Microporous Membrane with Temperature-Sensitive Breathability Based on PU/PNIPAAm Semi-IPN

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ABSTRACT: The semi-interpenetrating polymer network (semi-IPN) of thermoplastic polyurethane (TPU) and poly(*N*-isopropylacrylamide) (PNIPPAm) was synthesized and fabricated into microporous membranes with temperature-sensitive breathability. The chemical and physical structure of the semi-IPN was investigated by FTIR and thermo analysis including DSC and DMA. The results proved that the glass transition temperature of TPU and the LCST of PNIPAAm were shifted in the semi-IPN, revealing the formation of interchain interactions among the molecular chains of TPU and PNIPAAm. The swelling measurements revealed that the semi-IPN shows volume phase transition behaviors. The semi-IPN was therefore fabricated into microporous membranes and its volume phase transition property was employed to endow the membrane with temperature-sensitive breathability. The water vapor permeability of the membranes was measured and found to be significantly dependent on the temperature, which was enhanced remarkably when the temperature went up. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: E2–E8, 2012

Key words: polyurethane; semi-interpenetrating polymer networks (semi-IPNs); crosslinking; breathability

INTRODUCTION

Traditional waterproof fabrics are usually made from polyester and nylon. The high density and hydrophobic nature of traditional waterproof fabrics leads to a low permeability of moisture, resulting in poor breathability, which intensively impedes the evaporation of perspiration, and seriously debases the wearing comfort of waterproof garments. To endow the waterproof garments with high breathability, great effects have been taken in recent years searching for better materials. One of the most popular elements involved in modern breathable waterproof fabrics is microporous membrane. Large amount of micropores are introduced in the membrane, which are much smaller than water droplets from rain or snow, but large enough for water to be transmitted through in the form of single-molecular vapor. In this way, the two apparently contradictory properties of water-resistance and breathability are perfectly combined. Breathable fabrics can be found in various applications, such as sports wear, mountaineering suits, and military uniforms.

However, like the two faces of a coin, the enhancement on the breathability of fabrics inevitably decreases their thermal insulation, and the introduction of micropores greatly increases the evaporation of perspiration. Although this helps to keep human skin cool and dry in hot weather, it also results in serious loss of heat when the environmental temperature drops. This strictly restrains the applications of microporous membrane-based breathable garments, especially for the situations of outdoor activities, such as mountaineering and skiing. To solve this problem, the property of temperature sensitivity is required so that breathability should be reduced with the fall of environmental temperature. The special phase transition behavior of shape memory polyurethane was employed to fabricate temperature-sensitive fabrics.[1,2] However, the film has to be very thin if excellent permeability is required because of the solution-diffusion mechanism, which in turn reduces the mechanical stability of the film. PNIPAAm is a famous material with fine temperature-sensitivity. But the high glass transition temperature and low mechanical stability make it inappropriate for the application of fabrics. To achieve both high mechanical stability and

temperature sensitivity, IPN strategy was used to fabricate the blend of PU/PNIPAAm with various methods[3–7] in which the molecular chains of PU and PNIPAAm were combined by the interchain molecular interactions, such as hydrogen bonds. This novel material was widely applied in the process of medical treatment,[8–11] mainly based on its property of hydrophilic–hydrophobic transition.

Except for the hydrophilic–hydrophobic transition, PU/PNIPAAm IPN also shows a significant volume phase transition with the increase of temperature. In this work, we fabricated microporous membranes with PU/PNIPAAm semi-IPN. When the temperature decreases, the PNIPAAm in semi-IPN swells and the size of the micropores is reduced, leading to lower water vapor permeability. The membrane is therefore endowed with a fine temperature-sensitive breathability, and is very prospective in the applications of all-weather waterproof garments.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAAm) was purchased from Tokyo Chemical Industry Co., (TCI) and was used as received. Thermoplastic polyurethane (TPU, Estane 58887) was obtained from Lubrizol Advanced Materials, N,N′-methylene bisacrylamide (BIS) and azobisisbutyronitrile (ABIN) were recrystallized. Tetrahydrofuran (THF) and N,N′-dimethylformamide (DMF) were of analytical reagents and dried over 4 Å molecular sieve before use.

Preparation of the semi-IPN and fabrication of membranes

TPU was dissolved by the mixture of tetrahydrofuran(THF) and N,N′-dimethylformamide(DMF) (3 : 7, in volume ratio) to obtain a 10 wt % solution. NIPAAm, BIS, and AIBN were then added into the TPU solution with certain weight ratios. The *in situ* polymerization was then carried out under nitrogen atmosphere at 70°C for 6 h. In the end of the reaction, the solution was directly cast onto glass plate. After exposure in the air (15°C and 55% relative humidity) for 5 min, the membrane was immersed into water bath for 24 h. The membrane was then peeled off from the glass plate and washed by ultrasonication to remove unreacted NIPAAm monomer and then dried under vacuum for 24 h. For the characterization of semi-IPN material, samples of dense film was also prepared without the above phase-inversion steps.

Characterization of the semi-IPN

FTIR spectra were obtained by a NEXUS670 (Nicolet Instruments Corp.) spectrometer with 4 cm^{-1} resolution from 400 cm^{-1} to 4000 cm^{-1} to recognize the type of thermoplastic polyurethane and the successful synthesis of PU/PNIPAAm semi-IPNs. The film formed in water with 8%BIS was taken as a sample. Each sample was scanned 16 times at a resolution of 4 cm^{-1}, and the scan signals were averaged.

DSC measurement was carried out to study the change of LCST of PNIPAAm on a Mettler-Toledo Star DSC 204 F1 (Switzerland). The instrument was calibrated with an indium standard. The measurement was conducted under nitrogen atmosphere and the sample weight used in the DSC pan was kept within 4–6 mg. The samples of PU and PU/PNIPAAm semi-IPNs were immersed in water for 24 h and then wiped off the water on surface before the DSC experiments. The samples were heated up from 20 to 50°C at a rate of 3°C/min.

The storage modulus (E′), loss modulus (E″), and loss tangent (tan δ) of the semi-IPN material were measured with a Dynamic mechanical analyzer Q800-0678(TA Instruments, New Castle, DE) in tension mode. The sample was prepared in rectangular shape with the width of 5 mm and gauge length of 16 mm. The sample thickness was 0.1 mm. The testing was carried out at the temperature of 20°C and the relative humidity of 65 ± 2%. The dynamic mechanical properties of the samples were determined at frequency of 1 Hz. The heating rate was 3°C/min, and the temperature was scanned from −80°C to 60°C to record the T_g of TPU in semi-IPNs.

The volume phase-transition property of the semi-IPN was characterized by the equilibrium swelling ratio (ESR). The samples were immersed in water for 24 h, and then the samples were taken out and quickly blotted by tissue papers to remove free water on surface for gravimetrical measurement. Equilibrium swelling ratio was defined as

Equilibrium Swelling Ratio (ESR)
$$= (W_e - W_d)/W_d * 100\% \quad (1)$$

where W_e is the weight of swollen sample in equilibrium with water and W_d is the weight of the dried sample.

The mechanical properties of the semi-IPNs were characterized by tensile measurements on an SANS 8502 tensile tester (China) with a crosshead speed of 20 mm/min. The membrane sample was prepared in rectangular shape with the width of 10 mm and gauge length of 40 mm. The sample thickness was about 0.1–0.2 mm and measured by a micrometer screw clipper. The testing was carried out at the temperature of 20°C and the relative humidity of 65 ± 2%. The final results were reported as the average of five measurements.
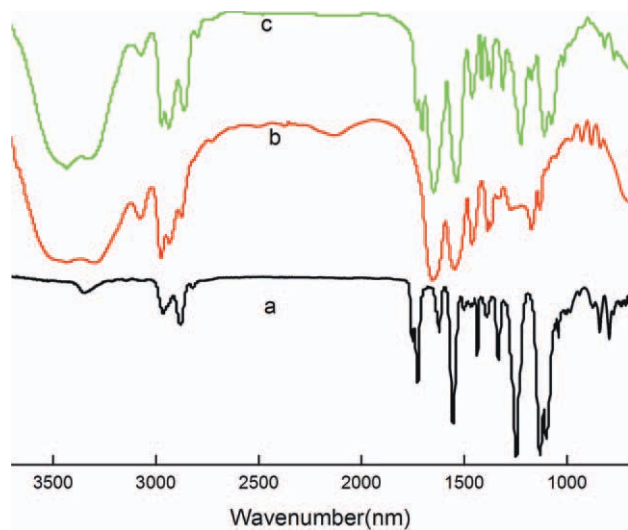
Figure 1 FTIR spectrum of polyurethane, PNIPAAm and PU/PNIPAAm semi-IPNs (a) PU; (b) PNIPAAm; (c) PU/PNIPAAm semi-IPNs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of the membranes

The morphologies of the membrane surface and cross-section were characterized by a field emission scanning electron microscope (JEOL JSM-5610, Japan) at the acceleration voltage of 15.00 kV after coating with an Au–Pd alloy layer.

The water vapor permeability (WVP) measurement of the membranes was carried out according to ASTM E96-80B method in which an upright cup, covered with the sample membrane and filled with fixed amount of water (10 mL), was placed in a controlled chamber at the relative humidity of 50% and various temperatures. WVP values were calculated according to Formula (2):

$$WVP = G/tA = (G/t)/A \qquad (2)$$

where G is the weight gain (g) of the test cup, t is the time length (h) of the WVP measurement, and A is the effective area (m^2) of the membrane.

RESULTS AND DISCUSSIONS

Structure properties of the PU/PNIPAAm semi-IPNs

The chemical structure of the semi-IPN was characterized by FTIR. The transmission IR spectra of TPU, NIPAAm and PU/PNIPAAm semi-IPNs were shown in Figure 1. In the spectra of TPU, the adsorption peaks at around 1640 cm^{-1} and 1550 cm^{-1} could be attributed to the adsorption bands of amide I and amide II, respectively. These two adsorption peaks could also be found in the spectra of PNIPAAm and semi-IPN. The band at 1223 cm^{-1} belongs to the ether linkage. The distinct band absorption 1730 cm^{-1} is

caused by the vibration of carbonyl groups. In the spectra of semi-IPN, all the above peaks are reserved. No new adsorption bands were discovered, indicating that there are no covalent bonds between TPU and PNIPAAm chains in the semi-IPN. On the other hand, the adsorption bands at 3300–3400 cm^{-1} in the spectra of PNIPAAM became narrower. This revealed that the free amino groups and hydroxyl groups in the PNIPAAm chains are fixed by the interchain hydrogen bonds with TPU chains in the semi-IPN.[4,12]

Although FTIR spectra had supplied some information about the structure of the semi-IPN, the most useful data was from the results of thermo analysis, including DSC and DMA, as shown in Figures 2 and 3.

As T_g of PU film is about $-21°C$ and it tends to melt at temperature above $100°C$, DMA was conducted at the temperature from $-80°C$ to $60°C$. The storage modulus, loss modulus, and tan δ of PU/PNIPAAm semi-IPNs with different BIS amount were identified by DMA measurement. The temperature associated with the peak magnitude of tanδ is defined as the glass transition temperature (T_g).[13]

The effect of NIPAAm content and BIS amount on T_g of PU and PU/PNIPAAm semi-IPNs films, and LCST values of PNIPAAm in PU/PNIPAAm semi-IPNs were recorded and listed. Figure 2 indicated that with the content of NIPAAm increasing, T_g of PU/PNIPAAm semi-IPNs went to a higher temperature, but changed not much when the content was higher than 25% (where the BIS amount was 5% relative to the weight of NIPAAm). The results of BIS amount on T_g of PU/PNIPAAm semi-IPNs and LCST of PNIPAAm (where NIPAAm content was 25%) illustrated that T_g of PU/PNIPAAm semi-IPNs went up when BIS amount was no less than 5% and did not change much when the amount of BIS was
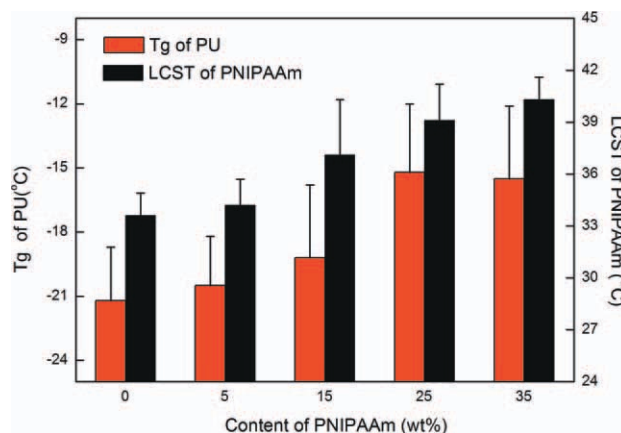

Figure 2 The effect of PNIPAAm content on the T_g and LCST of PU/PNIPAAm semi-IPNs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
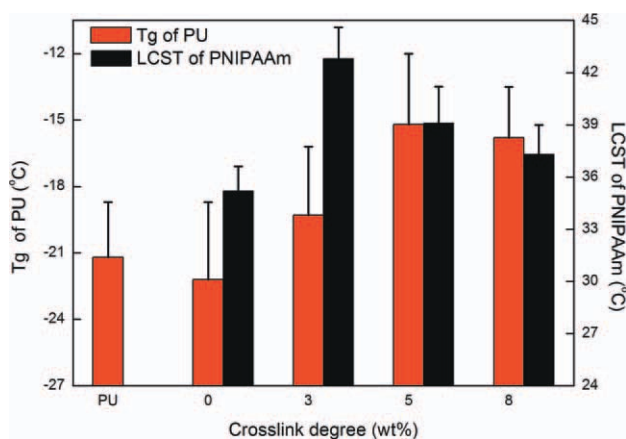
Figure 3 The effect of BIS amount on the T_g and LCST of PU/PNIPAAm semi-IPNs. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

8%. Those phenomena proved that PNIPAAm in PU/PNIPAAm semi-IPNs elevated the T_g of PU to a certain degree and its LCST dropped down with the increasing amount of BIS. T_g of PU/PNIPAAm semi-IPNs maintained on a certain level when NIPAAm content was more than 25% and BIS amount above 5%. That can be attributed to the saturation of intermolecular force, such as hydrogen bond force and Van der Waals force, between PNIPAAm and PU chains. The LCST in PU/PNIPAAm semi-IPNs was much higher than that of pure PNIPAAm, and dropped slightly due to the incorporation of BIS into the PNIPAAm chains. The acrylamide groups in polyurethane formed hydrogen bond force with groups in PNIPAAm, making the transformation of PNIPAAm more difficult. Conse-

quently, it needed more energy to turn the structure of PNIPAAm from hydrophilic to hydrophobic, leading to the rise of LCST. As previous studies have proved that the stability of the PNIPAAm structure is balanced by hydrophobic interaction energy among polymer chains and the bending energy of the aggregated polymer filament formed in the dense region. Structural heterogeneities are formed during the gel formation process. Therefore, during spinodal phase transition, the gel samples remember their history, that is, when temperature is increased above LCST during phase transition process, NIPAAm gel remembers its own heterogeneities created during gel formation process. These heterogeneities were produced depending on the BIS content, which the NIPAAm possessed. Gel with high BIS content inherits more heterogeneities during its formation process, so it goes through the spinodal decomposition much lower temperature than the low BIS content samples.[14]

Swelling properties of the PU/PNIPAAm semi-IPNs

The combination of PNIPAAm in the IPN endows the material with an obvious temperature sensitivity. To characterize this property, the equilibrium swelling ratios of the IPNs with various compositions at different temperatures were measured, as shown in Figures 4 and 5. The ESR of TPU itself was very low and increased slightly with temperature. This was resulted from the fact that the increase of temperature raised the free volume of TPU, leading to larger space for the inclusion of water molecules in the polymer matrix. With PNIPAAm introduced, the
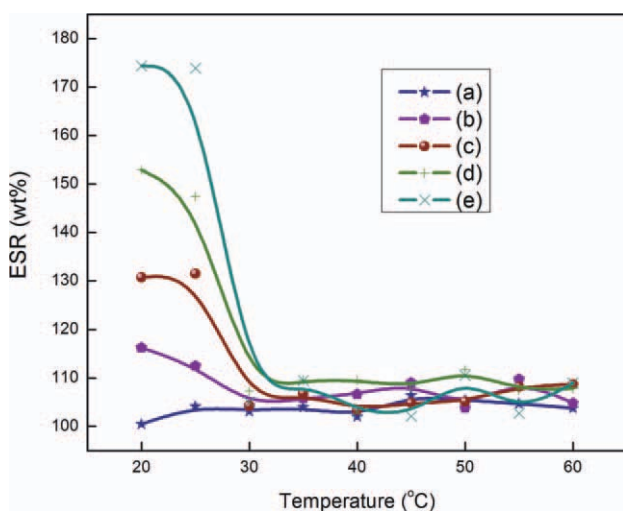

Figure 4 The ESR of PU/PNIPAAm semi-IPNs with varied PNIPAAm content at different temperature. (a) PU; (b) 15% PNIPAAm; (c) 25% PNIPAAm; (d) 35% PNIPAAm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
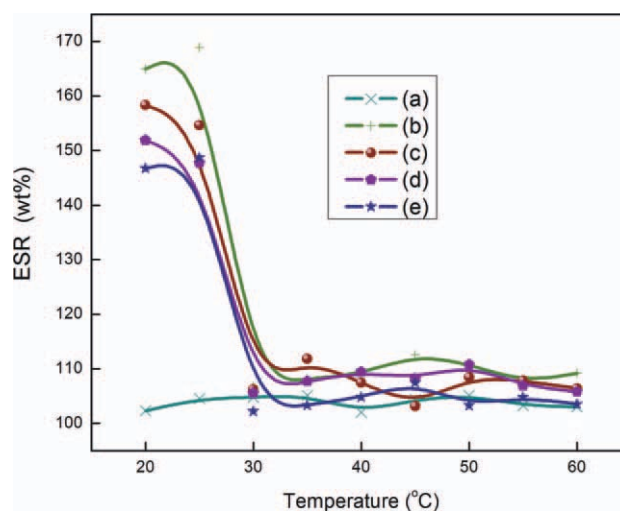

Figure 5 The ESR of PU/PNIPAAm semi-IPNs with different BIS amount at different temperature. (a) PU; (b) 0%BIS; (c) 3% BIS; (d) 5% BIS; (e) 8% BIS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
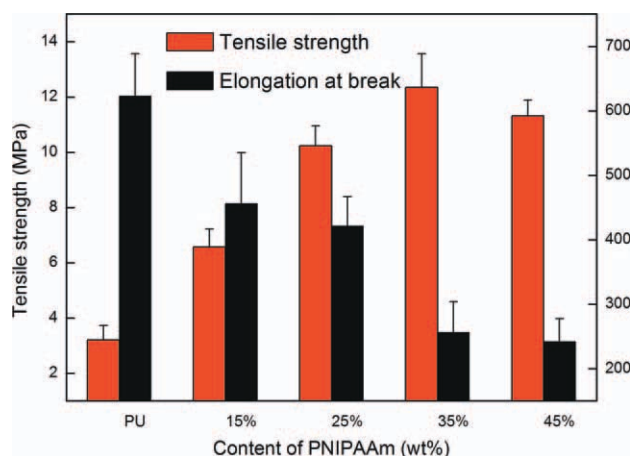
Figure 6 The mechanical properties of PU/PNIPAAm semi-IPNs with varied PNIPAAm content (a) PU; (b) 15% PNIPAAm; (c) 25% PNIPAAm; (d) 35% PNIPAAm. *The content of PNIPAAm was calculated with BIS amount fixed at 5%; and the percentage of BIS is relative to the weight of NIPAAm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ESR of the IPNs at low temperature (below 30°C) was enhanced significantly, and decreased remarkably when the temperature was raised from 30 to 50°C. The exclusion of water from the swollen hydrogel was caused by the hydrophilic-hydrophobic transition of PNIPAAm. However, the drop of ESR was not as sharp as that of pure PNIPAAm. The reason could be attributed to the hydrophobicity of TPU chains and the intensive interchain interactions of the IPN, which retarded the diffusion of water molecules through the material.

Quantitatively, the ESR of the IPN at low temperature was obviously affected by the content of PNIPAAm and its crosslinking degree. Higher content of PNIPAAm and less crosslinking led to more swelling at low temperature. On the other hand, the ESRs of the IPN at high temperature were quite close among various samples. Therefore, the high ESR at low temperature implied a better temperature sensitivity. As a result, the crosslinking degree and the content of TPU should not be too high to reserve the volume phase transition property of the semi-IPN material.

Mechanical properties of the PU/PNIPAAm semi-IPNs

Most PNIPAAm-based temperature-sensitive materials are of low mechanical stability due to the high swelling degree of PNIPAAm hydrogels.[15] This is fine for some of the applications, such as medical treatment. However, the high swelling property greatly inhibits their applications in the fields, such as smart breathable fabrics, where mechanical stability is required. Considering this, the mechanical

properties of the TPU/PNIPAAm semi-IPNs were measured and compared. Although the tensile strength of the semi-IPN obviously increased comparing with pure TPU, it was still at a low level, as shown in Figure 6. Therefore, the elasticity and ductility of TPU membrane could be reserved when the content of PNIPAAm was controlled in a low level (below 25 wt %). On the other hand, the influence of crosslinking of PNIPAAm was also discussed, as shown in Figure 7. Both tensile strength and elongation at break of the IPNs were slightly increased by more crosslinking when the crosslinking degree was low. However, over crosslinking would do harm to the flexibility of the membrane, which is caused by the destruction of TPU structure by the crosslinked PNIPAAm, and therefore high crosslinking degree should be avoided.

Morphology of the membranes

The mechanism of temperature-sensitive breathability of the membrane prepared in this work is based on the change of pore diameter with temperature. There are two factors important for the permeability of the membrane. The first one is the volume phase transition of the semi-IPNs, which has been discussed in the previous sections. The second factor is the pore structure of the membrane. The morphology of the membranes was investigated with the help of SEM (Figure 8). Generally, the membranes fabricated from the semi-IPN by the phase inversion method present an asymmetrical microporous structure, with the surface pore diameters of several micrometers, according to the preparation conditions. The semi-IPN membrane prefers to form smaller comb-like pores, whereas TPU membrane
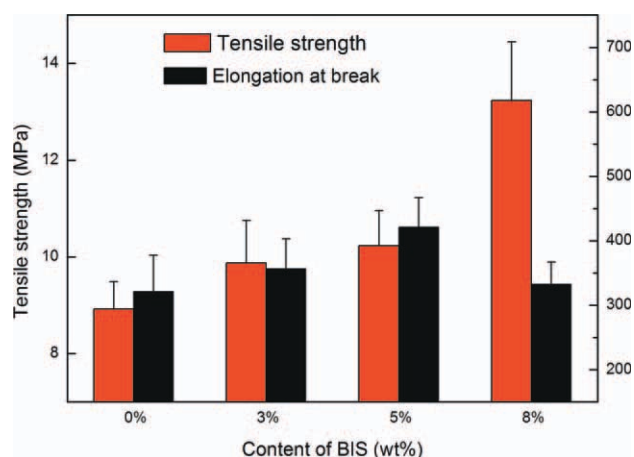

Figure 7 The mechanical properties of PU/PNIPAAm semi-IPNs with different BIS amount (a) 0% BIS; (b) 3% BIS; (c) 5% BIS; (d) 8% BIS. *The test was conducted with the content of PNIPAAm fixed at 25%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
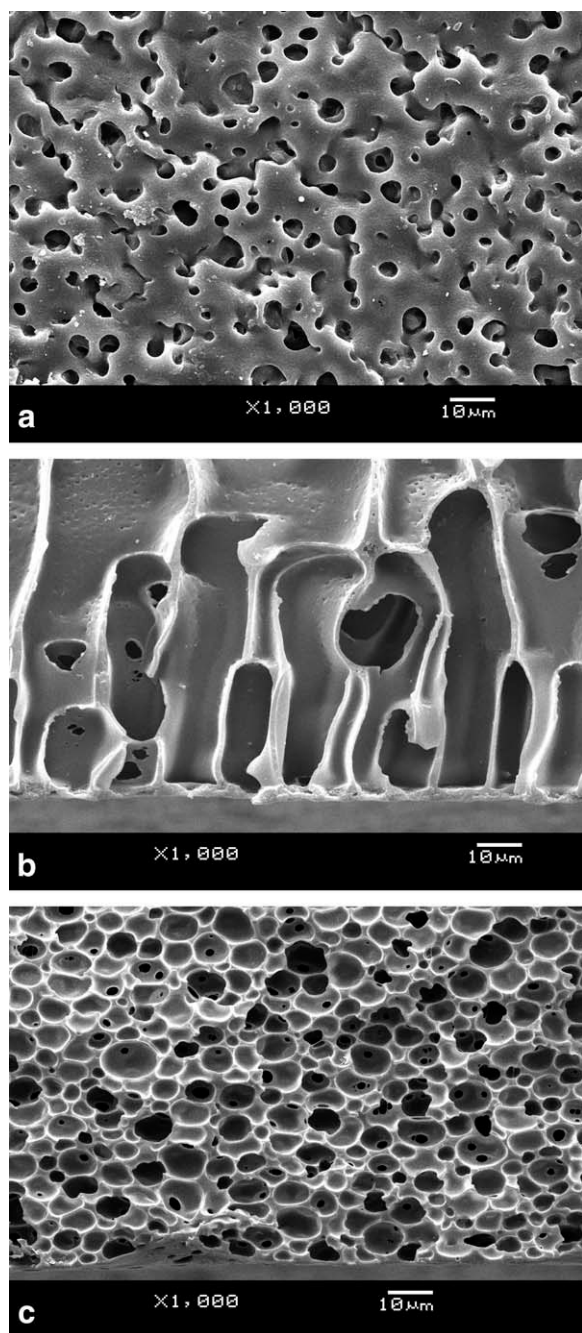
Figure 8 SEM of polyurethane and PU/PNIPAAm semi-IPNs film formed in water. (a) Surface of PU/PNIPAAm semi-IPNs; (b) cross section of PU film; (c) cross section of PU/PNIPAAm semi-IPNs.

tends to form larger finger-like pores. This could be attributed to the gelation of PNIPAAm, which slows down the exchange of water and DMF molecules, and inhibits the formation of large pores. Moreover, the crosslinking by BIS also increases the viscosity of the solution and further promotes the formation of small comb-like pores. The structure of the pores, such as the average diameter of the pores, and the porosity of the membrane could be controlled by the selection of proper membrane forming parameters,

which has been discussed in detail in our previous works.[16]

Water Vapor Permeability of the membranes

Unlike the previous report on temperature-sensitive breathable fabrics, the permeability of the membranes prepared in this work was determined by the microporous structure rather than the material itself. Therefore, high permeable membranes could be achieved by optimizing the pore structure. On the other hand, the WVP of the IPN membranes showed obvious temperature-dependent behaviors, comparing to the membranes fabricated from TPU. At low temperature, the WVP did not change much. However, when the environmental temperature was higher than 30°C, the WVP increased significantly with temperature. This property can be explained by the swelling of the IPN material and the average pore diameters of the membrane at different temperatures. At low temperature, the IPN material was hydrophilic and highly swollen, leading to smaller average pore diameters of the membrane. Thus, the membranes had low permeability. With the temperature going up, the IPN material turned from hydrophilic to hydrophobic. The water molecules were excluded and the shrinking of the IPN material caused the larger pore diameters. Therefore, the permeability of water vapor was enhanced, and high WVP was achieved at high temperature.

The influence of PNIPAAm content and crosslinking was also discussed, as shown in Figures 9 and 10. The permeabilities of the membranes are closely related to the volume phase transition behavior of
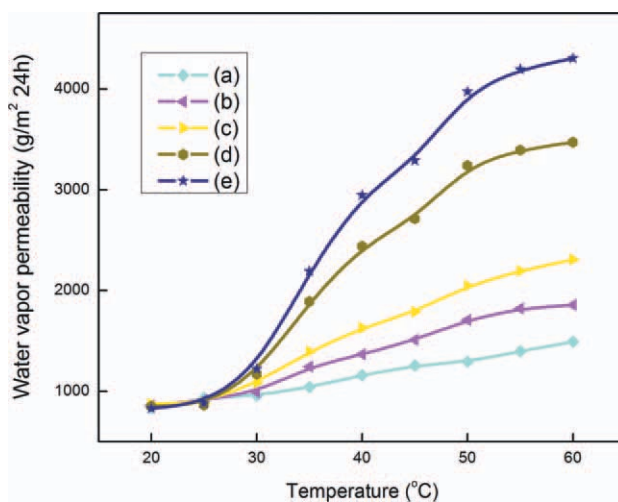

Figure 9 Water vapor permeability of PU/PNIPAAm semi-IPNs with varied PNIPAAm content at different temperature (a) pure TPU; (b) 5% PNIPAAm; (c) 15% PNIPAAm;(d) 25% PNIPAAm; (e) 35% PNIPAAm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
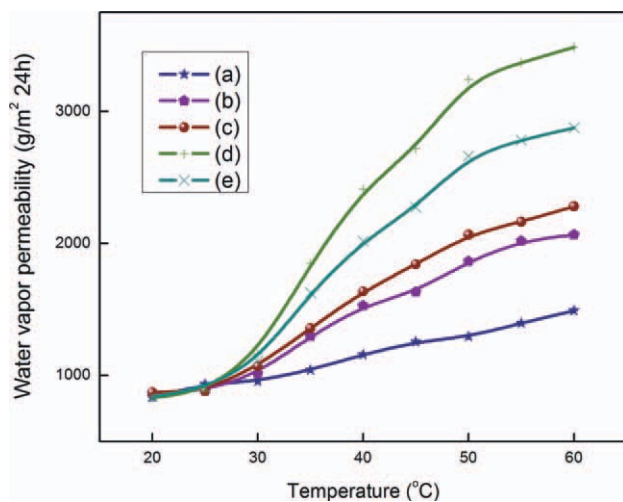
Figure 10 Water vapor permeability of PU/PNIPAAm semi-IPNs with different BIS amount at different temperature (a) pure TPU; (b) 0% BIS; (c) 3% BIS; (d) 5% BIS; (e) 8% BIS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the semi-IPN material. Therefore the increase of PNIPAAm content in the semi-IPN significantly enhances the temperature-sensitivity of the membranes. However, membranes with very high PNIPAAm content is not applicable to practical usage, since the semi-IPN material with high PNIPAAm content has a low mechanical stability, as illustrated in the previous sections. On the other hand, the influence of crosslinking on the WVP is complex. When the crosslinking degree is low, only microgel of PNIPAAm can be achieved, and the semi-IPN structure extending throughout the whole material cannot be formed. Therefore, although the ESR is very high, the temperature dependence of the swelling properties of the semi-IPN material can not be effectively converted to the temperature sensitivity of the permeability of the membrane. When the crosslinking degree is high, the semi-IPN material is less temperature-sensitive, and the permeability of the membrane is therefore less sensitive to temperature, too. Therefore, to fabricate membranes with better temperature sensitive permeability, semi-IPN material with an optimized crosslinking degree

should be used, which was found to be 5 wt % in this work.

CONCLUSIONS

The incorporation of PNIPAAm into PU bulks elevated the glass transition temperature of the films and the miscibility of PNIPAAm and PU was enhanced with the increasing amount of BIS. The PU/PNIPAAm semi-IPNs films formed in water exhibited the thermo-sensitivity of PNIPAAm, and their swelling ability and WVP were greatly improved. But the LCST of PNIPAAm was raised to a higher temperature because of the restriction and interaction of molecular chain. With the increasing of the content of PNIPAAm, the tensile strength of PU/PNIPAAm semi-IPNs was boosted to a certain degree, but their elongation at breaks reduced greatly when PNIPAAm was more than 25% and BIS amount was above 5 wt % (to the weight of NIPAAm).

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