

Thermosensitive Polyurethane Film and Finished Leather with Controllable Water Vapor Permeability

Huanhuan Shi, Yi Chen, Haojun Fan, Jun Xiang, Bi Shi

National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

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ABSTRACT: Three types of water based polyurethane (PU), i.e. one ordinary elastomeric polyurethane (EPU) and two thermosensitive polyurethane (TSPU), were synthesized and applied in leather finishing. Differential scanning calorimetry, positron annihilation lifetimes (PAL), water swelling, and water vapor permeability (WVP) were measured to evaluate how the structure of the synthesized PU and the temperature influenced the WVP of the PU finished leather. In contrast to EPU, TSPU(b) with a glass transition reversible phase and TSPU(c) with a crystal transition reversible phase showed an obvious phase separation structure and a phase transition in the normal wearing temperature range. PAL study indicated that when the temperature was higher than the designed phase transition temperature, the *ortho*-positronium lifetime (τ_3) and the average radius (R) of free volume of TSPU showed dramatic changes, whereas τ_3 and R of EPU remained unchanged.

The water swelling and WVP of TSPU finished leather were found to depend on the structure of the polymer and the temperature, and they gave different responses to temperature variation. When the temperature was higher than the designed phase transition temperature, a significant WVP increase from 3800 g/(m² 24 h) to 7830 g/(m² 24 h) for TSPU(b) finished leather and from 4100 g/(m² 24 h) to 9450 g/(m² 24 h) for TSPU(c) finished leather were observed. Whereas EPU finished leather showed low WVP, and increased slightly as temperature increased. Phase transition accompanying a significant change in WVP can be used to develop "smart leather" with controllable water vapor permeability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1820–1827, 2010

Key words: polyurethanes; coatings; structure–property relations; water soluble polymers; leather

INTRODUCTION

It has been widely recognized that shoes and garments must be water vapor permeable, or breathable, to be comfortable. This breathability allows perspiration to evaporate promptly when activity level increases; therewith the heat generated by metabolism can be continuously dissipated and regulated, guarding against a damp and roasted feeling.^{1–3} Leather has been used for the manufacture of shoes and garments since centuries. Generally speaking, unfinished leather has high water vapor permeability (WVP) because of its natural porous structure. But in order to modify the shade/gloss/handle, improve its physical properties (such as light/rub fastness and resistance to water/solvent/abrasion), and hide any defects or irregular appearance, leather needs to be finished.^{4,5} Water based elastomeric polyurethane (PU) resin is a popularly-

adopted material for leather finishing. The finishing layer formed by this resin has good resistance to the passage of water drops, but it simultaneously exhibits its low transport to water vapors, which significantly compromises the wear comfort of the final leather products.^{6–12} Previous literature reported that the WVP of PU finished leather decreases by 30–50% compared with the unfinished one. Especially as far as split leather for shoes is concerned, the WVP decreases from 1152 g/(m² 24 h) to 816 g/(m² 24 h) after traditional finishing, or to 600 g/(m² 24 h) after lamination coating.¹³ As a consequence, the accumulated sweat vapors will condense inside the leather shoes or garments, uncomfortable for the wearers and risking of bacterial contamination. Moreover, ordinary elastomeric PU finishing layer shows no thermosensitive feature in the normal wearing temperature range, i.e. the WVP shows no significant change as temperature increases, which is also responsible to the poor wear comfort of finished leather.

According to Fox and Flory's free volume theory, the volume of polymer is composed of two parts: one part is occupied by macromolecule itself, which is called occupied-volume; the other is free volume, which distributes in all polymers in the form of pores.¹⁴ As for a dense polymer film such as PU

Correspondence to: H. Fan (fanhaojun@163.com).

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TABLE I
Characteristics of the PU Synthesized

Sample	First step (mmol)			Second step (mmol)			NCO/OH (mole ratio)
	Diol	BDO	IPDI	DMPA	BDO	IPDI	
EPU(a)	20 (PPG3000)	9	61.8	31	–	–	1.03/1.00
TSPU(b)	20 (PPG600)	–	40	31	9	21.8	1.03/1.00
TSPU(c)	20 (PCL3000)	–	40	31	9	21.8	1.03/1.00

finishing layer for leather, its WVP is closely related to the size of free volume available in the polymer. Thus, how to efficiently-increase the size of free volume in the PU finishing layer is a crucial issue when finished leather with high WVP is to be manufactured.

Phase transition from a glassy state to a rubber state often accompanies great changes in physical properties of polymeric materials. These changes include a significant increase of free volume on heating through a glass transition temperature (T_g) or soft segment crystal melting temperature (T_m). Unfortunately, due to structure characteristic of ordinary elastomeric PU resin currently employed in leather industry for finishing, it undergoes no phase transition in the normal wearing temperature range. Therefore, the size of its free volume is hard to manipulate efficiently in this temperature range. If the T_g or T_m of the PU resin is designed to be in the normal wearing temperature range, its free volume will be too small to allow water vapor transportation when the temperature is lower than T_g or T_m . Thus under cold condition, a warm-keeping effect is achieved. When the environment temperature is higher than T_g or T_m , the significant increase of free volume will cause the WVP to increase dramatically.^{15–17} By this design, the WVP of PU finishing layer will respond automatically to the stimuli of external temperature and shows thermosensitive feature in the normal wearing temperature range.

In our previous work, we synthesized a type of solvent-based thermosensitive PU (TSPU) and studied its WVP as a function of temperature.^{18,19} The results indicated that this TSPU basically consisted of two phases (a reversible phase and a fixable phase) and showed independent phase transition temperature. The phase transition temperature of the reversible phase was in the normal wearing temperature range and defined as switch temperature (T_s). When the temperature varied from $T_s - 10^\circ\text{C}$ to $T_s + 10^\circ\text{C}$, the WVP of the TSPU film increased from 4100 g/(m² 24 h) to 10,400 g/(m² 24 h), showing obvious thermal sensitivity. As continuous work, two water based TSPU with a glass transition reversible phase and a soft segment crystal melting transition reversible phase, respectively, were synthesized and employed for leather finishing in this study. We

investigated how the structure of reversible phase and the temperature influenced the WVP of the TSPU finished leather. The aim of this study is to develop “smart leather” by finishing a layer of TSPU film with controllable water vapor permeability.

EXPERIMENTAL

Materials

Table I lists the basic formulation of this experiments. Polycaprolactone diols with molecular weight 3000 g/mol (PCL3000), poly propylene glycol with molecular weight 600 g/mol (PPG600), and 3000 g/mol (PPG3000) were purchased from Aldrich Chemical Co., (United States). They were dried at 100–120°C under 1–2 mmHg for 5 h before use. Extra pure grade of isophorone diisocyanate (IPDI), 1,4-butanediol (BDO), dimethylolpropionic acid (DMPA), and triethylamine (TEA) were obtained from Junsei Chemical Co., (Japan). They were used as received. Garment leather was obtained from a local tannery.

Synthesis of water based PU

Elastomeric polyurethane (a)

A 500 mL round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube was used as a reactor to prepare the PU. Dried PPG3000, IPDI, and BDO were charged into the dried flask. The reaction was carried out at 80°C for 2 h, followed by a chain-extension reaction with DMPA at 60°C for 2 h. The neutralization reaction by TEA was carried out at 40°C for 30 min. The mole ratio of TEA : DMPA was 1 : 1, and the final pH value of the prepolyurethane was about 7. Then the prepolyurethane was dispersed into distilled water with high stirring at room temperature for 1 h. Finally, a semitransparent emulsion with 30 wt % was obtained.

Thermosensitive polyurethane (b) and thermosensitive polyurethane (c)

TSPU(b) and TSPU(c) were synthesized with the same equipment, but in two steps. At the first step,

dried PPG600 or PCL3000 and twofold mole ratio of IPDI were charged into the flask. The reaction was carried out at 80°C for 2 h to form NCO-terminated soft segments. At the second step, hard components (IPDI, BDO, and DMPA) were charged into the flask to form hard segments at 60°C for 2 h. The molar ratio of OH : NCO in the hard components was 2 : 1, so that the hard components could react to form OH-terminated hard segments. Then the OH-terminated hard segments reacted with the NCO-terminated soft segments to form segmented polymer. Similarly, the neutralization reaction by TEA was carried out at 40°C for 30 min. The mole ratio of TEA : DMPA was 1 : 1, and the final pH value of the prepolyurethane was about 7. Then the prepolyurethane was dispersed into distilled water with high stirring at room temperature for 1 h. Finally, a semitransparent emulsion with 30 wt % was obtained.

Film casting and finished leather preparation

Films were prepared by casting emulsions on a glass plate with 5 cm × 5 cm × 1 mm. After standing at 60°C for 10 h, the films were further dried at 100°C under 2–4 mmHg for the next 10 h. The garment leather was finished by two finishing layers, and the total spraying amount was 150 g/m². The finishing material was formulated from PU samples (35 wt %), pigment (15 wt %, BASF Company), filler (5 wt %, BASF Company), release agent (0.1 wt %, Stahl Company), and distilled water (44.9 wt %). After finished by the first layer, the leather was predried at ambient temperature and plated at 100°C and 80 atm for 10 s. Then the second layer was sprayed and the finished leather was cured at 80°C for 1 h. The thickness of PU finishing layer was 0.15 mm.

Instrument analysis

The phase transition temperatures of the PU films were measured by using a DuPont 9900 thermal analyzer with a differential scanning calorimetry (DSC) module, which was purged with nitrogen gas and quenched with liquid nitrogen. The specimens were heated in sealed aluminum pans and scanned from –100 to 200°C with a heating rate of 10°C/min. To erase earlier thermal history of the sample, the DSC results relied on the second heating run instead of the first run.

Dynamic Mechanical Analysis (DMA) was performed in the tensile mode at a fixed frequency of 5, 10, and 15 Hz under nitrogen gas purging by a DuPont 983 DMA. To negate the DMA's dependence on the Poisson ratio, PU films with length-to-thickness ratio larger than 10 were used. The measured rectangular specimens were heated from –50 to

100°C with a heating rate of 5°C /min. The data of the storage modulus and Tan δ were recorded.

The positron annihilation lifetime (PAL) of PU films was determined by detecting the prompt gamma-ray (1.28 MeV) from the nuclear decay that accompanied the emission of a positron from the Na-22 radioisotope and the annihilation gamma-ray (0.511 MeV). A fast-fast coincidence circuit of the PAL spectrometer with a lifetime resolution of 290 ps as monitored with a Co-60 source was used to record all PAL spectra. The spectrum (1,000,000 counts) was collected at each temperature for a complete data analysis of lifetime distribution. The count rate was 200 counts/s and the channel width was 61 ps. Both RESOLUTION and POSITRON FIT programs in the PATFIT88 package were employed for data analysis.

Measurement of water swelling

Preserve the PU films in water at a certain temperature and measure the degree of water absorption after 2 and 24 h, respectively. The water swelling (%) was calculated by the following equation.

$$\text{Water swelling (\%)} = \frac{W - W_0}{W_0} \times 100\% \quad (1)$$

Where W_0 is the original film weight and W is the film weight after swelling. The reported value was mean ± standard deviation of five measurements for each sample.

Measurement of WVP

WVP of the PU finished leather was measured according to ASTM method E 96 Desiccant method, i.e. an open cup containing desiccant was sealed with the specimen 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 temperature of 15, 25, 35, 45, 55, 65, and 75°C with a constant relative humidity of 50%. Finally, the weight change of permeation cup with the specimen was recorded after 24 h and the WVP was calculated by the following equation.

$$\text{WVP} = \frac{a_1 - a_2}{S} \quad (2)$$

Where, $(a_1 - a_2)$: weight change of permeation cup with the specimen (g), S : area of permeation (m²). The reported value was mean ± standard deviation of five measurements for each sample.

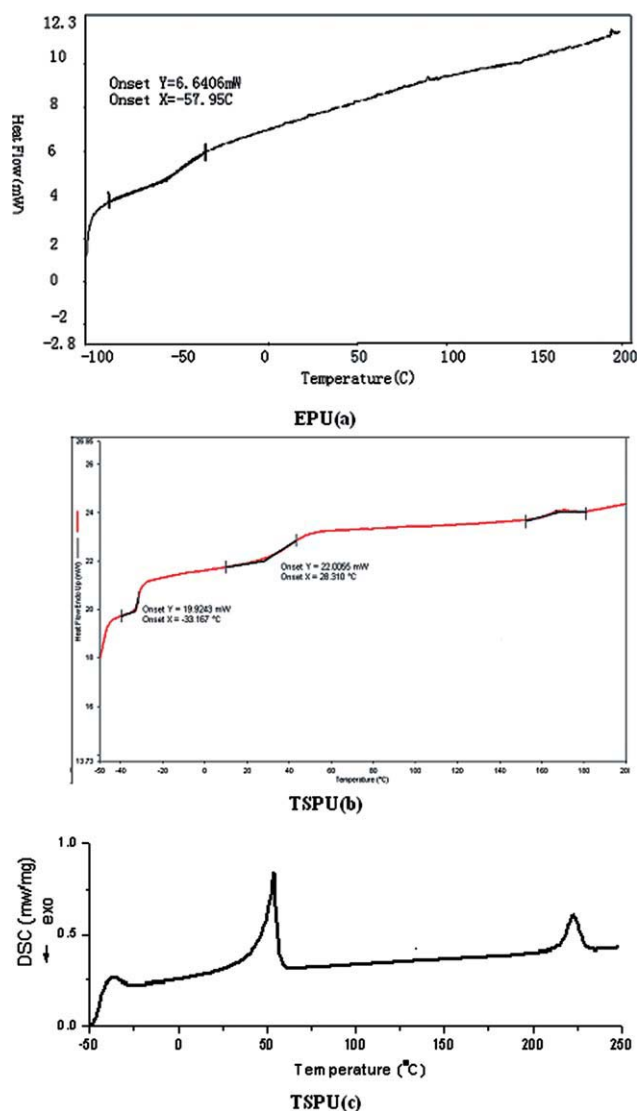


Figure 1 DSC curves PU films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Phase transition temperature of PU films

The compatibility between soft segments (reversible phase) and hard segments (fixable phase) of the synthesized PU can be characterized by DSC and DMA analysis. Figure 1 shows the DSC patterns of EPU(a), TSPU(b), and TSPU(c). The PU synthesized in this experiment were designed to have segmented structure except EPU(a). In Figure 1, we could see that EPU(a) did not show a phase transition in the normal wearing temperature range, but showed a glass transition at -57°C , which was the typical feature of PU elastomer rather than segmented PU. By contrast, TSPU(b) had an onset at -33.2°C corresponding to the glass transition of PU macromolecular chain, an onset at 28.3°C corresponding to the glass

transition of soft segments and a peak at 165°C corresponding to the phase transition of hard segments. For TSPU(c), two peaks at 49.8°C and 210°C corresponding to the crystal melting transition of soft and hard segments, respectively, were recorded, but the glass transition of the PU macromolecular chain could not be observed on the DSC curve. Figure 2 shows the DMA results of TSPU(c). It could be seen that glass transition of the TSPU(c) macromolecular chain is approximately -53°C , and the crystal melting transition of the soft segments is 50.1°C (almost the same as DSC result). The above results revealed that TSPU(b) and TSPU(c) were phase separated into soft segments and hard segments, and the incompatible soft and hard segments showed obviously independent phases and different phase transition temperatures.

These differences could be ascribed to the different composition and structure of EPU(a), TSPU(b), and TSPU(c). On one hand, PCL with molecular weight 3000 g/mol had an obvious melting point at $48\text{--}50^{\circ}\text{C}$,²⁰ but PPG with molecular weight 3000 g/mol was an amorphous polyol at room temperature. On the other hand, the assembly states of hard components were quite different in these PU because of the different synthesizing methods. In the case of EPU(a), hard components, such as BDO, IPDI, and DMPA were added separately, i.e. BDO and IPDI were added at the first step, and the DMPA was added at the second step in polymerization process. With this synthesizing method, these hard components were uneasy to form continuous hard segments, i.e. the hard segments were mostly dissolved into the soft segments. Therefore, no soft segment phase transition could be observed on the DSC curve

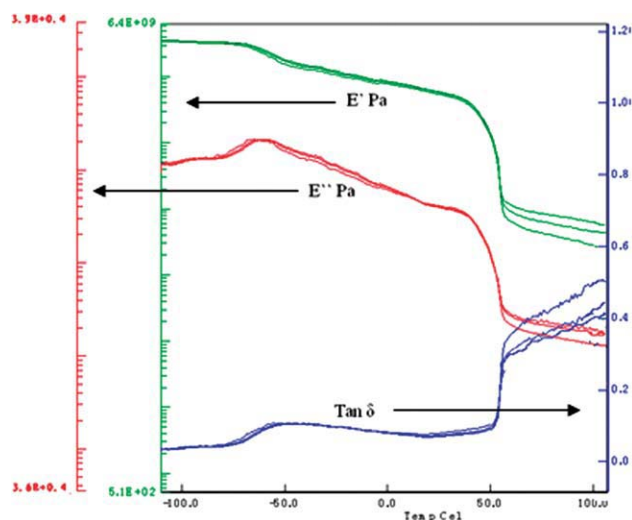


Figure 2 DMA patterns of the TSPU(c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Phase Transition Temperature and Enthalpy Change of PU films

Sample	T_g (°C)	T_s (°C)/ ΔH (J/g) Soft segments	T_m (°C)/ ΔH (J/g) Hard segments		
EPU(a)	-57	-	-	-	-
TSPU(b)	-33.2	28.3	23.2	165	4.21
TSPU(c)	-53 ^a	49.8	47.3	210	7.15

^a Observed from DMA; ΔH : Enthalpy change.

in the normal wearing temperature range except a glass transition at -57°C . However, TSPU(b) and TSPU(c) were prepared by two steps. At the first step, the NCO-terminated soft segments were formed. At the second step, the hard components (BDO, DMPA, and IPDI) were added simultaneously, so they would react with each other to form OH-terminated hard segments. Then these OH-terminated hard segments reacted with the NCO-terminated soft segments to form segmented polymer. In this method, the hard segments were not dissolved into the soft segments, so that the soft and the hard segments were separated enough to form independent phases. This was why there were two endothermic phase transition temperatures corresponding to the phase transition of soft and hard segments on the DSC curves of TSPU(b) and TSPU(c).

From Figure 1, we could also find that there was a sharp endothermic crystal melting peak at 49.8°C with a higher enthalpy change ($\Delta H = 47.3$ J/g) for TSPU(c) but only a small endothermic onset at 28.3°C with a lower enthalpy change ($\Delta H = 23.2$ J/g) for TSPU(b). Table II listed the enthalpy changes of three synthesized PU in the phase transition process. It is believed that reversible phase transition of soft segments from well organized state to amorphous state accompanies different changes in enthalpy (ΔH), which, to a great degree, reflects how well-organized the structure of the soft segments is.^{20,21} Generally speaking, the higher the enthalpy change is, the well the structure of soft segments organizes. Consequently, the reversible crystal soft segment of TSPU(c) showed a more well organized structure than that of TSPU(b).

The size of free volume in PU films

The PAL spectroscopy has been widely employed to study the microstructure of macromolecular, especially to determine the nanoscale free volume size (0.1–1.5 nm) in polymers.²² From the analysis of PAL spectroscopy, we can obtain the data of *ortho*-positronium (*o*-Ps) lifetime (τ_3) and *o*-Ps intensity (I_3), and then the average radius (R) of free volume holes can be calculated by the following semiempirical equation.¹⁵

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1} \quad (3)$$

Where, $R_0 = R + \delta_R$; $\delta_R = 0.166$ nm, which is the fitted empirical electron layer thickness.¹⁶

Furthermore, the average volume of free volume holes (V_h) can be calculated by the following equation.

$$V_h = \frac{4}{3} \pi R^3 \quad (4)$$

On one hand, the *o*-Ps lifetime (τ_3) is related to the size scale of free volume holes, and higher τ_3 value means larger average radius (R) of free volume holes. Correspondingly, the average volume of free volume holes (V_h) also shows a larger value. On the other hand, the *o*-Ps intensity (I_3) is proportional to the amount of free volume holes, and higher I_3 value means larger amount of free volume holes.^{15,22} Figure 3 described the τ_3 , I_3 , R , and V_h of PU films as a function of temperature. From this figure, we found that in all temperature range, the parameters including τ_3 , I_3 , R , and V_h , of EPU(a) showed little changes as temperature increased, and the maximum radius of free volume holes (0.311 nm) was lower than the average radius of water vapor (0.4 nm). This indicated that EPU(a) film had a barrier function to moisture. However, as for TSPU(b) and TSPU(c), when the temperature was lower than the phase transition temperature of their soft segments, two samples showed a relatively lower τ_3 , I_3 , R , and V_h value compared with EPU(a). Because at low temperature, TSPU(b) and TSPU(c) were in well organized glassy state and all movements of the macromolecular chain were frozen, so they showed lower τ_3 , I_3 , R , and V_h value. When the temperature exceeded the phase transition temperature of their soft segments, both TSPU(b) and TSPU(c) underwent a change from glassy state to rubbery state, which resulted in a dramatic changes in τ_3 , I_3 , R , and V_h . In this condition, the radius of free volume holes ($R_b = 0.418$ nm, $R_c = 0.467$ nm) in TSPU(b) and TSPU(c) was larger than the average radius of water vapor. Lower τ_3 , I_3 , R , and V_h value at lower temperature and higher τ_3 , I_3 , R , and V_h value at high temperature implied that TSPU(b) and TSPU(c) films had good moisture barrier effect at low temperature but a higher WVP at higher temperature.

The water swelling of PU films

Table III showed the water swelling of three types of PU films at phase transition temperature of soft segments $\pm 10^\circ\text{C}$. It is believed that the water swelling of PU films is related to their assembly state and temperature. In a temperature range from ambient

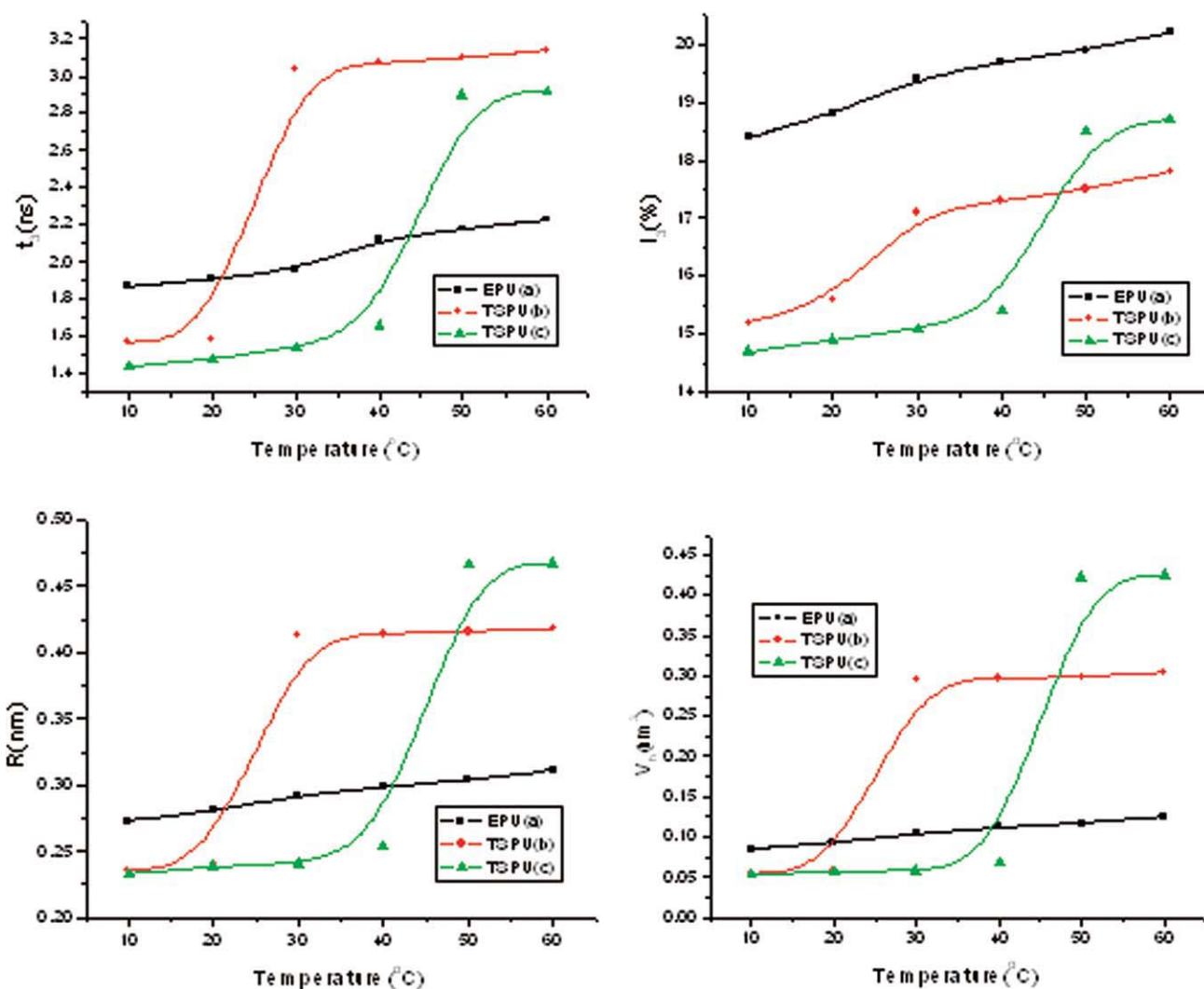


Figure 3 The τ_3 , I_3 , R , and V_h of PU films as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature to 55°C, the macromolecular chain of EPU(a) was still in a rubbery state, so the temperature had little effect on the average radius of free volume. Therefore the penetration and absorption of water did not show significant changes in response to temperature variation. However, in the same temperature range, the temperature played an important role in controlling the size of free volume

holes for TSPU(b) and TSPU(c) because of the existence of phase transition. When the temperature was 15°C, macromolecular chain of both TSPU(b) and TSPU(c) is in a glassy state, and the average radius of free volume holes was too small to allow water vapor penetration. Therefore, lower water swelling at low temperature was obtained. When the temperature was higher than 55°C, the soft segments of

TABLE III
Water Swelling of PU Films

Sample	State of the polymer		Water swelling (%)	
	15°C	55°C	15°C ²	55°C
			2 h/24 h	2 h/24 h
EPU(a)	Rubbery	Rubbery	2.03 ± 0.12/4.38 ± 0.10	3.34 ± 0.11/4.61 ± 0.09
TSPU(b)	Glassy	Rubbery	1.43 ± 0.15/1.96 ± 0.16	4.32 ± 0.12/8.34 ± 0.17
TSPU(c)	Glassy	Rubbery	0.91 ± 0.17/1.64 ± 0.12	4.62 ± 0.13/9.18 ± 0.19

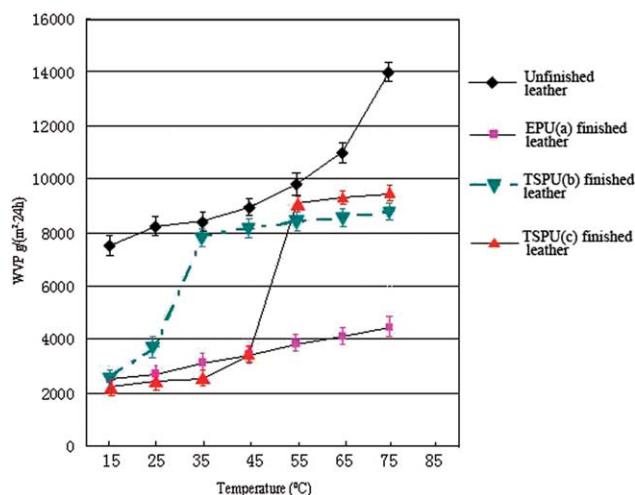


Figure 4 WVP of PU finished leather and unfinished leather. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TSPU(b) and TSPU(c) changed from glassy state to rubbery state. Simultaneously, the frozen macromolecular chain was released, and the significantly enhanced free volume hole size allowed the water penetration and caused the water swelling to increase markedly. In contrast to TSPU(b), the water swelling of TSPU(c) was lower at low temperature and higher at high temperature, showing a more sensitive characteristic to thermal stimulus. This was related to the more well organized soft segments of TSPU(c), because these dense soft segments were more beneficial for hindering water penetration at low temperature.

The WVP of PU finished leather

The WVP of PU finished leather and unfinished leather as a function of temperature was shown in Figure 4. The WVP of all specimens increased with an increase of temperature. Unfinished leather showed relatively higher WVP all over the temperature range due to its natural porous structure. Unfortunately, this inherent virtue was dramatically reduced after the leather was finished. PU finishing layers undoubtedly retarded water vapor diffusion and penetration, which led to low WVP. But this retarding effect was quite different among the three types of PU synthesized in this study due to their different structure.

As mentioned earlier, no phase transition occurred in the normal wearing temperature range for EPU(a), thus the free volume did not undergo a significant change as temperature increased. Therefore the WVP of EPU(a) finished leather showed kept at a low level all over the temperature range. However, this was not the case for TSPU(b) and TSPU(c) finished leather. When the temperature was lower than

the phase transition temperature of soft segments of TSPU(b), both TSPU(b) and TSPU(c) were in the glassy state, so the WVP of TSPU finished leather showed a very low value. However, as the temperature exceeded the phase transition temperature of soft segments of TSPU(b) but was still lower than the phase transition temperature of soft segments of TSPU(c), EPU(a) was still in the rubbery state and TSPU(c) was still in the glassy state, so their WVP showed little changes. While the TSPU (b) had a phase transition from the glassy state to the rubbery state, and the significantly enhanced free volume hole size caused the WVP of TSPU(b) finished leather to increase from 3800 g/(m² 24 h) at 25°C to 7830 g/(m² 24 h) at 35°C. When the temperature exceeded the phase transition temperature of soft segments of TSPU(c), similarly, TSPU(c) underwent a phase transition, so the WVP of TSPU(c) finished leather changed from 3600 g/(m² 24 h) at 45°C to 9450 g/(m² 24 h) at 55°C, showing an improvement as high as 162%.

Although the WVP of both TSPU(b) and TSPU(c) finished leather showed thermosensitive feature, the response of WVP to the temperature change was quite different. Obviously, the change of WVP was greater for TSPU(c) finished leather than for TSPU(b) finished leather. This was due to the fact that the reversible phase of TSPU(c) was a crystal segment, which showed a well organized morphological structure. Therefore, in the phase transition process from a well organized state to an amorphous state, the free volume hole size of TSPU(c) changed more sharply, causing the WVP to increase more markedly. This conclusion was well consistent with the analysis of the enthalpy changes of TSPU(c) and TSPU(b). According to this phenomenon, it was easy to understand that the well organized structure of reversible phase was necessary for TSPU finished leather to achieve more sensitive feature to thermal stimulus.

To sum up, it was very interesting that leather finished by TSPU showed a relatively higher WVP at high temperature but very low WVP at low temperature compared with EPU finished leather, providing a guidance to develop "smart leathers" with controllable water vapor permeability.

CONCLUSIONS

1. Two types of thermosensitive polyurethane (TSPU) and a polyurethane elastomer (EPU) were synthesized and applied in leather finishing. TSPU showed a phase separated behavior and a phase transition temperature in normal wearing temperature range. In contrast to EPU, the *o*-Ps lifetime (τ_3) and the average radius (*R*)

of free volume holes of TSPU showed dramatic changes when the temperature exceeded the phase transition temperature. While as for EPU, no phase transition could be observed, and τ_3 and R remained unchanged in the same temperature range.

2. As temperature exceeded the phase transition temperature, TSPU with a more well organized reversible phase showed a more significant increase of free volume hole size.
3. Leathers finished with TSPU had lower WVP at low temperature and higher WVP at high temperature, showing a thermosensitive feature. This provided an application of developing "smart leather" with controllable WVP.

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