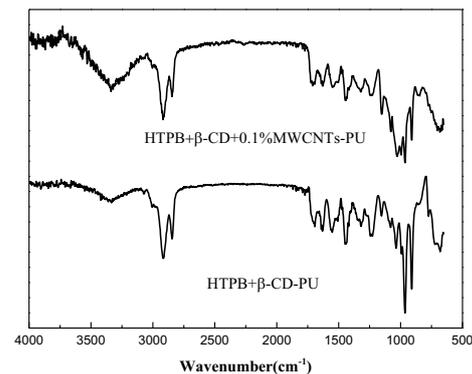


Figure 3. FTIR spectra of modified PU membranes

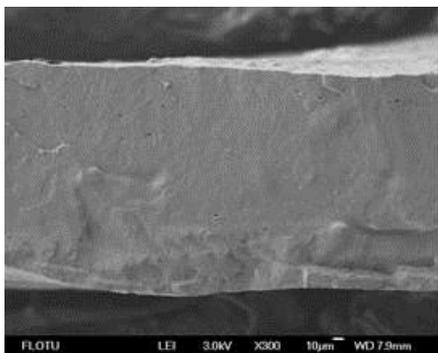
Figure 3 is the FTIR characterization of HTPB+β-CD+0.1% MWCNTs-PU and HTPB+β-CD-PU. From that, both membranes with or without CNT show obvious characteristic peak at 3300 cm^{-1} due to N-H

stretching. Besides, the peak from PUCD is stronger than that from CD-CNT-PU, which is probably due to more polar groups such as $-OH$ or $-COOH$ on CNT surface. The peaks from these polar groups overlap those from N-H, so 3300cm^{-1} peak from HTPB+ β -CD+0.1% MWCNTs-PU is stronger.

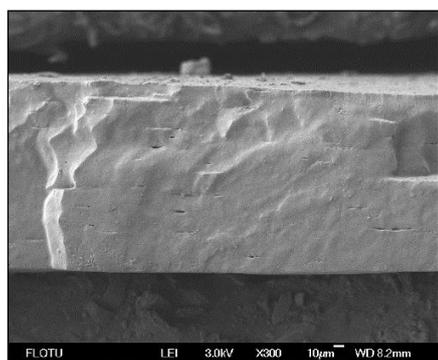
Both kinds of membranes show some common absorption peaks: 1720cm^{-1} related to stretching of C=O group, 1540cm^{-1} related to bending vibration of N-H group and the obvious bands from 2800cm^{-1} to 3000cm^{-1} related to C-H stretching vibration.

The peak at 2270cm^{-1} attributed to $-NCO$ group from TDI cannot be observed in FTIR spectra. That means $-NCO$ has been totally reacted. The characteristic peaks of urethane group and absence of $-NCO$ can prove a successful synthesis of PU material to some extent.

3.2 SEM



(a) HTPB+ β -CD+0.1% MWCNTs-PU membrane



(b) HTPB+ β -CD-PU membrane

Figure 4. SEM morphology of modified PU membranes

Figure 4 is cross section morphology of HTPB+ β -CD-PU. From that, thickness of membranes can be determined as about $100\ \mu\text{m}$. Both two kinds of PU membranes are smooth.

Comparing HTPB+ β -CD+0.1% MWCNTs-PU

shown in Figure 4 (a) with HTPB+ β -CD-PU shown in Figure 4 (b), no any aggregates are observed in CNT-modified PU membranes, which indicates a good dispersion of carbon nanotube in PU matrix. There is also no CD aggregates in HTPB+ β -CD-PU membrane, which means CD has reacted and entered into polymer network.

SEM can provide another evidence to prove successful reaction.

3.3 DSC and TGA

DSC and TGA are both common characterization methods to test thermal properties of materials.

Figure 5 shows DSC curves of several modified PU membranes. From that, glass transition temperature (T_g) can be determined. All membranes show only one T_g attributed to the soft segment of HTPB, and no T_g of hard segment is observed. It can be concluded that there is no obvious micro-phase separation in these membranes. That is also supported by SEM results and can be explained by high content ($\sim 80\%$) of soft segments in these materials. The less polar hard segments are dispersed in more soft hydrophobic HTPB areas and difficult to be gathered into a large area. As a result, T_g of hard segment is not shown in DSC curves.

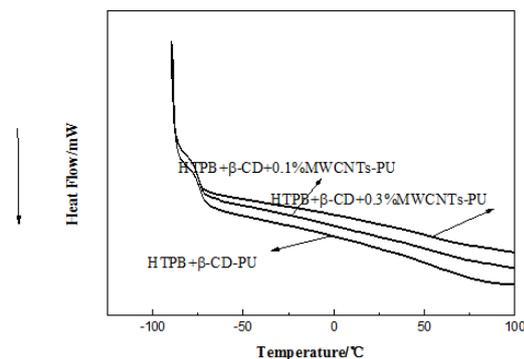


Figure 5. DSC curves of modified PU membranes

In detail, the soft T_g of HTPB+ β -CD-PU, HTPB+ β -CD+0.1%MWCNTs-PU and HTPB+ β -CD+0.3% MWCNTs-PU are respectively $-75.7\ ^\circ\text{C}$, $-75.1\ ^\circ\text{C}$ and $-73.9\ ^\circ\text{C}$, following the order HTPB+ β -CD+0.3% MWCNTs-PU > HTPB+ β -CD+0.1% MWCNTs-PU > HTPB+ β -CD-PU. So it can be seen that T_g increases with the increasing content of carbon nanotube. The mobility of HTPB will be hindered by carbon nanotube.

Figure 6 is TGA curves of HTPB+ β -CD+0.1% MWCNTs-PU, HTPB+ β -CD+0.3% MWCNTs-PU and HTPB+ β -CD-PU membranes. As shown in Figure 6, three kinds of modified membranes start showing weight loss at about $200\ ^\circ\text{C}$ following two-stage process. The first stage is during $280\text{--}350\ ^\circ\text{C}$ when $-NHCOO-$ group in hard segment begins to decompose; the second stage is over $400\ ^\circ\text{C}$ when soft seg-

ment of HTPB begins to decompose. The temperatures with 5wt% weight loss are respectively 302.5 °C for HTPB+ β -CD-PU, 310.3 °C for HTPB+ β -CD+0.1% MWCNTs-PU and 316.2 °C for HTPB+ β -CD+0.3% MWCNTs-PU. The addition of carbon nanotube improves the thermal stability of organic membrane. The operation temperature of pervaporation is during 40–80 °C, and good thermal stabilities of these membranes can ensure the steady running in separation process.

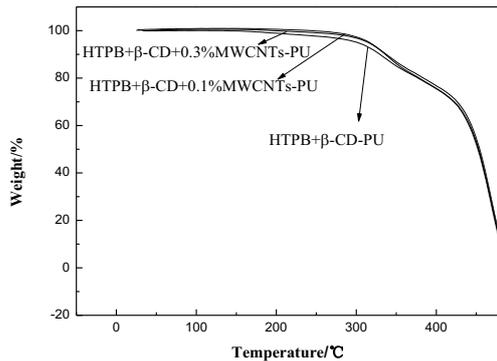


Figure 6. TGA curves of modified PU membranes

3.4 Effects of modification on PV performances

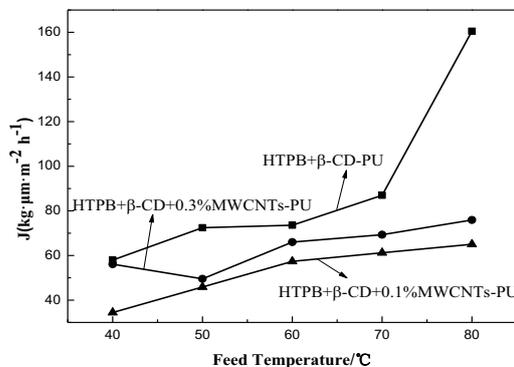


Figure 7. Permeation flux of modified PU membranes

As shown in Figure 7, three kinds of membranes, HTPB+ β -CD+0.1%MWCNTs-PU, HTPB+ β -CD+0.3%MWCNTs-PU and HTPB+ β -CD-PU all demonstrate increasing total flux with increasing temperature.

The rising temperature induces strengthening motion of polymer chain segments with more free volume or void. That is a new path to water and phenol to pass through the membrane with less resistance. What's more, phenol and water get better mobility when heated and will diffuse through the membrane more rapidly. As a result, all membranes show the

increasing permeability. Among these membranes, HTPB+ β -CD-PU possess highest flux from 58.0 $\text{kg}\cdot\mu\text{m}^2\cdot\text{h}^{-1}$ to 160.5 $\text{kg}\cdot\mu\text{m}^2\cdot\text{h}^{-1}$; while the β -CD+0.1%MWCNTs-PU has the lowest flux from 34.4 $\text{kg}\cdot\mu\text{m}^2\cdot\text{h}^{-1}$ to 65.0 $\text{kg}\cdot\mu\text{m}^2\cdot\text{h}^{-1}$.

Comparing different membrane materials, the flux follows the order HTPB+ β -CD-PU>HTPB+ β -CD+0.3%MWCNTs-PU>HTPB+ β -CD+0.1%MWCNTs-PU. It can be seen that the addition of CNTs decreased the permeability of PU membrane. CNT is a kind of nanometer materials without through-hole in it. So it will become an obstacle between polymer chain to the diffusion of water and phenol.

As the content of CNT is concerned, PU membrane with 0.3wt% obtains higher flux than that with 0.1 wt%. It is induced by interface gap between inorganic CNT and organic PU, which provides more broad permeation path through the membrane. It can be concluded that a little addition of nano-filler to organic matrix probably has great effect on separation performances.

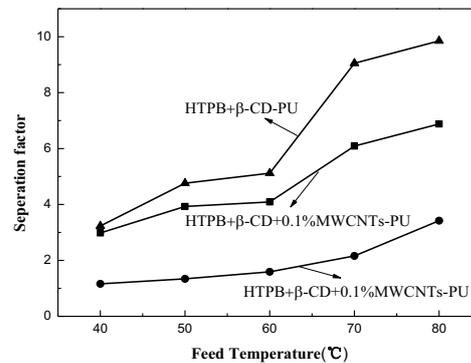


Figure 8. Selectivity of modified PU membranes

Figure 8 shows that the effect of temperature on separation factor of pervaporation. As shown in Figure 8, with feed temperature increasing, the separation factor of three kinds of membranes also increased during 40–80 °C. The relative selectivity order is HTPB+ β -CD-PU>HTPB+ β -CD+0.1%MWCNTs-PU>HTPB+ β -CD+0.3%MWCNTs-PU.

In the research of pervaporation membrane separation, most membranes usually have increased flux and decreased separation factor with increased feed temperature. That is called a “trade-off” phenomenon. But in our study, both permeation and selectivity increase with temperature, and that is anti-trade-off but advantageous for application. In previous study, Zhang^[8] added ZSM-5 zeolite into PU membrane for the separation of ester from water and found similar results. It was considered that water molecule existed not in the form of a single molecule, but a cluster composed of several water molecules when feed temperature was increased. Because the size of water cluster was bigger than that of single water molecule, these clusters were

difficult to diffuse than ester. As a result, the water flux decreased and the selectivity was increased. Furthermore, Yang^[9] used ZSM-5 zeolite to fill polymer membranes such as PU and PEBA to recover organics from water, and the similar anti-trade-off was observed. They considered that the activation energy of organics was higher than water, so the increase of organics flux was more sensitive to temperature and elevated to more extent with increased temperature. The further research is needed to reveal this phenomenon.

Comparing two kinds of CNT modified PU membranes, HTPB+ β -CD+0.1%MWCNTs-PU shows a higher selectivity than HTPB+ β -CD+0.3%MWCNTs-PU. On one side, more CNT will occupy the free volume of polymer chain and result in the decreased flux of water and increased separation factor. On the other side, the interval between CNT and polymer provides more broad space for diffusion than original free volume, and water will pass through membrane easier than phenol due to smaller size.

In this study, the latter is predominant. So HTPB+ β -CD+0.1%MWCNTs-PU shows higher selectivity than HTPB+ β -CD+0.3%MWCNTs-PU.

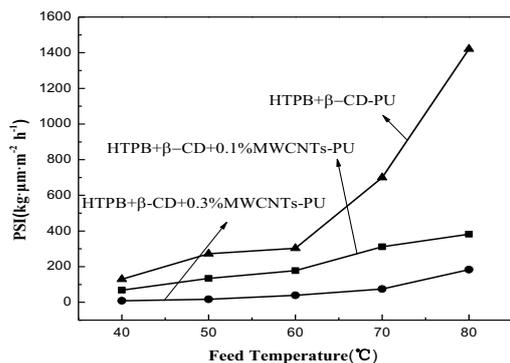


Figure 9. PSI of modified PU membranes

PSI is an important index to evaluate the comprehensive performances of membranes. It includes both permeability and selectivity. Usually, the high PSI value means great potential to develop or apply. Figure 9 shows that the effect of temperature on PSI of pervaporation. As shown in Figure 9, with feed temperature increasing, the PSI of three kinds of membranes also increased during 40–80 °C just as flux and separation factor. HTPB+ β -CD-PU has the highest PSI value and the potential to further application. But when the stability is concerned, CNT modified membranes will be suggested for its better thermal stability.

In many studies, the comprehensive performances of membranes in this study are better than other previous research. So HTPB+ β -CD-PU and CNT modified HTPB+ β -CD-PU membranes can be developed for the treatment of waste water in more industry application. Particularly, the process of synthesis and

preparation is simple and the cost of relative material is low. And more industrial investigation should be started.

4 CONCLUSIONS

Three kinds of modified PU membranes with CD or carbon nanotube were prepared successfully. The results from FTIR show that the characteristic peaks of urethane group and absence of –NCO. DSC curves prove that Tg increases with the increasing content of carbon nanotube. The mobility of HTPB will be hindered by carbon nanotube and no obvious micro-phase separation is observed. TGA shows that three kinds of modified membranes have enough thermal stability to afford pervaporation test and start weight loss at about 200 °C. In pervaporation, the total flux, separation factor and PSI value all increase with increased feed temperature. That is anti-trade-off phenomenon. Among these membranes, HTPB+ β -CD-PU shows the best comprehensive performance at 80 °C and has great potential for further application.

ACKNOWLEDGEMENT

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