

# Water vapor permeability of nonwoven fabric coated with thermosensitive polyurethane films obtained from isophorone diisocyanate and polyester or polyether polyol

A. Morel<sup>1,2</sup>, G. Bedek<sup>2</sup>, D. Dupont<sup>2</sup> and F. Salaün<sup>\*1</sup>

<sup>1</sup>ENSAIT, GEMTEX - Laboratoire de Génie et Matériaux Textiles, F-59000 Lille, France

<sup>2</sup>HEI-Yncréa, GEMTEX, F-59000 Lille, France

The aim of this work is to develop a thermosensitive membrane allowing a temperature-controlled water vapour permeability to enhance the comfort and the safety of firefighters. Membranes with different chemical structure were synthesized from segmented polyurethane. The influence of the polyol type, its length and the hard segment content was studied. These films were laminated onto nonwoven fabric in order to analyse the vapour water transfer mechanisms. Two kinds of mechanisms were identified depending on the chemical structure as a bulk modification and a surface modification, that change moisture management properties. The systems polyurethane-textile keep the properties of the polyurethane film and show controlled water vapour permeability according to the temperature changes.

**Keywords:** smart textile; thermosensitive membrane; polyurethane; water vapor permeability; nonwoven

## 1. Introduction

Thermal comfort is closely related to changes in physiological variables, such as skin and core temperature, environmental factors such as humidity, air velocity, air temperature; the activity level of the individual, and clothing properties, in which the insulation value of the fabric as well as the water vapor permeability play a main role [1]. The term 'thermal comfort' refers also to the mind condition which expresses satisfaction with the thermal environment [2] and it is closely related to clothing comfort. Thus, when it is provided by clothing, it is mainly affected by tactile perceptions meaning sensorial comfort including warm-cool feeling of the fabric, moisture and thermal interactions which influence the human perception [3]; and also related to the way clothing interacts with metabolic heat and moisture dissipation, i.e. thermophysiological comfort. In hot environments, a large amount of moisture accumulates in the garment and interferes with heat transfers by modifying thermal properties of the textile system [4]. This moisture is responsible for hot steam burn injuries, which occur when moisture vaporises since it cannot diffuse outside the garment and thus returns to the skin. This phenomenon is enhanced by energy storage due to the high insulation of the system. After exposition to radiant heat flux, the system is cooling but heat transfers are still coming towards the skin, which hinders skin cooling and promotes injuries even when the person is no longer exposed to heat. Thus, preventing steam burn injuries is an important issue in the improvement of fire protective clothing and the safety of firefighters [5].

Thus, the use of smart textiles, and more specially a protective coating, is one of the possible ways to enhance thermal comfort for firefighters to improve human thermoregulation by transmitting their metabolic heat and sweat vapor, and avoidance of burn injuries.

In this context, the development of fabrics for thermal protective clothing takes in account three main fabric components, i.e. shell fabrics, thermal liners, and moisture barriers; which are used in combination to produce the composite fabric [6]. Fabric moisture management is crucial in extreme activity conditions, and it appears that two conflicting requirements compete each other, i.e. (i) protecting clothing which is required to prevent the body burning from the external heat source; and (ii) an highly insulative protective layer that can shut down the channels for sweat evaporation and thereby the body's release of heat stress. To improve it and to allow the dissipation of the sweat vapor generated, moisture barriers have been mainly developed with a microporous or hydrophilic lamination/coating or a membrane [7]. In this context, polymeric material can offer many concrete opportunities for the design of adaptive layer, having the ability to transport water vapor and then yielding a microclimate in the garment complex.

Furthermore, it was found by Keiser et al. that the moisture content is mainly dependent on the textile complex structure [8], and hydrophobic underwear, such as aramid, can transport the moisture to adjoining layers. And under high heat flux, the water vapor accumulation inside the fabric and transmission toward firefighters' skins may cause steam burns [9]. Thus, water vapor permeability is one of the most main textile properties to protect against steam exposure, and the presence of a membrane inside the textile complex reduces burn injuries by preventing steam transfers [10].

Taking in account that a cooling effect is obtained when there is a negative water vapor pressure gradient, the water vapor diffusion properties of the polyurethane thermosensitive membranes may be used for this kind of application [11].

Indeed, moisture is transferred by sorption, diffusion, and desorption in non-porous membrane, which is related on the water molecules dilution and their subsequent diffusion due to a concentration gradient through it [12, 13].

Therefore, thermosensitive polyurethane membranes are recognized as smart material, according to the temperature

range they present either good moisture barrier effect or higher water vapor permeability. Thus, Chen et al. have observed that the WVP of finished leather increased by over two-fold from either side of the switch temperature [14].

This latter can be the glass transition temperature and the crystalline melting transition temperature of soft segment in the polyurethane membrane [15]. Since, these materials can show microphase-separated structure, they can offer a large range of physical properties according to the composition of soft and hard segments. The water vapor permeability can be controlled by free volume, depending on the chemical composition, and hydrophilicity of membranes [16], and also to the crystallization of soft segments and bulk modifications improving the diffusion property [5]. Beside, even if the polyurethane membranes are not well organized, they can also show high swelling abilities or sorption capacity related to the surface changes. Furthermore, it was also observed that the textile coated or laminated with polyurethane membranes show significant transition in moisture permeability from either side of the switch temperature [17], resulting from the smart permeability characteristics of the PU [18, 19]. As described by Lei et al. [20] water vapor permeation occurs in two consecutive steps, *i.e.* (i) water vapor absorption and (ii) desorption, in which the hydrophilic property of the membrane play the main role.

Driven the great application potential of polyurethane membrane, we aimed at developing thermosensitive coated textile to improve fire fighter comfort and protection. In this contribution, three kinds of PU membranes were prepared and applied onto an aramid nonwoven fabric by compression molding. The synthesized membranes were characterized in terms of moisture vapor transfer and related to their thermo-mechanical properties to determine the influence of the formulation parameters on this behavior. And, the water vapor permeability of the three different PU coated fabrics were investigated to evaluate the effect of the textile substrate on the temperature dependency of the moisture management.

## 2. Experimental

### 2.1 Materials

Two polytetrahydrofurans (POTM) ( $2000 \text{ g.mol}^{-1}$ ), polycaprolactone diol (PCL) ( $2000 \text{ g.mol}^{-1}$ ), isophorone diisocyanate (IPDI) 98%, dimethylol propionic acid (DMPA), triethylamine (TEA) and 1,4-butanediol (BDO) were purchased from Sigma Aldrich and were used without further purification. The aqueous dispersion is obtained using deionized water.

A 100% aramid nonwoven fabric (perforated needle-felt made of aramid microfibers), ISO'AIR® PER 4659, having a surface weight of  $60 \text{ g.m}^{-2}$ , density of  $45 \text{ kg.m}^{-3}$  and a thickness of 1.23 mm and obtained from Dufлот Industrie (France) was used as textile specimen. It was conditioned for 48 h in the atmospheric conditions of temperature  $20 \pm 2 \text{ }^\circ\text{C}$  and relative humidity  $65 \pm 2\% \text{ RH}$ , before the various tests.

### 2.2 Polyurethane film synthesis

The synthesis is based on a two-step polymerization. The first step corresponds to the formation of a prepolymer from two semi-crystalline polyols and an excess of diisocyanate. The second step corresponds to the chain extension. The prepolymer preparation is carried out in a 250 ml four-necked round-bottomed flask equipped with a mechanical stirrer and a nitrogen inlet. POTM (polyether-polyol) and IPDI or PCL (polyester-polyol) and IPDI mixture was heated to  $80^\circ\text{C}$ , and stirred for 1h under inert atmosphere at 300 rpm. Afterwards, DMPA was added and the reaction was carried out at  $95^\circ\text{C}$  for 70 min. DMPA was used as an emulsifier that provides hydrophilic groups within the prepolymer structure to improve its dispersion in water. The NCO-terminated prepolymer was dispersed in deionized water containing TEA (1 equiv. per DMPA) at  $28^\circ\text{C}$  at high speed to produce the polyurethane dispersion, and BDO chain extender was then added. The reaction proceeded for 70 min at 500 rpm. TEA was used to neutralize the carboxylic group of the DMPA. This neutralization leads to the formation of an ammonium salt enhancing the stabilization of the dispersion. Then, methanol was introduced to modify the end-groups and to block the residual NCO functions. The corresponding polyurethane films were obtained by casting the dispersion into a Teflon mold, and drying at room temperature for 24h, followed by drying at  $60^\circ\text{C}$  during one night. The obtained films were stored in a desiccator at room temperature. Three formulations were chosen, and the resultant films were designated as X-polyol<sub>Y</sub>, *i.e.* 17-POTM<sub>2000</sub>, 36-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub>, where X is the hard segments content (%), and Y, the molecular length of the polyol ( $\text{g.mol}^{-1}$ ) (Table 1).

**Table 1** Composition of polyurethane films.

Samples	Feed ( $\times 10^3 \text{ mol}$ )					HSC (wt%)
	Polyol	IPDI	DMPA	TEA	BDO	
17-POTM <sub>2000</sub>	27.3	19.3	7.75	7.75	2.25	17
36-POTM <sub>2000</sub>	20.0	38.6	15.5	15.5	4.5	36
36-PCL <sub>2000</sub>	20.0	38.6	15.5	15.5	4.5	36

### 2.3 Polyurethane complexes – dry heat lamination

The resulting polyurethane membranes were then applied on an aramid nonwoven by compression molding at 100°C, between two PTFE plates, by using a Dolouets hydraulic press. They were pressed at 10 bars during 5 min, and were finally cooled to room temperature under pressure.

### 2.4 Analytical methods

#### 2.4.1 FTIR spectroscopy analysis

Fourier-transformed infrared spectroscopy (FTIR) studies were performed using a FT-IR Nicolet Nexus spectrometer in the ATR mode. The number of scans per experiment was 128 and the resolution was 4 cm<sup>-1</sup>. To put an interpretation on a more quantitative basis, the deconvolution of the spectra using peakfit 4.0 software (Jandel, San Rafael, CA) in the 1800-1650 cm<sup>-1</sup> range into Gaussian peaks was used. Position, bandwidths, and amplitudes of the peaks were varied until: (i) the resulting peaks had reasonable half-widths (<20-25 cm<sup>-1</sup>), and (ii) good agreement between the calculated sum of all components and experimental spectra was achieved (r<sup>2</sup>>0.99). The results of three independent experiments were averaged.

#### 2.4.2 Wetting measurement

Surface hydrophobicity and wettability of the samples were evaluated by contact angle measurements using a Digidrop GBX contact angle meter equipped with a diffuse light source and a CCD camera at 25 frames per second. A droplet of test liquid (6 µl) was deposited on the film, and the image was analyzed to determine the contact angle between the liquid and the solid. The surface tension (γ) of the films was obtained from a combination of the dispersive (γ<sup>d</sup>) and polar (γ<sup>p</sup>) components of the surface tension. The three test liquids were water (γ=72.8 mN/m, γ<sup>d</sup>=21.8 mN/m, γ<sup>p</sup>=51.0 mN/m), methylene iodide (γ=50.8 mN/m, γ<sup>d</sup>=48.5 mN/m, γ<sup>p</sup>=2.3 mN/m) and dodecane (γ=25.4 mN/m, γ<sup>d</sup>=25.4 mN/m, γ<sup>p</sup>=0 mN/m). At least ten measurements were made with each liquid and the mean contact angle was used to calculate the polar and dispersive contributions to the surface tension of the samples according to the Owens and Wendt method with the referent liquids used [21]. The tests were realized at room temperature and after a conditioning at 60°C to investigate the influence of the temperature on the surface tension of samples.

#### 2.4.3 Thermal analysis

The thermal behaviour of the samples was recorded using a DSC 2920 TA instrument piloted on PC with TA Advantage control software. Indium was used as a standard for temperature calibration. The analysis was conducted under a constant stream of nitrogen at a heating rate of 10 °C.min<sup>-1</sup> in the temperature range from -20 to 200 °C. Samples were placed in aluminium pans that were hermetically sealed prior to be placed on the calorimeter thermocouples.

Thermogravimetric analyses were carried out using a TGA 2950 TA Instrument at a heating rate of 10 °C.min<sup>-1</sup> under a constant stream of nitrogen. The weight of the samples used was kept around 10 mg in an open platinum pan. The scans were performed at a temperature range from room temperature to 500 °C.

#### 2.4.4 Evaporative dish method

Water vapor permeability (WVP) was measured using a DSL Atlas turning table by placing the samples on a 31.0 x 10<sup>-6</sup> m<sup>2</sup> diameter flask filled with a predetermined amount of distilled water. Eight flasks were put on the turning table that is placed at room temperature or inside a climate chamber regulated at 50 °C. Each flask was weighed after 1h and 16h of conditioning. The water vapor permeability was determined from the Eq. (1).

$$WVP = \frac{G}{A \times t} \quad (1)$$

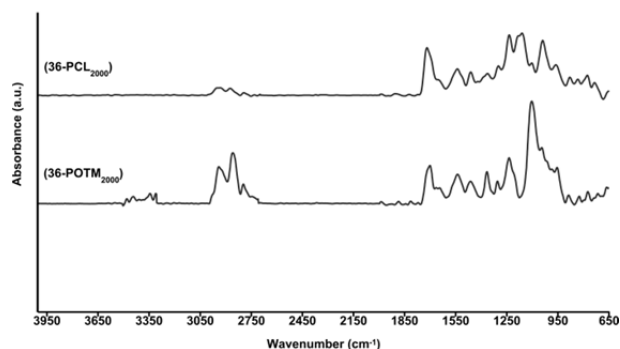
where G is the weight change in g, t is the duration of the test in days, A is the exposed film area (m<sup>2</sup>) and WVP is the water vapor permeability (g.m<sup>-2</sup>.day<sup>-1</sup>).

The sorption capacity of the polyurethane films was characterized by swelling G (wt-%) [12] that was calculated from the mass uptake,  $m - m_0$ , of the membrane at the equilibrium and the mass of the dry polymer  $m_0$  (Eq. (2)).

$$G(\text{wt} - \%) = \frac{m - m_0}{m_0} \times 100 \quad (2)$$

## 3. Results and discussion

### 3.1 Structure of the polyurethane films

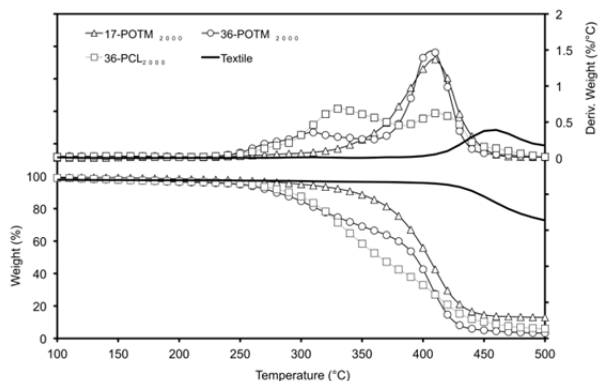


**Fig. 1** FTIR spectra of 36-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub>.

Structure of the obtained polyurethane films was analyzed by ATR-IR method, the spectra of 36-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub> are shown in Figure 1. The characteristic absorption peaks of urethane groups were observed at 1730 cm<sup>-1</sup> (C=O stretching) and 1650 cm<sup>-1</sup> (hydrogen bonded amide I). The absorption band at 1102 cm<sup>-1</sup> was attributed to the ether groups of the soft segments. The isocyanate (-N=C=O) absorption band at 2270 cm<sup>-1</sup> and the -OH large absorption band at 3300 cm<sup>-1</sup> that belongs to the diisocyanate and the polyol were not present, this suggested that the reaction was completed. The shoulder at 1040 cm<sup>-1</sup> was attributed to the C-O stretching of the DMPA. The absorption bands at 1235 cm<sup>-1</sup> and 1305 cm<sup>-1</sup> were assigned to the amide group. The stretching vibrations of the -CH<sub>3</sub> and -CH<sub>2</sub> groups appear at 2923 cm<sup>-1</sup>, 2853 cm<sup>-1</sup>, 1365 cm<sup>-1</sup> and 1460 cm<sup>-1</sup>. N-H bending and C-N stretching at 1540 cm<sup>-1</sup>, 1305 cm<sup>-1</sup> and 1235 cm<sup>-1</sup> were also detected. Furthermore, it was distinguished on the two spectra the presence of polyurea stretching vibration bands at 1500-1400 cm<sup>-1</sup> and 1050-1000 cm<sup>-1</sup> overlapped with C-O of DMPA. The presence of the absorption band of the carbonyl group at a range of 1660-1625 cm<sup>-1</sup> was related to a side reaction to form urea related to the reaction with water during the chain extension reaction step, even if it was limited due to the protection of the polymer particles by hydrophilic moieties in the particle outer part. Hard segments were formed from the diisocyanate and the chain extender, and were the same for all the polyurethane films. The difference in the intensity of the peaks attributed to the soft and hard segments was ascribed to the influence of the kind of polyol used. The absorption bands at 1715 cm<sup>-1</sup> and 1695 cm<sup>-1</sup> were related to amorphous conformation of hydrogen bonding and crystalline conformation of hydrogen bonding [22], respectively.

### 3.2 Thermal properties of the laminated textiles

Polyurethanes display several thermal transitions, in which the soft phase shows glass and melting transitions when they are semicrystalline, and the hard phase may present multiple melting transitions depending on its content. Endothermic phase transitions disappear during the second heating cycle, except for the 17-POTM<sub>2000</sub> complex. Thermograms are similar to those of membranes alone [23]. The characteristic temperature,  $T_{Tr}$ , of the 36-PCL<sub>2000</sub> film is 42°C, and increases up to 46°C after heat lamination, due to the reorganization of the macromolecular chains at 100°C. The temperature of 17-POTM<sub>2000</sub> is lower when it was laminated, i.e. 21°C and 38°C for the coated textile, compared to 48°C for the raw film. Furthermore, it was also noted that this lower  $T_{Tr}$  was related to the sticky behaviour of this sample after lamination process. The sample organization of flexible segments was unchanged for laminated textiles compared to raw films.

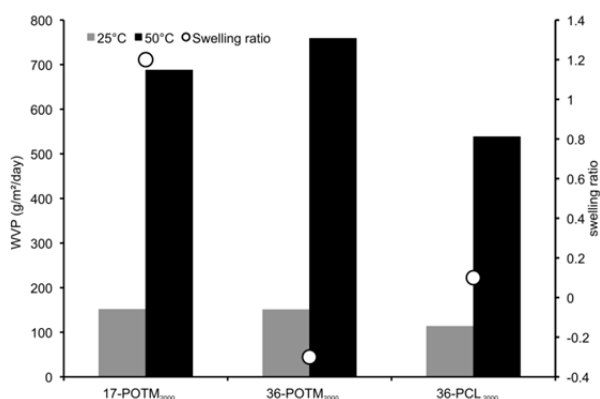


**Fig. 2** TG and DTG curves of laminated textiles with 17-POTM<sub>2000</sub>, 36-POTM<sub>2000</sub>, 36-PCL<sub>2000</sub>, and pristine fabric.

Thermal degradation of polyurethane occurs in two steps with a complex mechanism due to the formation of various products during the heating process. Thus, the early degradation step is related to the hard segments which generally starts at about 200°C, and the soft segment one occurs at higher temperature and is responsible of the second step. The presence of multiple peaks on the DTG curves is mainly related to the interactions between the thermal degradation

process of hard and soft segments. TG and DTG of the textile and laminated textiles are shown in Fig. 2. In inert atmosphere, pristine fabric undergoes single stage degradation between 400 and 500°C and leads to the formation of a condensed residue about 85 % of the initial mass. The degradation of the two laminated textile samples with the higher hard segment content occurs in a double stage, i.e. (i) from 280 to 360 °C, and (ii) from 360 to 450°C. Sample based on 17-POTM<sub>2000</sub> has a single degradation step with a maximum degradation rate about 410 °C, related to the interactions between soft and hard segments due to their reorganization during the heating process. Therefore, soft and hard segment cannot segregate and form separated independent domains. Furthermore, its HSC value is probably too low to induce the formation of hard domains and promote phase separation. The effect of the chemical composition of the polyol used on the thermal stability of the laminated samples, 36-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub>, is relatively low until 350°C, on the other more interactions between hard and soft segments, detected with the presence of multiple peaks on the DTG curves, contribute to enhance the thermal stability of the sample laminated with 36-PCL<sub>2000</sub> at higher temperatures in regard to the other sample.

### 3.3. Thermosensitivity properties



**Fig. 3** Water vapour permeability measurements at 25°C and at 50°C, and swelling ratio of laminated textile samples.

Water vapor permeability and swelling ratio (Fig. 3) were measured to determine the influence of the chemical composition of the polyurethane samples on the behavior of the laminated textile. The WVP value of each laminated textile sample is temperature dependent, since it increases with the increase of temperature. Nevertheless, the increasing trend is quite different between the POTM-based polyurethane series samples due to their hard segment content, and between the polyester- and polyether-based polyurethane. The water vapour permeability of the pristine fabric (1200 g.m<sup>-2</sup>.d<sup>-1</sup>) textile at room temperature is higher than that of the laminated samples. The membranes are poorly breathable at room temperature, creating a high vapour pressure gradient to promote the diffusion of moisture above the transition temperature of the polyurethane membrane. The water vapour permeability of the 36-POTM<sub>2000</sub> laminated sample is higher than that of the other two membranes. At room temperature, it is lower for complexes, which can be explained by the presence of textiles. It can also be denoted that the membrane in WVP between the raw film and the laminated sample based on 36-POTM<sub>2000</sub> membrane has the most higher difference between the kind of morphology [5]. The post-treatment at 100°C was able to rearrange the polymer chains, modifying the volume free, which varies the vapour permeability. This result can also be explained by the appearance of the complexes, i.e. the surface complexes have a permeability to the higher water vapour than core complexes.

At 25°C, both samples are in the glassy state and the WVP of each sample shows a very low value. Furthermore, the WVP of 36-POTM<sub>2000</sub> textile sample is slightly higher than the other samples, this can be related to the increase of free volume just before the crystal melting point. The higher degree of crystallinity of soft segment for 17-POTM<sub>2000</sub> limits the water vapor transport, and therefore its WVP value is lower. Above the soft segment crystal melting point (50°C), free volume increases that enhances the WVP. The sensitivity of WVP to thermal stimuli is greater for nonwoven coated with 36-POTM<sub>2000</sub> than for the two others laminated fabrics. The phase separation of the polyurethane film is one of the parameters governing the WVP behaviour. Thus, for samples laminated with 17-POTM<sub>2000</sub> or 36-PCL<sub>2000</sub> films, as low phase separation polyurethane, the measured WVP are lower than the 36-POTM<sub>2000</sub> one at 25°C and at 50°C. This result is also related to the influence of free volume on the degree of phase separation. Furthermore, the increase in WVP with increasing hard segment content is due to a greater mobility of the soft segments. Since, the water vapour permeability is also related to the existence of a sufficient free volume and hydrophilicity of the samples [24], it is interesting to note the sample based on 36-PCL<sub>2000</sub> has a lower WVP value than the sample based on 36-POTM<sub>2000</sub>. This difference can be due to the presence of carboxylic group in the first sample, which induces strong interactions between the polymeric chains and the water vapor molecules, and therefore reducing the permeability. Moreover, the

difference between WVP values at room temperature and 50°C is higher for the 17-POTM<sub>2000</sub> and 36-POTM<sub>2000</sub> laminated fabrics than for 36-PCL<sub>2000</sub>, which denotes their higher thermosensitivity. Therefore, since during the phase transition from a well-organized state to an amorphous state, the free volume changes induce the increase of WVP, which is consistent with the enthalpy changes determined by DSC. Furthermore, the phase separation of the polyurethane samples also influences the WVP behavior. Thus, the WVP values of the samples having no or low phase separation such as 36-PCL<sub>2000</sub> is lower than the 36-POTM<sub>2000</sub> one at 25°C. This result is also related to the influence of free volume on the degree of phase separation.

### 3.4. Mass transfer mechanisms

Mass transfers in non-porous membranes occur by sorption-diffusion-desorption [25]. The swelling ratio, depicted in Figure 3, corresponds to the ratio between the swelling at 50°C and at room temperature. Higher swelling ratio was calculated for 17-POTM<sub>2000</sub>, which exhibited weak melting transitions that may be related to the sorption increase in amorphous structure [26]. The water swell decreases as the hard segment content at 25°C increases. This seems to be due to the decrease of hydrophobicity, which reduces the solubility of water vapor molecule (Table 2).

**Table 2.** Comparison of water swelling of POTM<sub>2000</sub> based polyurethane and PCL<sub>2000</sub> based polyurethane.

Sample	Water swelling (%)		ratio
	25°C	50°C	50°C/25°C
17-POTM <sub>2000</sub>	1.7	3.7	1.2
36-POTM <sub>2000</sub>	3.6	2.4	-0.3
36-PCL <sub>2000</sub>	6.3	6.8	0.1

Moreover, when the temperature was 25°C, macromolecular chains of both samples, excepted 17-POTM<sub>2000</sub> are in a glassy state, and as described by Shi et al., the average radius of free volume was too small to allow sufficient water vapor penetration [27]. Therefore, lowest water swelling values were obtained. The presence of carboxylic groups in the 36-PCL<sub>2000</sub> laminated sample induces a strong interaction between polymer chains and water vapor molecules, thus its water swelling is higher than the 36-POTM<sub>2000</sub> one. The decrease or the weak increase of swelling with increasing temperature for the samples labelled 36-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub>, cannot be related to the change from the glassy state to the rubbery one, there the enhancement of free volume does not allow the water penetration due to the lamination with the textile. The difference in swelling ratio between the various fabrics denotes that the sorption property is influenced by the composition of the polyurethane and the temperature. This behavior is quantified by the contact angle measurements (Table 3).

**Table 3.** Effect of temperature on surface energy ( $\gamma$ ) of solid samples by Owens and Wendt method and their polar and dispersive components

Sample	25°C			60°C		
	$\gamma^d$	$\gamma^p$	$\gamma$	$\gamma^d$	$\gamma^p$	$\gamma$
	(mN.m <sup>-1</sup> )	(mN.m <sup>-1</sup> )	(mN.m <sup>-1</sup> )	(mN.m <sup>-1</sup> )	(mN.m <sup>-1</sup> )	(mN.m <sup>-1</sup> )
17-POTM <sub>2000</sub>	30.5 (±4.4)	3.2 (±1.9)	33.7 (±3.3)	34.2 (±3.3)	2.5 (±1.1)	36.6 (±2.1)
36-POTM <sub>2000</sub>	34.8 (±1.4)	5.0 (±1.7)	39.8 (±0.9)	32.4 (±2.0)	7.5 (±2.4)	39.8 (±1.5)
36-PCL <sub>2000</sub>	29.2 (±9.7)	14.2 (±17.4)	43.4 (±8.7)	34.2 (±3.7)	8.3 (±3.4)	42.4 (±1.7)

The hard segment content modifies not only the bulk polyurethane but also its surface [28]. Indeed, when microphase separation occurs, reorganization of soft segments in the film leads to promote a more hydrophobic surface, in the same time the polar component for the samples 17-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub> decreases. Furthermore, the dispersive component increases with temperature, excepted for sample based on 36-POTM<sub>2000</sub>, which implies that molecular packing increases due to microphase separation. This phenomenon is intensified at the transition temperature by the higher mobility of the soft segments.

Characterization of laminated polyurethane nonwoven textile presented in this study emphasizes two types of mechanisms. On the one hand, 36-POTM<sub>2000</sub> exhibits a low endothermic transition, which means that its soft segments are not sufficiently organized. The surface energy related to state surface modification varies few according to the temperature. Nevertheless, the high swelling ratio induces the increase in surface sorption, which suggests a change in the bulk with rising temperature. On the other hand, 17-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub> contain well-organized soft segments with surface modification. The WVP of these two laminated samples are lower the other one as well as the difference between the WVP measured at room temperature and at 50°C. In this case, the water vapor diffusion of the polyurethane laminated samples is related to the changes at the surface with rising temperature. The crystallization of

the soft segments is a key parameter governing this behavior. Furthermore, the mobility of the no-crystallized soft segments allows bringing some surface changes. Therefore, these latter contribute to the sorption of the laminated textiles, and the moisture diffusion is enhanced.

#### 4. Conclusion

The mechanical properties of the laminated nonwovens increase with the presence of the polyurethane film, and their water vapour permeability properties depends on the temperatures related to the possibility of microphase separation between room temperature and 50°C. The switch in temperature also causes a change in the surface energy of the samples. Thus, for the samples labelled 17-POTM<sub>2000</sub> and 36-PCL<sub>2000</sub> laminated fabrics, the dispersive component increases while their polar one decrease, for the 36-POTM<sub>2000</sub> it is the opposite. These results also suggest two kinds of mechanisms, i.e. one is related to the surface change, the other one is due to the macromolecular chains reorganisation during the process.

Polyurethane membranes with a rigid segment content about of 36% present a surface aspect allowing their use in a textile structure. The laminating of polyurethane films, on the surface or in the core of the non-woven backing, limits the swelling ratio between 25 and 50°C, thus promoting vapour permeability. In addition, in the case of ether polyol (36-POTM<sub>2000</sub>), the complex has a higher WVP than the raw film. The polar component of this complex increases at 50°C, which makes its surface more hydrophilic. The presence of the textile reduces the swelling ratio, which promotes vapour permeability. The reorganization of the macromolecular chains of the 36-PCL<sub>2000</sub> laminated sample following thermal post-treatment increases its  $T_{Tr}$  to 46°C and the mechanical properties provided by the textile are better than for the film. This WVP is similar to that of the film, whatever the temperature, although slightly lower, this which results from the reorganization of the chains. The WVP values are about 113 g.m<sup>-2</sup>.day<sup>-1</sup> at 25°C and 539 g.m<sup>-2</sup>.day<sup>-1</sup> at 50°C. The surface of this laminated textile becomes hydrophobic to this last temperature, which can promote the diffusion of moisture to the outside.

**Acknowledgements** The authors thank HEI and the region Nord/Pas-de-Calais for funding this research.

#### References

- [1] Bedek G, Salaün F, Martinkovska Z, Devaux E, Dupont D. Evaluation of thermal and moisture management properties on knitted fabrics and comparison with a physiological model in warm conditions. *Applied Ergonomics*. 2011; 42(6):792-800.
- [2] ASHRAE. ASHRAE Standards 55-2004. Thermal Environmental Conditions for Human Occupancy. New York 2004.
- [3] Sukigara S, Niwa M. Analysis of “wet” sensation for lingerie fabrics. *Int J Cloth Sci Technol*. 1997; 9(3):214-9.
- [4] Das B, Das A, Kothari VK, Fanguiero R, de Araujo M. Moisture transmission through textiles: Part I: Processes involved in moisture transmission and the factors at play. *Autex Research Journal*. 2007; 7(2):100-10.
- [5] Morel A, Salaün F, Bedek G, Dupont D, Giraud S. Water vapor permeability of thermosensitive polyurethane films obtained from isophorone diisocyanate and polyester or polyether polyol. *Journal of Materials Science*. 2017; 52(2):1014-27.
- [6] Song G, Mandal S, Rossi R. Development of high performance thermal protective clothing. In: Song G, Mandal S, Rossi R, editors. *Thermal Protective Clothing for Firefighters*: Woodhead Publishing; 2017. p. 27-55.
- [7] Holmes DA. Performance Characteristics of Waterproof Breathable Fabrics. *Journal of Coated Fabrics*. 2000; 29(4):306-16.
- [8] Keiser C, Becker C, Rossi RM. Moisture Transport and Absorption in Multilayer Protective Clothing Fabrics. *Textile Research Journal*. 2008; 78(7):604-13.
- [9] Keiser C, Wyss P, Rossi RM. Analysis of steam formation and migration in firefighters' protective clothing using X-ray radiography. *Int J Occup Saf Ergon*. 2010; 16(2):217-29.
- [10] Rossi R, Indelicato E, Bolli W. Hot steam transfer through heat protective clothing layers. *Int J Occup Saf Ergon*. 2004; 10(3):239-45.
- [11] Bajaj P, Sengupta AK. *Protective Clothing*. Manchester, UK: Textile Institute; 1992.
- [12] Jonquière A, Clément R, Lochon P. Permeability of block copolymers to vapors and liquids. *Prog Polym Sci*. 2002; 27(9):1803-77.
- [13] Wijmans JG, Baker RW. The solution-diffusion model: a review. *Journal of Membrane Science*. 1995; 107(1-2):1-21.
- [14] Fan H, Li L, Fan X, Shi BI. The water vapour permeability of leather finished by thermally-responsive polyurethane. *Journal of the Society of Leather Technologists and Chemists*. 2005; 89(3):121-5.
- [15] Chen Y, Liu Y, Fan H, Li H, Shi B, Zhou H, et al. The polyurethane membranes with temperature sensitivity for water vapor permeation. *Journal of Membrane Science*. 2007; 287(2):192-7.
- [16] Mondal S, Hu JL, Yong Z. Free volume and water vapor permeability of dense segmented polyurethane membrane. *Journal of Membrane Science*. 2006; 280(1-2):427-32.
- [17] Hu J, Chen S. A review of actively moving polymers in textile applications. *J Mater Chem*. 2010; 20(17):3346-55.
- [18] Cho JW, Jung YC, Chun BC, Chung Y-C. Water vapor permeability and mechanical properties of fabrics coated with shape-memory polyurethane. *J Appl Polym Sci*. 2004; 92(5):2812-6.
- [19] Mondal S, Hu JL. Water vapor permeability of cotton fabrics coated with shape memory polyurethane. *Carbohydr Polym*. 2007; 67(3):282-7.

- [20] Lei H, Luo Y, Ge Z, Li X, Wang S. Preparation and properties of waterborne siloxane-containing polyurethane for moisture permeable textile coating. *e-Polymers*. 2011; 11(1).
- [21] Owens DK, Wendt RC. Estimation of the surface free energy of polymers. *J Appl Polym Sci*. 1969; 13(8):1741-7.
- [22] Rueda-Larraz L, d'Arlas BF, Tercjak A, Ribes A, Mondragon I, Eceiza A. Synthesis and microstructure–mechanical property relationships of segmented polyurethanes based on a PCL–PTHF–PCL block copolymer as soft segment. *Eur Polym J*. 2009; 45(7):2096-109.
- [23] Morel A, Salaün F, Bedek G, Dupont D, Giraud S. Water vapor permeability of thermosensitive polyurethane films obtained from isophorone diisocyanate and polyester or polyether polyol. *Journal of Materials Science*. 2016:1-14.
- [24] Mondal S, Hu JL, Yong Z. Free volume and water vapor permeability of dense segmented polyurethane membrane. *Journal of Membrane Science*. 2006; 280(1-2):427-32.
- [25] Hu J, Mondal S. 7 - Temperature sensitive shape memory polymers for smart textile applications A2 - Mattila, H.R. *Intelligent Textiles and Clothing*: Woodhead Publishing; 2006. p. 104-23.
- [26] Hu J. 1 - Introduction. *Shape Memory Polymers and Textiles*: Woodhead Publishing; 2007. p. 1-27.
- [27] Shi H, Chen Y, Fan H, Xiang J, Shi B. Thermosensitive polyurethane film and finished leather with controllable water vapor permeability. *J Appl Polym Sci*. 2010:NA-NA.
- [28] Nakamae K, Nishino T, Asaoka S, Sudaryanto. Microphase separation and surface properties of segmented polyurethane—Effect of hard segment content. *Int J Adhes Adhes*. 1996; 16(4):233-9.