Study on Hole Filling of Porous PU/PEG Membrane and Its Mechanical Properties

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Abstract: This study attempted to introduce porous technology into functional textile's formation, and developed a new way to improve working materials content in phase change material. Porous polyurethane (PU)/ polyethylene glycol (PEG) membrane was prepared and selected as a supporting material. Considered to be convenient for filling, anhydrous ethanol was used to decrease PEG viscidity according to the rule of similarity. The solution of PEG and anhydrous ethanol were filled into porous PU/PEG membrane by vacuuming and then PU dry-film technology was used for the sealing of the membrane hole. The effects of PEG mass percentage in ethanol solution on filling rate and the filling rate on the membrane morphology and mechanical properties were studied. The results show that, the filling rate increased with the increase of PEG content in the blending solution. As the filling rate increased, the elongation at break decreased obviously, while the initial modulus increased largely. After sealing the filled membrane using PU dry-film technology, the initial modulus of the membrane decreased, while the elongation at break increased. In addition, DSC analysis indicates that the sealed membrane and pure PEG show similar thermal properties, while the compound membrane can retain its solid shape during phase change.

Keywords: Porous phase change membrane, polyurethane, polyethylene glycol, filling, mechanical properties.

1. Introduction

Technology development and the improvement of people's lifestyle brought forward higher demands to textile comfort performance. Self-adaptive textiles with heat storage and preservation function thus came into being and then the representative materials are phase change materials (PCMs) and corresponding techniques [1-4]. Among all the studies, new compound solid-solid PCMs are paid more and more attention [5-10]. Porous materials have light mass and big porosity. The combination of porous material and phase change material (PCM) is one method to obtain compound solid-solid PCMs. Porous composite phase change materials have been used as heat preservation materials in buildings. And relative study has being done widely at home and abroad [11-16]. The control of pore structure and PCM content are two key problems in porous composite PCM study. PCM content decides heat storage density and temperature adjusting ability of the composite material [17]. Pore structures and characters not only effect PCM content but also heat insulation [18]. For the present study, there are still problems such as low latent heat during phase change and separation of work material and supporting material [19]. And polyurethane membrane as porous skeleton in phase change composite material is seldom reported.

In this study, porous polyurethane (PU)/ polyethylene glycol (PEG) membrane was prepared and selected as supporting material and PEG was selected as filling component. For pure PEG has high viscidity hole of the PU/PEG membrane was shaped as a beehive, it was hard to fill PEG into the membrane fully if only rely on soaking and wicking. To improve the filling effect, PEG and anhydrous ethanol was blended in a certain proportion to reduce PEG viscidity based on the law of similar mutual solubility. Porous PU membrane was soaked in the blended solution and the filling of the membrane with PEG was fulfilled under a certain vacuum degree. And PU dry film was used for the sealing of the filled membrane.

2. Experimental section

2.1 Materials and reagents

PEG2000, N, N-Dimethylformamide (DMF) and anhydrous ethanol were of chemical grade and supplied by Shanghai Sinopharm Chemical Reagent Co. Inc. Liquid PU (solid content 30wt%) was of chemical grade and purchased from Kunshan Gaoding Chemicals Industry.

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2.2 Preparation of porous PU/PEG membrane

The homogenous mixture solution was obtained by dissolving PU and melted PEG in DMF by vigorous stirring. When the mixture solution was cooled down to room temperature, 28.6wt% $(NH_4)_2CO_3$ superfine powder was dispersed in DMF and the emulsion was added into the mixture and stirred vigorously for 1h to form a homogenous solution. After degassing, the resulting solution was cast onto a plane glass model using a glass bar. The cast film was placed at ambient temperature for 2min, and then immersed into water at room temperature for 3 min. And then the model was taken out of water and dried in air for about 5h. Finally the membrane was removed from the model and placed in climatic chamber at temperature 50℃ and 70~80% R.H. for at least three hours. After steam treatment, the films were stored in a ventilated environment for at least one week before measurements.

2.3 Filling and sealing of the membrane

Melt PEG and anhydrous ethanol were mixed up in different mass ratio till a white transparent solution obtained. Then the porous membrane was vacuum-impregnated (vacuum degree 0.1MPa) with the blended solution. The membrane was taken out when no bubble appeared in the solution and was dried until anhydrous ethanol volatilized entirely.

14~19wt% PU (30wt%PU diluted with solvent DMF) was poured into a self-made glass plate and scrapped to film formation with a glass bar. The cast film was dried at 25~60℃ for 1~10min and then covered with the filled membrane (loosen bottom down). Then the combined membrane was flattened and treated at 20~30℃ for 5~30min under 60~80% relative humidity. After becoming stable, the film was peeled off and stored in sealed container for measurement.

2.4 Characterization

2.4.1 Morphology observation

Pore morphology of PU/PEG membrane and the surface of the sealed membrane were investigated using a scanning electron microscope (SEM) (HITACHI, model X-450).

2.4.2 Void fraction measurement of the membrane

Void fraction of the porous PU membrane was calculated according to Eq.1:

$$V = (V_1 - V_0)/V_1 \times 100(\%) \qquad (1)$$

where V is void fraction of the membrane,%; V_0 is entity volume of the membrane (Assuming the membrane has no pore.); V_1 is real volume of the membrane.

2.4.3 Viscosity measurement of blended PEG and anhydrous ethanol

PEG and anhydrous ethanol were blended evenly by different mass ratio. The viscidity of the mixture was measured using NDJ-79 rotational viscometer.

2.4.4 Filling rate of PEG into porous PU/PEG membrane

Filling rate was calculated according to Eq.2:

$$W\% = \frac{W_1 - W_0}{W_1} \times 100\% \qquad (2)$$

where W is the filling rate of PEG into PU/PEG membrane; W_1 is the dry weight of the filled membrane; W_0 is the dry weight of the membrane before filling.

2.4.5 Mechanical property measurement

Mechanical performance test of the membrane was carried out using Instron5566 apparatus with 50mm gauge at a crosshead speed of 100mm/min, using rectangular (100mm×50mm) type tensile bars as testing samples.

2.4.6 DSC Measurement

Differential scanning calorimetry (DSC) was carried out using a DSC 204 F1 (NETZSCH). Samples (5~10 mg) were sealed in aluminum pans and measurements were performed in nitrogen atmosphere (60ml/min) at a heating rate of 10 ℃/min in a temperature range of 0 to 100 ℃. In the first scanning, the sample was kept at 0 ℃ for 10 min and heated to 100 ℃, then kept at this temperature for 10 min. In the second scanning, the sample was cool down to 0 ℃ and the second scan was measurements were recorded.

3. Results and discussion

3.1 Porous PU/PEG membrane morphology

Figure 1 is the SEM image of PU/PEG membrane sublayer. It can be seen that porous structure of the membrane was formed. It is observed that in the sublayer round pores or likeness as beehive presents for a certain distribution. And it shows the pore grows along the thickness direction of the membrane to shape like a finger. The formation of porous structure resulted from instant phase separation between PEG continuous phase and PU dispersed phase and thermal decomposition of $(NH_4)_2CO_3$ powder.

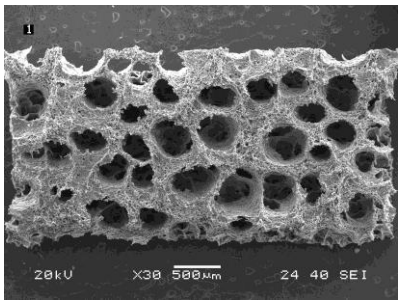


Figure 1 SEM image of PU/PEG membrane.

3.2 Effects of PEG Mass Percentage on filling rate

The relationship between PEG mass percentage in anhydrous ethanol solution and filling rate is shown in Figure 2. It shows that as mass ratio of PEG to anhydrous ethanol increased, the filling rate increased gradually and reached stability.

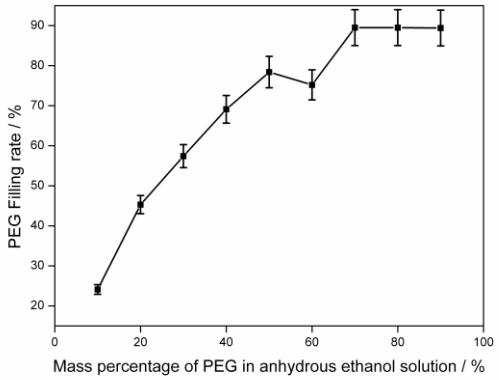


Figure 2 The relationship of PEG mass percentage in ethanol solution and filling rate.

Viscosity measurement results are listed in Table 1, which show that the viscosity of the blended solution increased as PEG proportion increased. It means the solution of low mass ratio was easy to flow into the membrane hole, but low PEG content resulted low filling rate. Though filling rate increased as mass ratio increased, at the same time, solution viscosity increased, which hindered flow of the solution, and thus filling rate tends to be stable.

In addition, during experiment it is observed that as mass percentage of PEG reached 50%, membrane shape changed obviously; when at 90%, the membrane swelled and the appearance changed totally which was due to the increase of PEG viscidity and the formation of PEG layer at the bottom of the membrane.

Table 1 Viscosity of PEG and anhydrous ethanol blend

P	10	20	30	40	50	60	70	80	90
V	4	4	8	13	25	35	59	91	920

*P is the mass percentage of PEG in blend solution, % and V is the viscosity of the blended solution, mPa s.

3.3 Effects of filling rate on mechanical properties of PU/PEG membrane

Mechanical properties of the membrane with different filling rates are presented in Table 2.

Table 2 Mechanical properties of the porous membrane with different PEG content

Filling rate (%)	Breaking strength (MPa)	Breaking extension (mm)	Breaking work (J)	Initial modulus (N/mm^2)
0	5.083	490.6	10.44	0.678
24.10	3.426	384.0	7.644	1.699
45.26	3.380	401.4	9.015	4.142
57.39	3.346	369.6	6.985	5.284
69.06	1.751	117.0	2.827	12.450
78.36	1.470	11.6	0.630	34.890
89.53	1.108	3.4	0.356	111.700

It is obvious that breaking strength and breaking extension decreased with the increase of PEG filling rate, namely the tenacity of the membrane. And the evident increase of initial modulus meant the membrane turned to become brittle. Especially when filling rate exceeded 69.06wt%, breaking extension decreased drastically, which demonstrated further that PEG filling played evident negative role on mechanical properties of the membrane. Excessive PEG addition made the soft film sub-layer become tight and hard. PEG viscidity limited macromolecular stretching, which resulted in the large macromolecule amounts

loaded at the same time of reduction and thus the non-simultaneous breakage of the membrane increased. Considering the mechanical properties, high PEG filling rate was not suitable.

3.4 Mechanical properties of the sealed membrane

The membrane with 69.06wt% filling rate was sealed and the feature of sealing layer and the filled membrane are shown in Figure 3.

Mechanical properties of the sealed membrane are shown in Table 3. The results show that breaking strength reduced further after the membrane was sealed. However, breaking extension of the sealed membrane increased and initial modulus decreased compared to the filled membrane, but was still lower and higher than the unfilled membrane respectively. As stated above, the flexbility of porous PU/PEG membrane reduced after filling, however, when the membrane is being sealed by casting solution using dry method, DMF in the solution results in volatized and corroded, sub-layer and cortex layer of the filled membrane, which reduced initial modulus of the sealed membrane. The increase of breaking extension was due to PU layer formed after sealing.

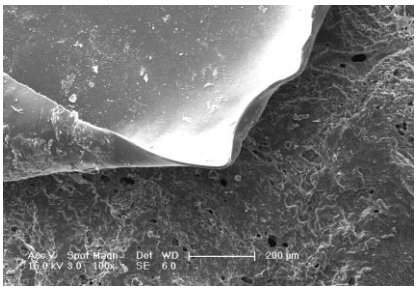


Figure 3 SEM photo of the sealed membrane.

Table 3 Mechanical properties of the membrane

Sample	Breaking strength (MPa)	Breaking extension (mm)	Breaking work (J)	Initial modulus (N/mm^2)
Unfilled	5.083	490.6	10.44	0.6780
Filled	1.751	117.0	2.827	12.45
Sealed	0.5889	263.4	2.743	7.679

3.5 Phase change behavior of the sealed membrane

DSC curves of the sealed film and PEG2000 are shown in Figure 4, and the data of their transition temperature and enthalpy are summarized in Table 4. The results show that heating and cooling DSC curves of the sealed membrane and pure PEG show similar characterization, and there was a melting peak at about 56.9℃ in the heating direction for both, which indicated they had similar thermal properties. However, for the sealed membrane, initial temperature decreased and final temperature increased in the heating direction; initial, final and peak temperature decreased in the cooling direction; and the enthalpy was obviously lower than that of pure PEG. The difference implies that the PU blocked PEG to carry out phase change and reduced its sensitivity to temperature; when PEG was crystallized, PU weakened the PEG crystallization integrity, which reduced the transition temperature.

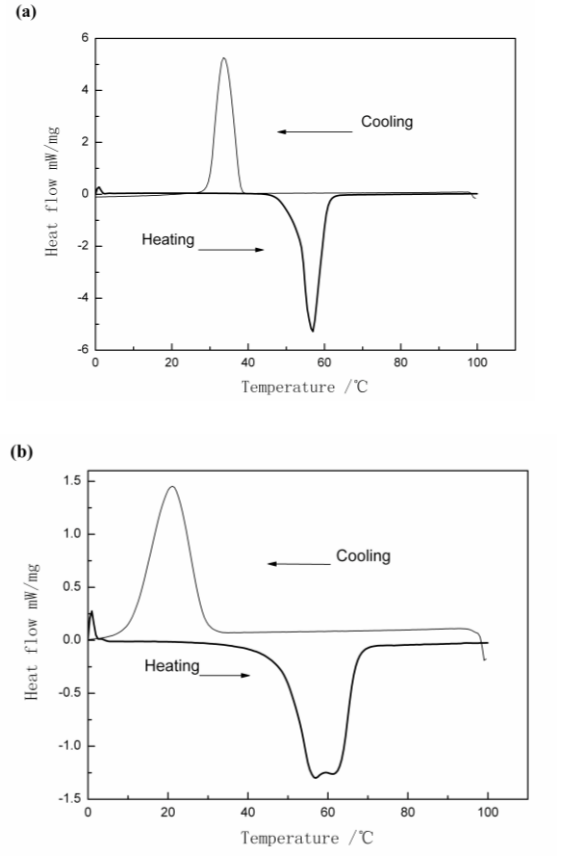


Figure 4 DSC curves of PEG and the sealed film (a) PEG2000; (b) the sealed film.

Table 4 Transition temperature and enthalpy of the sealed film and pure PEG

Sample		T_{on} (℃)	T_p (℃)	T_{end} (℃)	$\triangle H_1$ (J/g)
PEG2000	Heating	53.2	56.9	60.8	178.7
	Cooling	38.0	33.7	29.8	160.4
Film	Heating	49.4	56.9	67.1	107.5
	Cooling	29.0	21.2	11.0	95.6

* T_{on}: initial temperature; T_{end}: final temperature; T_p: peak temperature; $\triangle H$: enthalpy.

In addition, the enthalpies of the positive process (107.5J/g) and the reverse process (95.6J/g) are close, and the temperature decides the direction, which indicates that the sealed membrane was a transition reversible latent storage material [20]. Moreover it was observed that the sealed membrane can keep its solid shape during phase change. Namely stable or shape stabilized compound PCM with high PEG content was obtained.

4. Conclusion

Porous PU/PEG membrane was prepared and taken as a supporting material. Blended solution of PEG and anhydrous ethanol was filled into the porous membrane under vacuum. Filling rate increased with the increase of mass ratio of PEG to anhydrous ethanol until it reached stability. Filling rate increase resulted in the decrease of membrane tenacity and membrane shape deformation. PU dry-film technology was used for the sealing of the membrane pore. After sealing, initial modulus of the membrane decreased, and breaking extension increased. The sealed membrane and pure PEG show similar thermal properties, but phase change enthalpy reduced and temperature range changed, except the increase of final temperature in the heating direction, other initial and final temperatures decreased.

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