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Water vapor permeability of cotton fabrics coated with shape memory polyurethane

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Abstract

In this paper, we have investigated the water vapor permeability of shape memory polyurethane (SMPU) coated cotton fabrics. The SMPUs were tailor made in order to obtain the phase transition temperature (soft segment crystal melting temperature) in the room temperature range. SEM studies were carried out in order to investigate the surface structure of coated and uncoated fabrics. The temperature sensitive water vapor permeability at soft segment crystal melting point was observed for SMPU coated fabrics. When the experimental temperature reached the soft segment crystal temperature of SMPU, an abrupt change of water vapor permeability of SMPU coated fabrics were observed. The significant change of water vapor permeability of SMPU coated fabrics is due to the phase change of SMPU which causes density changes inside the membranes due to micro-Brownian motion of soft segment, therefore, enhanced the water vapor permeability through the coated fabrics. The water vapor permeability of coated fabrics was also dependent on the primary structure of SMPU. When polycaprolactone glycol (PCL, M_n 3000 g mol^{-1}) was introduced in the polytetramethylene glycol (PTMG, M_n 2900 g mol^{-1}) based SMPU, the water vapor permeability decreases due to the increased interaction between the polymer chains due to presence of ester groups. In contrast increase of polyethylene glycol (M_n 3400 g mol^{-1}) in the SMPU backbone, the WVP increases due to the increasing hydrophilicity of the SMPU.

Keywords: Shape memory polyurethanes; Water vapor permeability; Soft segment crystal melting temperature; Phase transition

1. Introduction

The development of shape memory polymers (SMPs) is currently of great interest (Hayashi, Ishikawa, & Jiordano, 1993; Tobushi, Hara, Yamada, & Hayashi, 1996) because of light weight, high shape recovery, ease in manipulation and low cost as compared with shape-memory alloy. SMPs are a novel class of functional materials which have developed quickly in the last decades. Shape-memory polymers are stimuli-responsive polymeric materials. They have the capability of changing their shape upon the application of an external stimulus. Shape memory behavior can be triggered by heat, light, electric filed, magnetic field, chemical, moisture, pH, and other external stimuli (Irie, 1998; Mondal, Hu, Yang, Liu, & Szeto, 2002). Among them, the thermally stimulated shape memory polymers, whose shape can be easily changed and recovered through the temperature change, have tremendous potential applications in breathable textiles field. Change in shape caused by change in temperature is called a thermally induced shape-memory behavior (Chen, Zhu, & Gu, 2002).

Phase transition accompanies a great change in thermo-mechanical properties of polymeric materials. A large drop of modulus and an enhanced micro-Brownian motion of polymer chains on heating through the glass transition temperature or crystal melting temperature can be used in the molecular design of shape memory polymers (Jeong, Ahn, Cho, & Kim, 2000; Jeong, Ahn, & Kim, 2000; Kim, Shin, Cho, & Jeong, 2000). Shape memory polyurethane (SMPU) basically consists of two phases, a frozen phase

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and a reversible phase. SMPUs have microphase separated structure due to the incompatibility between the constituent domains (Jeong et al., 2000). According to the literature, the crystallinity of the soft segments and the formation of the physical cross-link structure of the hard segments in the segmented polyurethanes are two necessary conditions for their good shape memory behaviors (Jeong et al., 2000; Lee, Chun, Chung, Sul, & Cho, 2001). Therefore, the shape memory behavior could be controlled by varying the molecular weight of the soft segment, mole ratio of soft and hard segments, and the polymerization process (Takahashi, Hayashi, & Hayashi, 1996; Lai, Quinn, & Valint, 1995). By proper selection of hard and soft segments, the phase transition temperature (soft segment crystal melting point temperature) of SMPU could be made close to ambient temperature for breathable textiles applications.

Cotton is a cellulosic fiber which took highest place among the family of fibers including natural and synthetic. Owing to the several good properties it has (including comfort), cotton plays most prominent role in apparel industry. It is best suited next to the skin. In order to make the cotton fabric suited for multipurpose use, we often need to coat the fabric with polymer. However, condensation is of particular interest in a discussion of the merit of coated fabrics. Several characteristics (including flexibility and soft hand) would make polyurethane especially suited for the use in breathable textiles. For the application of polyurethanes in breathable textiles, the temperature dependency of water vapor permeability is an important factor to be considered for the effective utilization of this kind of materials. For example, in order to improve the user comfort of coated/laminated textiles with shape memory polyurethanes, the coated/laminated textiles should have high water vapor permeability at higher temperature and low water vapor permeability at lower temperature (Jeong et al., 2000). The advantage of SMPU coating over conventional polymer coating is that to control the permeability, according to both the surrounding temperature and body temperature which derives the development of smart garments. In this paper, we have investigated the water vapor permeability of three different SMPU coated fabrics.

2. Methods

2.1. Shape memory polyurethanes

Three different shape memory polyurethanes were used in this study and their compositions were given in Table 1. Shape memory polyurethanes (SMPU) were synthesized from bifunctional diisocyanate (4,4′-diphenylmethane di-isocyanate, MDI), and diol (polyol) viz. Polytetra methylene glycol (M_n 2900 g mol^{-1}, PTMG 2900) and/or Polycaprolactone diol (M_n 3000 g mol^{-1}, PCL 3000), and Polyethylene glycol (M_n 3400, PEG 3400), and chain extender (1,4-butane diol, 1,4-BDO), by two or three steps polymerization process. The details synthesis process was given elsewhere (Mondal & Hu, 2006; Mondal & Hu, 2006). The shape memory behavior of SMPU was reported in our previous paper (Mondal & Hu, 2006).

2.2. Coating of fabrics

Scoured and bleached white cotton fabrics of weight 118 g m^{-2} was coated by knife over roller machine (Weamer Mathis AG, Switzerland). The coated fabrics were dried at 90 °C for 20 min in order to remove the *N*,*N*-dimethyl formamide and then cured at 120 °C for 10 min. The thicknesses of the uncoated and coated fabrics were 0.21–0.22 and 0.23–0.50 mm, respectively, measured by Mitutoyo thickness gauge (accuracy 0.001 mm). In order to easily identify the coated and uncoated fabrics throughout the discussions, the samples are coded and tabulated in Table 2.

The add-on % on the coated fabric was about 30% and calculated by using the following formula:

$$\text{Add-on}(\%) = [(Y - X)/X] \times 100, \quad (1)$$

where X is the conditioned weight of the control fabric and Y is the conditioned weight of the coated fabric.

2.3. Equipments and measurements

The surface of coated and uncoated fabric was observed by scanning electron microscope (SEM) with a Leica Stereoscan 440 equipped with an Oxford energy dispersive X-ray system, operating at 20 kV.

Differential scanning calorimetry data for SMPUs were obtained by Perkin-Elmer DSC 7. Each sample was scanned from −50 to 120 °C at scanning rate of

Table 2
Coding of coated and uncoated fabrics

Sample code	Descriptions
F_0	Uncoated fabrics
F-PTMG-PEG10	Coated fabrics with SMPU sample of PTMG-PEG10
F-PTMG-PEG15	Coated fabrics with SMPU sample of PTMG-PEG15
F-PCL-PEG10	Coated fabrics with SMPU sample of PCL-PEG10

Table 1
Composition of SMPU

Samples	Feed (×10^3 mol)				
	Polyol	PEG 3000	MDI	1,4-BDO	Wt % of PEG
PTMG-PEG10	8.9 (PTMG 2900)	1.18	32.03	21.89	10
PTMG-PEG15	10 (PTMG 2900)	1.77	17.77	6.0	15
PCL-PEG10	10.17 (5.0 PCL3000 & 5.17PTMG2900)	1.2	18	7	10

10 °C/min under dry nitrogen purge. All runs were carried out with sample weight of 5–10 mg.

Mass transfer of coated and uncoated fabrics was measured by water vapor permeability (WVP) measurements. The WVP was measured according to ASTM E 96-80B. Round mouth conical plastic cups with diameter of 60 mm and a height of 90 mm were filled with deionized water. The coated and uncoated fabrics were placed over the top of the cups, and secure the perfect sealing between cup and fabric sample. The gap between the fabric and water surface was about 4 mm. Cups were placed in a constant temperature chamber at the desired temperature (12, 18, 25, 35, or 45 °C). During all WVP measurements, air surrounding the fabric had a constant temperature and 70% of relative humidity. An average of 3 different samples were used for each WVP measurements, which are calculated by using the following formula and expressed in units of $g\,m^{-2}\,d^{-1}$, where d is a day (24 h).

$$\mathrm{WVP} = G/tA = (G/t)/A, \tag{2}$$

where G = weight change in gm. t = duration test in hour A = test area in m^2.

Tensile properties of coated and uncoated fabrics were measured according to the ASTM standard, 1 in. strip and 75 mm gauge length by Instron 4411.

3. Results and discussion

3.1. SEM micrograph

Observation of the uncoated fabrics [Fig. 1 (a)] by SEM revealed that the surfaces are porous. In contrast inter filamental gaps are filled up by polymer after coating [Figs. 1 (b) & (c)]. The nonporous SMPU layer was formed continuously over the surface of the coated fabric. The presence of nonporous SMPU layer suggested that water vapor permeability of coated fabrics is originated from the property of SMPU itself. Therefore the chemical structure of SMPU plays a major role in the breathability of coated fabrics.

3.2. Differential scanning calorimetry

Thermal properties of SMPUs used in the present study have been quantified previously by the present authors (Mondal & Hu, 2006; Mondal & Hu, 2006) by using differential scanning calorimetry (DSC). From the results of DSC measurements (the data listed in Table 3 and shown in Fig. 2), we have previously made the following conclusions: (1) soft segment (polyol) form crystalline structure in the phase separated SMPU due to their long and regular polymer chains. However, hard segment act as reinforcing filler in soft matrices and hinders the crystallization process of soft domain. (2) In a mixed soft segment block SMPU, each soft block form crystalline structure separately in the resultant SMPU. Therefore, separate endothermic peaks have been appeared for subsequent blocks. (3) However, hard

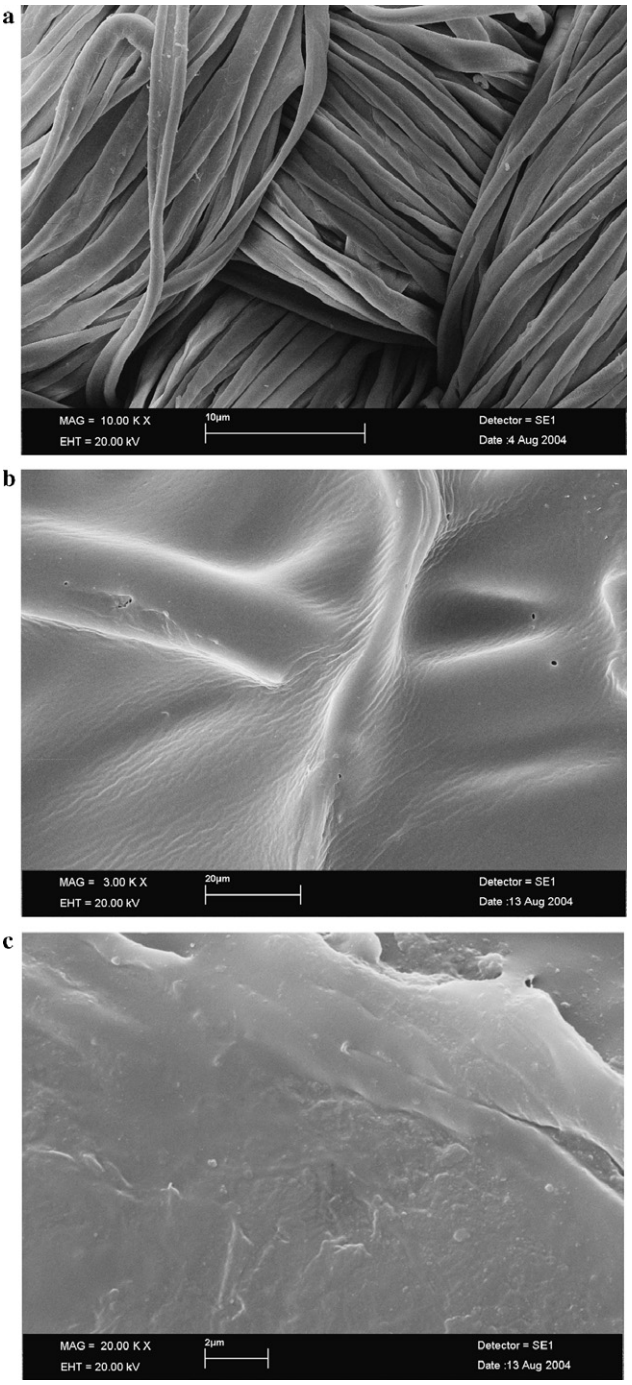

Fig. 1. SEM image of (a) uncoated fabric, (b) coated fabric with PTMG-PEG10, and (c) coated fabric with PCL-PEG10.

domain aggregation in the SMPU was not observed, may be their less quantity (about 20%) as compared to soft segment do not provide favorable condition for crystallization. (4) As the hydrophilic segment (PEG 3400) content in SMPU was increases from 10 wt% to 15 wt%, it enhances the shifting of primary endothermic peak due to the ordering of crystalline PEG 3400 domain. From the experimental results (Table 3 and Fig. 2), we can see that, there are two soft segment crystal melting temperature of tailor made SMPU.

Table 3
Thermal property of SMPUs

Sample code	First endothermic peak (°C)			Second endothermic peak (°C)		
	$(T_{ms1})_{start}$	$(T_{ms1})_{peak}$	$(T_{ms1})_{end}$	$(T_{ms2})_{start}$	$(T_{ms2})_{peak}$	$(T_{ms2})_{end}$
PTMG-PEG10	8.2	22.2	28.0	34.4	38.5	41.2
PTMG-PEG15	7.1	19.0	22.0	31.8	38.6	44.0
PCL-PEG10	9.0	19.2	26.2	33.8	46.8	53.2

T_{ms1} – first endothermic peak, T_{ms2} – second endothermic peak, $(T_{ms})_{start}$ – starting point of crystal melting, $(T_{ms})_{peak}$ – peak of crystal melting, $(T_{ms})_{end}$ – end point of crystal melting.

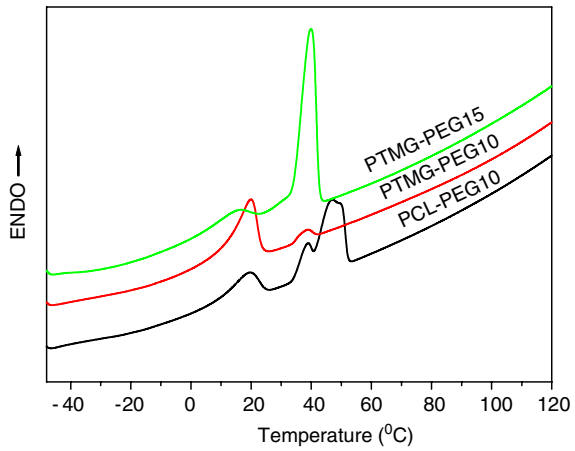

Fig. 2. DSC heating thermogram of PU samples.

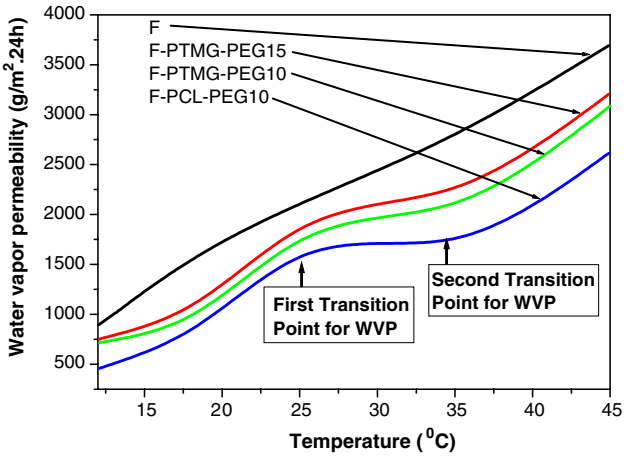

Fig. 3. Water vapor permeability of SMPU coated fabrics.

One around room temperature and another around human body temperature range which would be suitable for making smart breathable fabrics.

3.3. Water vapor permeability

Water vapor permeability (WVP) results of coated and uncoated fabrics are shown in Fig. 3 and data are tabulated in Table 4. From the Fig. 3 we can see that WVP for uncoated fabric was increase linearly with temperature. The increase of temperature will increases the difference in saturation vapor pressure between the cup and surroundings (Fig. 4) which will enhance the permeability through the coated and uncoated fabrics.

SEM pictures shows thin layer of nonporous polymeric films on the coated fabric, therefore the SMPU film properties will plays major role for the permeability of coated fabric. The permeation of small molecules through nonporous polymer film would enhance when their solubility and diffusivity in polymer would increases. Water vapor permeability would be occurred through nonporous membrane in three stages i.e., sorption–diffusion–desorption. The water vapor permeability of SMPU coated fabrics increases abruptly at soft segment crystal melting point of SMPU due to the increasing mobility of soft segment (polyol) phase which is enhanced at melting temperature of soft domain. At the phase transition temperature of SMPU (soft segment crystal melting point temperature) discontinuous density change would occur in the polymer membrane which provides more gaps for water vapor molecules to pass through the membranes. The micro-Brownian motion of soft segment at crystal melting point temperature (T_{ms})

Table 4
Water vapor permeability results of coated and uncoated fabrics

Samples	12 °C	18 °C	25 °C	35 °C	45 °C
F_0	880	1587	2125	2751	3701
F-PTMG-PEG10	715	990	1735	2117	3086
F-PTMG-PEG15	750	1079	1851	2271	3215
F-PCL-PEG10	455	848	1572	1760	2625

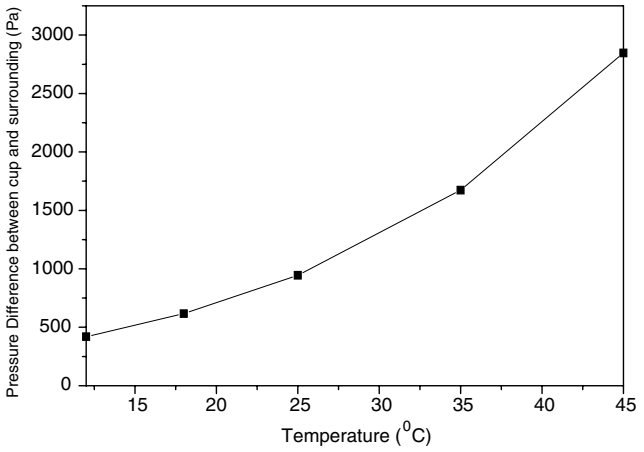

Fig. 4. Effect of temperature on difference of saturation water vapor pressure inside cup and surroundings.

obviously would increase the intermolecular gap large enough to allow water vapor molecule to pass through the polymer films (Hu, Zeng, & Yan, 2003). The soft segment crystal melting temperature increases the void volume between the molecules and drug diffusion become easier which will helps for the penetration of water vapor molecules. In the interpretation of DSC and WVP results, we can see that, the WVP of coated fabrics have two transitions due to the soft segment crystal melting. The first transition point is at about 20 °C (room temperature) and another at around 37 °C (human body temperature). Phase transition accompanies large changes in visco-elastic properties of shape memory polyurethane. A large drop in modulus and an enhanced segmental mobility on heating through soft segment crystal melting temperature make soft segment into a larger volume which results in an increase in free volume of SMPU and permits the water vapour molecules to transmit through the polymer films easily. The water vapor permeability of coated fabrics would also be depends on the primary structure of SMPU as well. In this study we have used PTMG 2900 and PCL 3000 based SMPU with hydrophilic segment content of 10 and 15 wt%. From the Table 4 and Fig. 3, we can see that WVP of PTMG 2900 based SMPU coated fabric is higher than that of PCL 3000 based SMPU coated fabrics, the reason is due the loose structure of PTMG 2900 based (Hsieh, Tsai, & Tseng, 1990) SMPU which helps to transport the water vapor molecules easily. When PCL segment was introduced in the PTMG based SMPU backbone, the decrease of water vapor permeability of resultant SMPU coated fabrics is due to the presence of ester groups which will increases the inter-chain interaction and prevent the water vapor molecules to pass through the membrane. When the hydrophilic segment content in the SMPU increases, the WVP would also increases, because the water vapor permeability occurred in the nonporous membrane in the molecular mechanism i.e., sorption–diffusion–desorption, more hydrophilic group enhance the sorption of polymer membrane (Hu & Mondal, 2005). Once the water vapor molecules absorbed by the polymer membrane, it will diffused across the membrane and comes to the other side of membrane, and finally release to the environment due to the concentration differences. The temperature sensitive water vapor permeability of coated fabrics with tailor made SMPU will have great potential in the development of smart clothing.

3.4. Mechanical properties of fabrics

Mechanical property of coated fabric is also important from application point of view. The tensile strength of the coated fabrics is the manifestation of visco-elastic nature of polymer, and interaction of polymer and filaments of the coated fabrics. In general, the application of coating tends to increase the tensile strength of coated fabrics. The longitudinal tension applied to the fabric during coating, stretches the warp thread yarn system and increases its orientation. This helps to "lock" the yarn in place by the coating materials. Thus the warp yarns are essentially in plane to any longitudinally applied stress and better able to support the applied load, hence the increases in tensile strength (Wilkinson, 1996). The tensile properties of the coated and uncoated fabrics are tabulated in Table 5. Tensile strength in both warp and weft direction increases for the coated fabrics, since the base fabrics are porous which would allow sufficient penetration of polymer to achieve some chemical and mechanical adhesion of filaments. Coated fabric is a composite of SMPU and fabrics, and final tensile properties of the coated fabrics are function of the base fabrics and the polymeric materials. The tensile strength of fabrics coated with PTMG 2900 based SMPU is higher than that of the PCL 3000 based SMPU due the strong interaction of PTMG-PEG polymer and filaments. The strength of coated fabrics with the SMPU containing higher PEG content (PTMG-PEG15) is higher than that of the sample with lower PEG content (PTMG-PEG10) due to the increase of polar groups which will increases the adhesion between the filaments. After coating the fabric becomes stiffer, which decreases the breaking strain in both directions.

Table 5
Tensile properties of coated and uncoated fabrics

Samples	Breaking load (*N*)		Breaking strain (%)	
	WP	WF	WP	WF
F_0	247.18	147.40	21.12	15.971
F-PTMG-PEG10	285.43	172.00	20.01	15.667
F-PTMG-PEG15	312.18	175.22	18.50	14.05
F-PCL-PEG10	271.35	174.04	17.37	12.93

4. Conclusions

Nonporous SMPU layer was formed on the coated fabrics surface, which signifies the control of water vapor permeability through the coated fabrics by polymer films. The tailor made SMPU has two soft segment crystal melting point temperature (phase transition temperature). The water vapor permeability of SMPU coated fabric was triggered around the soft segment crystal melting point temperature of SMPU, when the chain mobility of soft segment enhanced by phase transition. Water vapor permeability of SMPU coated fabrics was also influenced by primary chemical structure of SMPU. The water vapor permeability of PTMG based SMPU coated fabrics was decreases when PCL block was introduced in the SMPU backbone. In contrast, water vapor permeability was enhances with increasing the hydrophilic block in the SMPU backbone. Mechanical properties of SMPU coated fabrics were depended on the interaction of polymers and fibers. The temperature sensitive water vapor permeability of tailor made SMPUs coated fabrics would be applicable in developing smart clothing.

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