

Water Vapor Permeability of the Polyurethane/TiO₂ Nanohybrid Membrane with Temperature Sensitivity

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ABSTRACT: A novel thermal-sensitive polyurethane (TSPU)/TiO₂ nanohybrid membrane was successfully prepared via *in situ* process and used for controllable water vapor permeation. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) were employed to reveal the nanohybrid mechanism between TSPU and TiO₂ and the thermal sensitive characteristics of TSPU/TiO₂ nanohybrid membranes. FTIR analysis demonstrates that the highly active nano-TiO₂ particles produced by the hydrolysis of the nanoprecursor (tetrabutyl titanate) have reacted with the active groups of TSPU. And some new peaks assigned to the Ti—O—C, Ti—C, and Ti—O—Ti bonds occur in the FTIR spectra of TSPU/TiO₂ nanohybrid membrane; these chemical bonds are believed to contribute to the higher mechanical properties of nanohybrid samples. DSC study indicates that nanohybridization does not disrupt the intrinsic phase-separated structures and thermal-sensitive characteristics of pure TSPU, the difference in behavior is the phase transition temperature (defined as

switch temperature, T_s) of the reversible phase shifting from 50.1 to 53.4°C. SEM analysis shows that the nano-TiO₂ particles are evenly distributed in TSPU and the size of the nano-TiO₂ is lower than 100 nm. In addition, the water vapor permeability (WVP) of nanohybrid membrane is found to depend on the TiO₂ content. To be specified, when TiO₂ content is lower than 5.0 wt %, the nanohybrid samples show lower WVP at low temperatures and higher WVP at high temperatures than pure TSPU. Especially, when the temperature exceeds the T_s , for example from 50 to 60°C, the WVP of pure TSPU show improvement by 114%, whereas the WVP of the nanohybrid TSPU with 5.0 wt % TiO₂ content shows improvement by 145%, the latter shows more sensitivity to thermal stimuli. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3002–3007, 2008

Key words: polyurethanes; nanocomposites; stimuli-sensitive polymers; thermal properties; water vapor permeability

INTRODUCTION

Thermal-sensitive polyurethane (TSPU) has often been observed with a block or segmented structure, which consists of two phases, i.e., a thermally reversible phase (soft segment) and a fixed phase (hard segment). In many cases, a phase transition temperature (crystalline melting transition or glass transition temperature) of the thermally reversible phase can be used as a switch temperature (T_s) for controllable water vapor permeability (WVP).¹

In our previous work, a kind of segmented TSPU membrane with functional gates was synthesized and used for water vapor permeation. When the temperature varied from $T_s - 10^\circ\text{C}$ to $T_s + 10^\circ\text{C}$, the average radius (R) of free volume (FV) holes in this polymer showed dramatic change from 0.23 to 0.467 nm, as a result, the WVP of this membrane sensed

and responded to external thermal stimuli and showed significant improvement. TSPU with a well-organized reversible phase showed large augment in FV holes size and much sensitive characteristic to thermal stimuli, as a result, exhibited high increase in water vapor permeability.^{1,2}

When a TSPU is utilized in outdoor garments, the vegetable compartments of refrigerators or membrane materials, some important factors, such as controllable water vapor permeability, high mechanical properties, and high thermal, chemical stability should be considered. In the past several years, inorganic particles, especially nanoparticles, were widely introduced into polymeric matrix to improve the mechanical and thermal properties of polymeric membranes.^{3,4} On the other hand, nanoparticles had been proved to disrupt the polymer chain packing and increased the FV available for gas/vapor permeation.^{5–7} The introduced nanoparticles to polymer membranes might be silica,⁸ Al₂O₃,⁹ Fe₃O₄,¹⁰ ZnO,¹¹ TiO₂,^{12–14} and polymeric nanoparticles.¹⁵ Among different metal oxide nanoparticles, TiO₂ has received the most attention because of its stability, availability, and promise for application such as painting,

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catysis and photocatalysis, battery, cosmetic, etc.¹⁶ Hence, to prepare nanohybrid membrane with improvement of the mechanical and thermal properties, and gain higher WVP of nanohybrid membrane above the T_g , we introduced the nano-TiO₂ particles into the TSPU matrix via *in situ* nanohybrid process. The main purpose of this study was to investigate how the nanoparticles influenced the morphological structure, mechanical properties, thermal-sensitive characteristics, and WVP of TSPU/TiO₂ nanohybrid membranes, finally, to develop a novel intelligent membrane with higher performance and controllable gas/water vapor permeability.

EXPERIMENT

Materials

Polycaprolactone diols (PCL, Daicel, Japan) with molecular weight 4000 g/mol were dried at 100–120°C under high vacuum (0.5 mmHg) for 12 h before use. Extra pure grade of 4,4'-diphenylmethane diisocyanate (MDI, Aldrich Chemical) and 1,4-butanediol (BDO, Aldrich Chemical) were used with PCL to prepare TSPU. Dimethylformamide (DMF, Kelong Co., China) was used as solvent with further purification to remove trace water. Extra pure grade of tetrabutyl titanate (TBT, Merck) was used as nanoprecursor, and acetylacetone was used as chelator in the hybridization process.

Preparation of TSPU

A 500-mL round-bottomed four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with a drying tube was used as a reactor to prepare TSPU. Dried PCL (0.02 mol) and MDI (0.04 mol), which would provide the soft-segment formation reaction, were charged into the dried flask. The soft-segment formation reaction was carried out in DMF at 80°C for about 2.0 h, followed by hard-segment formation reaction with MDI (0.04 mol) and BDO (0.06 mol) at 80°C for 2.0 h. Finally, a viscous, transparent polymer solution was obtained.

Preparation of nanoprecursors

The nanoprecursor consists of the dispersion supporter (DMF), quantitative tetrabutyl titanate, and acetylacetone. These nanoprecursors are easily dispersed in the TSPU solution and can produce nano-TiO₂ at the given condition.

Preparation of TSPU/TiO₂ nanohybrid membranes

The TSPU/TiO₂ nanohybrid membranes were prepared via *in situ* nanohybrid process: At first, TSPU solution and quantitative acetylacetone and nanopre-

cursors were mixed by a magnetic stirrer for 1.0 h. Membranes were prepared by casting TSPU solution on a cellophane paper and immersed in 20 : 80 (wt %) = DMF : water solution with pH = 1.5 at 25°C for 30 min, and then the pH of the bath was slowly adjusted to 2.5 in the next 60 min. In this case, the tetrabutyl titanate hydrolyzed and *in situ* produced nano-TiO₂ particles in polymer base; as a result, an organic–inorganic nanohybrid reaction occurred between TSPU and nanoparticles. Finally, the nanohybrid membranes were taken out from the DMF solution and washed with distilled water to remove solvent and acid, then dried at 40°C under vacuum condition (1 mmHg) for the next 10 h.

Instrumental analysis

Fourier transform infrared (FTIR) spectra of the nanohybrid membranes were performed on Nicolet 560 ultrared spectra meter (USA) in the 4000–450 cm⁻¹ wave number range. Samples for FTIR were prepared in the film method. The phase transition temperature of the TSPU was measured by Dupont 9900 thermal analyzer (USA) with a DSC module, which was purged with nitrogen gas and quenched with liquid nitrogen. The TSPU samples (5–10 mg) were heated in sealed aluminum pans and scanned from -50 to 250°C with a heating rate of 10°C/min. To erase earlier thermal history of the sample, the results of DSC analysis relied on the second heating run instead of the first run. The size scale and distribution of nano-TiO₂ in TSPU was measured by SEM (Hitachi Model S-520, Japan). The membranes were cryogenically fractured in liquid nitrogen and then sputtered with platinum. The SEM micrographs were taken at certain magnifications. The thin membranes, with almost no volatile solvents, was cast to be a dumbbell shape with a narrow width of 5 ± 0.5 mm and a narrow length of 10 ± 0.5 mm, and used for tensile and elongation test with an Instron GT-AI-7000s (Gotech Testing Machine, China). The testing rate is at 50.0 mm/min, and an average of six parallel samples was used for each measurement.

Measurement of WVP

The WVP of the TSPU and TSPU/TiO₂ nanohybrid membrane were measured according to ASTM method E 96 Desiccant method, i.e., an open-cup containing desiccant was sealed with the specimen membrane in such a manner that the cup mouth defined the area of the specimen exposed to the vapor pressure of the environment. The edges of the specimen were thoroughly sealed to prevent the passage of water vapor into, out of, or around the specimen edges or any portion thereof. Then the assembly was placed in a test chamber at the different

temperatures of 20, 30, 40, 50, 60, and 70°C with a constant relative humidity of 60%. Finally, the weight change of permeation cup with the specimen was recorded and the WVP was calculated by the following equation. The degree of water vapor permeability was expressed as $\text{g}/\text{m}^2 \text{ day}$:

$$\text{WVP} = 24(a_1 - a_2)/T \cdot S$$

where $a_1 - a_2$ is the weight change of permeation cup with the specimen (g), T is the assembly time in the test chamber (h), and S is the area of permeation (m^2). An average of three parallel samples was used for each WVP measurement.

RESULTS AND DISCUSSION

Size scale and distribution of nano-TiO₂ in TSPU membranes

Figure 1 shows the SEM photographs of the nano-TiO₂ grain size and distribution in TSPU membranes (circular particles are TiO₂ and the background is TSPU, which acts as a continuous phase). According to Figure 1, most of the TiO₂ particles produced from the hydrolyzed precursors are evenly distributed in TSPU and no coagulation can be found. This should be the reason that, on one hand, both the polymer networks and chelators control the growth of the nanoparticles and stabilize the nanoparticles to prevent them from coagulation. On the other hand, the nano-TiO₂ may link with the active groups of TSPU as soon as it is formed. In addition, as shown in Figure 1, the porous structure of nanohybrid membrane is observed, which may be caused by volatilization of the DMF and water in the dry process.

Figure 2 is the particular size of some nano-TiO₂ in Figure 1. Obviously, the particle size of TiO₂ prepared under this condition is lower than 100 nm.

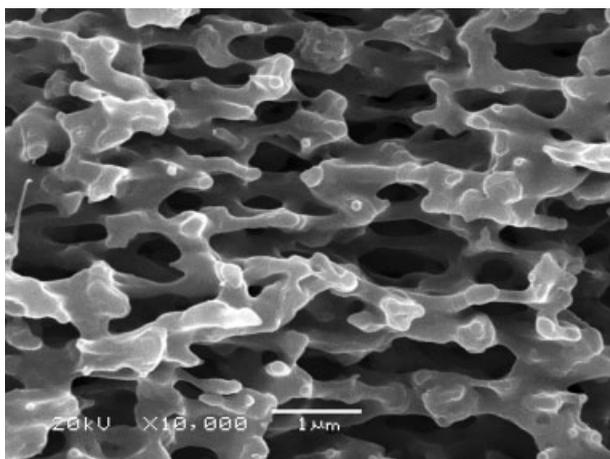


Figure 1 SEM photograph of cross section of the TSPU/TiO₂ nanohybrid membrane (5.0 wt % TiO₂).

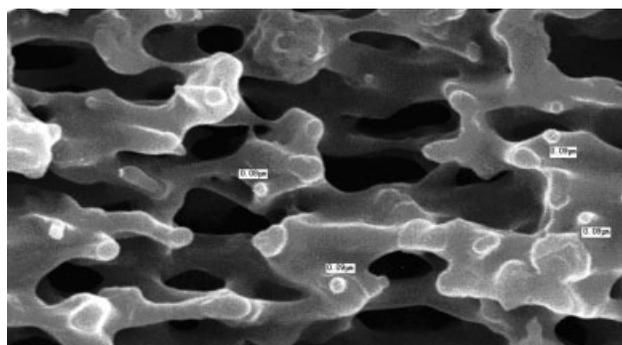


Figure 2 The size of some nano-TiO₂ particles in Figure 1.

Interaction between nano-TiO₂ and TSPU

To explore the nanohybrid mechanism between TSPU and nano-TiO₂, FTIR was employed to analyze group changes before and after hybridization. Figure 3(a,b) shows the FTIR spectra for TSPU/TiO₂ nanohybrid membrane and pure TSPU membrane, respectively. Comparing the two FTIR spectra, it is found that the adsorption peak of pure TSPU at 3107, 3033, 912, and 650 cm^{-1} [assigned to $-\text{C}-\text{H}$ of Aromatic ring (Ar)] disappears while an additional signal in the spectrum of nanohybrid TSPU at 1030 cm^{-1} (assigned to $\text{Ti}-\text{C}$ of $\text{Ti}-\text{Ar}$) appears, which indicates that nano-TiO₂ particles produced by the hydrolysis of tetrabutyl titanate have reacted with the $\text{Ar}-\text{H}$ on the backbone of TSPU. Additional adsorption peak in spectrum of TSPU at 1080 cm^{-1} (assigned to $-\text{C}-\text{O}$ of $-\text{CH}_2-\text{OH}$) weakens markedly and a peak at 3538 cm^{-1} (assigned to $-\text{OH}$ of $-\text{CH}_2-\text{OH}$) disappears, which reveals that, as the condensation reaction of tetrabutyl titanate proceeded, the terminal hydroxyl groups of TSPU may react with the $\text{Ti}-\text{OH}$ and form new $\text{Ti}-\text{O}-\text{C}$ bonds at 1191 and 1235 cm^{-1} . Moreover, there is an additional signal in the spectrum of nanohybrid TSPU at 598 cm^{-1} (assigned to $\text{Ti}-\text{O}-\text{Ti}$), which comes from the self-condensation reaction of $\text{Ti}-\text{OH}$. From the earlier discussion, we can easily

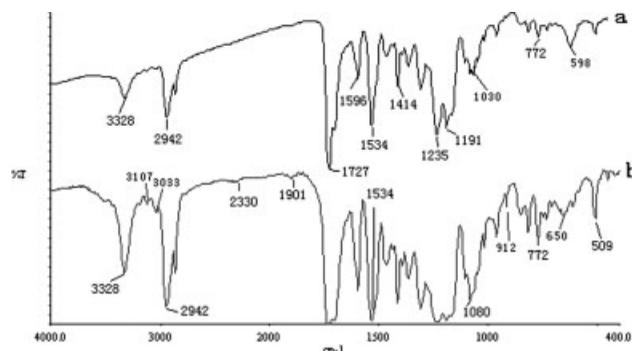


Figure 3 FTIR spectra for (a) TSPU/TiO₂ and (b) TSPU.

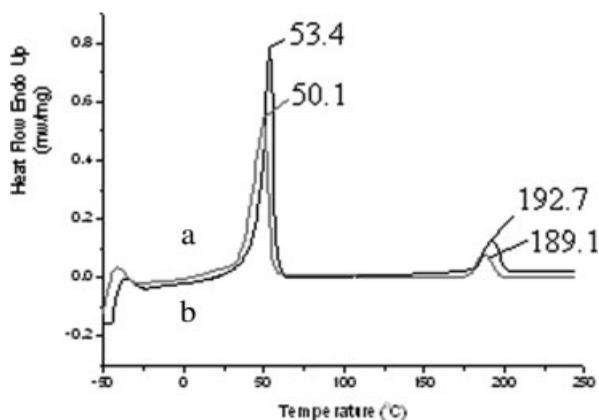


Figure 4 DSC curves of TSPU (a) and TSPU/TiO₂ nanohybrid composite (b, 5.0 wt % TiO₂).

conclude that the nano-TiO₂ particles have reacted with the active groups on the backbone of TSPU. These reactions between nano-TiO₂ and TSPU seem to be contributed to higher mechanical properties.

The segmented structure and phase transition temperature of TSPU/TiO₂ nanohybrid composites

DSC analysis can be used to investigate the segmented structure and phase transition temperature (T_s) of TSPU/TiO₂ nanohybrid composites. According to the DSC curves in Figure 4, two peaks at 50.1 and 189.1°C for TSPU and at 53.4 and 192.7°C for nanohybrid sample, corresponding, respectively, to the phase transition of the reversible phase (soft segment) and the fixed phase (hard segment) are found, which reveals that two samples show similar phase transition behavior and are all phase-separated into a soft segment and a partially hard segment, and the incompatible soft and hard segments show obviously independent phases and different phase transition temperatures. In comparison with the pure TSPU, the T_s of the nanohybrid sample shifts from 50.1 to 53.4°C, showing 3.3°C higher than that of the TSPU. This should be attributed to the interactions between the organic and inorganic phases. These interactions, on one hand, enhance the rigidity of the hard segments,¹⁷ on the other hand, limit the movement or motions of the soft segments, therefore, increase the phase transition temperatures of the nanohybrid membrane.

Another difference in behavior involves the melt enthalpy change (ΔH) in reversible phase transition process. It is well-known that phase transition from well-organized state to amorphous state often accompanies changes in melt enthalpy (ΔH), which, to a great degree, reflects how well-organized is the degree of the reversible phase.^{18,19} From the results in Figure 4, it can be seen that there is an endothermic peak at 53.4°C with an enthalpy change ($\Delta H =$

34.65 kJ/kg) for the nanohybrid sample, while a little smaller endothermic peak at 50.1°C with a lower enthalpy change ($\Delta H = 29.62$ kJ/kg) for pure TSPU, which reveals that the well-organized degree or the crystallinity of the soft segment is greater for nanohybrid sample than that for pure TSPU. This means the introduction of nano-TiO₂ particles is beneficial for the formation of well-organized reversible phase.

Mechanical properties of TSPU/TiO₂ nanohybrid membranes

The comparison of mechanical properties of pure TSPU and nanohybrid TSPU membranes are given in Figure 5. It can be revealed that as the TiO₂ content rises from 0.0 to 5.0 wt %, the tensile strength of nanohybrid TSPU membranes increases from 1.5 to 2.0 MPa and the broken elongation increases from 92.2 to 105.8%, showing an improvement by 33.3% and 14.8%, respectively. This reinforcement effect is believed to be the interfacial interaction between the nano-TiO₂ particles and the polymer. Nanoparticles, due to their small size, abundant of un-pair-atom and high surface energy, show a high combination potentiality with polymer substrate,²⁰ which is beneficial for the increase of the mechanical properties of the polymer. Moreover, nanoparticles have the ability to transfer the applied load to nano-TiO₂ particles themselves during the deforming process,²¹ so the nanohybrid membranes show much higher broken elongation than that of the pure TSPU.

Nevertheless, the tensile strength and the broken elongation then tend to decrease thereafter as the TiO₂ content is further increased from 5.0 to 7.5 wt %. These may be attributed to the TiO₂ agglomerates with large size scale that are easily formed with excessive precursors added into the TSPU resin, and these TiO₂ agglomerates have already lost their

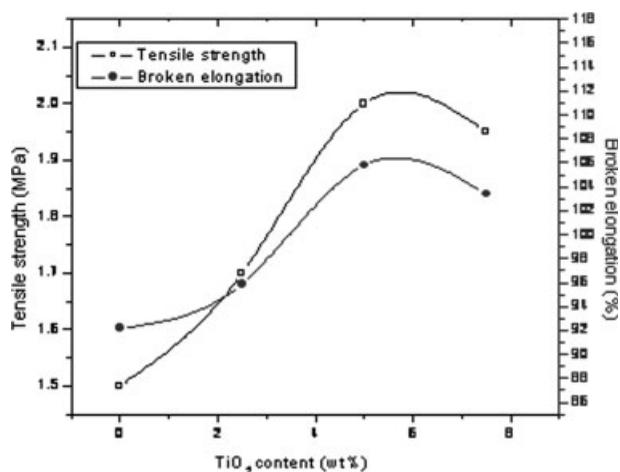


Figure 5 Mechanical properties of TSPU/TiO₂ nanohybrid membranes as a function of the TiO₂ content.

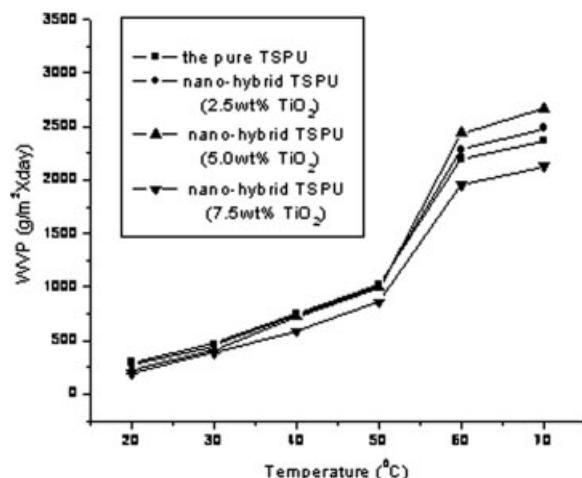


Figure 6 The WVPs of the pure TSPU and TSPU/TiO₂ nano-hybrid membranes as a function of temperature.

nanocharacteristics, resulting in no interfacial interaction formed between the organic and the inorganic phases. In addition, nonuniform distribution of TiO₂ particles will cause uneven stress in the TSPU membranes when an external force is applied, which also brings on the decreased tensile strength and broken elongation of the nano-hybrid samples. As a matter of fact, this unusual behavior in nanocomposites mentioned earlier has also been observed by many researchers concerning the mechanical properties of polymer in the presence of nanoparticles.²²

Water vapor permeability of TSPU/TiO₂ nano-hybrid membranes

In our previous study, TSPU with a well-organized reversible phase showed larger changes in average radius (R) of FV holes and much more sensitive characteristic to thermal stimuli, as a result, exhibited higher WVP changes.² According to the DSC analysis, we found that nano-hybridization could efficiently enhance the well-organized degree of reversible phase, so in the phase transition process from the well-organized state to the amorphous state, the nano-hybrid membrane would yield much more changes in FV hole size and micro-Brownian motion, as a result, would yield higher WVP changes.

Figure 6 is the comparison of the water vapor permeability among TSPU and nano-hybrid TSPU membranes as a function of the temperature. It was also found that the WVP of nano-hybrid membranes depend on the TiO₂ content. Although the WVPs of all specimens increase with increase of temperature and show sensitive characteristic to thermal stimuli, the responses of WVP to the temperature changes are quite different. To be specified, when TiO₂ content is lower than 5.0 wt %, the nano-hybrid samples show lower WVP at low temperatures ($<T_g$) than the

pure TSPU. This may be the reason that nano-TiO₂ particles enhance the well-organized degree of the soft segment in the polymer, as a result, limit the water vapor transport. Nevertheless, in the next temperature range from 50 to 60 °C, the pure TSPU and nano-hybrid TSPUs undergo a phase transition from the glassy state to the rubbery state,^{23,24} with the FV hole size and micro-Brownian motion of the macromolecules enhanced leading the WVP of membrane to increase, showing a significant improvement by 114, 126, and 145%. Obviously, the sensitivity of WVP to thermal-stimuli is greater for nano-hybrid TSPU membrane than that for pure TSPU membrane. This may be the reason that the nano-hybridization, on one hand, results in a more well-organized soft segment for TSPU at low temperatures ($T > T_g$), on the other hand, disrupts the polymer chain packing at high temperatures ($T > T_g$),^{5,6} both lead more changes of FV hole size available in polymer for water vapor transport. So when the temperature exceeds the T_g , the nano-hybrid samples show much more changes in WVP.

However, it is not the case for nano-hybrid TSPU with higher TiO₂ content (7.5 wt %), the WVP of nano-hybrid sample tends to decrease gradually in all temperature ranges. As already known, when the TiO₂ content is higher than 5.0 wt %, the TiO₂ agglomerates may be easily formed in the hybrid TSPU membranes. These agglomerates will block the FV holes in the membranes and force the water vapor molecules to follow a more tortuous path as they diffuse through the membranes,⁵ as a result, decrease the water vapor permeability.

CONCLUSIONS

Through the analysis and discussion earlier, this work intends to provide the following tentative conclusions:

1. The reaction mechanism between TSPU and nano-TiO₂ study indicates that the highly active nano-TiO₂ particles or Ti—OH produced by the hydrolysis of the precursor (tetrabutyl titanate) has bonded with the active groups of TSPU and formed three chemical bonds of Ti—C, Ti—O—C, and Ti—O—Ti, which seems to contribute to the higher mechanical properties of the polymer.
2. The particle size of nano-TiO₂ in the TSPU was lower than 100 nm, and most of the nano-SiO₂ particles were evenly distributed in TSPU and no coagulation could be found.
3. In contrast to the pure TSPU, TSPU/TiO₂ nano-hybrid sample shows well-organized morphological structure and higher phase transition temperature, i.e., the T_g increases from 50.1 to 53.4 °C.

4. Nanohybridization can efficiently enhance the WVP of the TSPU membrane above the T_s . Especially, when the temperature covers the T_s , for example, varies from 50 to 60°C, the WVP of membranes show improvement by 114% for TSPU membrane and 145% for TSPU/TiO₂ nanohybrid membrane with 5.0 wt % TiO₂ content, the latter shows much higher WVP change and much more sensitivity to thermal stimuli.

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