

# Water Vapor Permeability and Mechanical Properties of Fabrics Coated with Shape-Memory Polyurethane

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**ABSTRACT:** Water vapor permeable fabrics were prepared by coating shape-memory polyurethane (PU), which was synthesized from poly(tetramethylene glycol), 4,4'-methylene bis(phenylisocyanate), and 1,4-butanediol, onto polyester woven fabrics. Water vapor permeability and mechanical properties were investigated as a function of PU hard-segment content or polymer concentration of the coating solution. Water vapor permeability of PU-coated fabrics decreased dramatically with increased concentration of coating solution, whereas only a slight change was observed with the control of PU hard-segment content. The coated fabric showed the clear appearance of a nonporous PU surface according to SEM measurements. Attainment of high water permeability in PU-coated fabrics is considered to arise from the smart permeability characteristics of PU.

Mechanical properties of coated fabrics, although there was some variation depending on the concentration of coating solution, were primarily affected by PU hard-segment content. Fabrics coated with PU hard-segment content of 40% showed the lowest breaking stress and modulus as well as the highest breaking elongation, which could be interpreted in terms of the dependency of mechanical properties of coated fabrics on PU hard-segment content and the yarn mobility arising from a difference in penetrating degree of coating solution into the fabric. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2812–2816, 2004

**Key words:** water vapor permeability; shape-memory polyurethane; mechanical properties; fibers/fabrics; coatings

## INTRODUCTION

Research on shape-memory thermoplastic polyurethane (PU) has been of great interest because it is light, high in shape recovery, easy to manipulate, and economical compared with shape-memory alloy. PU is composed of hard and soft segments, and is usually obtained by polymerization of bifunctional diisocyanate, polyol, and chain extender. The shape-memory effect is known to originate from the phase-separated structure between hard and soft segments, and the reversible phase transformation of the soft segment. Thus, shape-memory characteristics can be controlled by varying the molecular weight of the soft segment, mole ratio of soft and hard segments, and the polymerization process.<sup>1–6</sup> The combination of such structure-controlling factors can also be used to tailor the glass-transition temperature of shape-memory PU for specific uses, leading to application of PU in other fields such as medicine, industry, sports, and textiles. Shape-memory PU has potential application in the

development of highly vapor permeable thin film, given its high vapor permeability at warm temperatures and low permeability at cold temperatures. Based on this, breathable fabrics,<sup>7–9</sup> impermeable to liquid water and permeable to water in the vapor phase, can be obtained by coating shape-memory PU onto polyester, nylon, cotton, or silk fabrics. The advantage over conventionally coated fabrics in controlling the permeability, according to both the surrounding temperature and the body temperature, is one of the reasons that drives development of this smart fabric. In this article, the influences of PU hard-segment content and concentration of coating solution on water vapor permeability and mechanical properties of PU-coated fabrics were investigated.

## EXPERIMENTAL

### Polymer synthesis

Synthesis of PU was carried out in a two-step process as described in our previous report.<sup>10</sup> First, prepolymer was prepared from a reaction of 4,4'-methylene bis(phenylisocyanate) (MDI) and poly(tetramethylene glycol) (PTMG; MW = 1830) at 80°C for 3 h. At the second stage, the chain extender 1,4-butanediol (BD) was added to this prepolymer and the final PU block copolymer was synthesized. PU film was obtained

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**TABLE I**  
Composition and Characterization of  
PU Block Copolymers

Mol%			Hard segment content (%)	MW <sup>a</sup>	$T_g$ (°C) <sup>b</sup>
MDI	PTMG	BD			
5.0	1.0	4.0	50	55,000	1.5
4.0	1.0	3.0	40	113,000	-2.4
3.0	1.0	2.0	30	105,000	-3.6

<sup>a</sup> Average molecular weight obtained from gel permeation chromatography.

<sup>b</sup> Glass-transition temperature determined from the loss tangent experiment.

from casting the PU solution in dimethylsulfonic acid. Table I presents the composition and some properties of PUs used in this investigation.

### Coating of PU onto the fabrics

PU, at different concentrations (10, 15, 20, and 25%), was dissolved homogeneously in dimethylsulfonic acid. The PU solution was coated evenly using a knife coater on poly(ethylene terephthalate) fabric of a plain weave with warp and weft densities of 120 ends/in. and 80 picks/in., respectively. Then, some tension in both the warp and weft directions was applied to the substrate fabric during coating. After the coating, the fabric was dried by a hot air flow at 80°C for 5 min.

### Water vapor permeability

The coated fabric samples were placed over a dish containing water and left to condition in an oven (36°C). The volume of water in the dish was adjusted to allow an air gap between the water and inner face of the fabric, and a fabric-covered ring was then sealed over the dish using a fixed cap. Water vapor permeability of the cast film or coated fabric was measured by the time-transfer method.<sup>11,12</sup> Water vapor transfer or the weight of moisture permeated through the fabric per unit area was measured at 1-h intervals for 28 h. Water vapor permeability (in  $\text{g mm}^{-2} 24 \text{ h}^{-1}$ ) was calculated from the steady-state permeation rate or a slope between water vapor transfer and time.

### Mechanical property

Tensile testing of PU films and PU-coated fabrics was performed using a universal testing machine (UTM LR50K; JJ Lloyd, Centre for Materials Research, University of London, London, UK) and the gauge length and crosshead speed were 25 mm and 10 mm/min, respectively. At least five samples were tested and the average was used.

### Thermomechanical property

The shape-recovery effect of PU film was measured by an interrelationship between stress, strain, and temperature, using a UTM equipped with a temperature-controlled thermal chamber. The thermomechanical test was carried out in the following order: (1) deformation ( $\epsilon_m$ ) was applied to the sample with a constant crosshead speed of 10 mm/min at  $T_h$ , (2) sample was cooled to  $T_l$  with the same deformation, (3)  $T_l$  was maintained for 5 min with removal of the load, and (4) temperature was raised from  $T_l$  to  $T_h$  and kept at  $T_h$  for 5 min. Under these conditions, shape retention and shape recovery are defined as follows:

$$\text{Shape retention (\%)} = \frac{\epsilon_f}{\epsilon_m} \times 100 \quad (1)$$

$$\text{Shape recovery (\%)} = \frac{\epsilon_m - \epsilon_f}{\epsilon_m} \times 100 \quad (2)$$

where  $T_h = T_g + 20^\circ\text{C}$ ,  $T_l = T_g - 20^\circ\text{C}$ ,  $\epsilon_m$  is the strain at 50% elongation,  $\epsilon_f$  is the retention at  $T_g - 20^\circ\text{C}$ , and  $\epsilon_r$  is the recovery at  $T_g + 20^\circ\text{C}$ .

### SEM observation

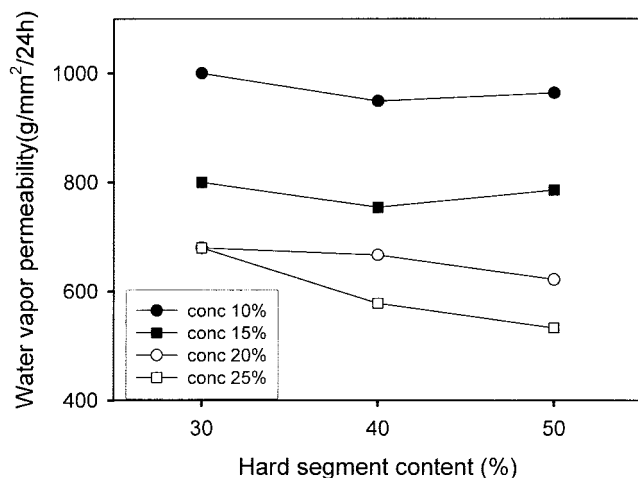
The surface and cross section of PU-coated fabrics were observed using a scanning electronic microscope (SEM, Alpha 25A).

## RESULTS AND DISCUSSION

Tensile and thermomechanical properties of PUs were obtained from the stress-strain and stress-strain-temperature relations, respectively. The breaking stress, breaking elongation, and tensile modulus of PU versus hard-segment content are represented in Table II. It can be seen that 30 and 40% hard-segment PU can be easily elongated up to more than 100% of its original length, whereas it is not possible for 50% hard-segment PU to stretch that much because of the increased rigidity in the PU. This is attributed to the difference in interchain attraction among PU polymeric chains, resulting from the interactions of hard segments<sup>13-15</sup> by

**TABLE II**  
Mechanical and Thermomechanical Values of PU Block Copolymers

Hard segment content (%)	Breaking stress (MPa)	Breaking elongation (%)	Modulus (MPa)	Shape retention (%)	Shape recovery (%)
50	7.2	52	33	—	—
40	5.3	120	14	92	95
30	3.9	165	13	90	83



**Figure 1** Water vapor permeability of coated fabrics versus PU hard-segment content at different concentrations of coating solution.

hydrogen bonding between carbamoyl group and carbonyl group of the hard segment and dipole–dipole interaction between carbonyl groups of hard segments.<sup>10,16</sup> Similarly, breaking stress and tensile modulus increased when the hard-segment content was increased. The high jump in modulus at 50% hard-segment content reflects an increase in stiffness resulting from the increase of high hard-segment content. Thus, from the tensile behavior of the PU, it was determined that the breaking stress, breaking elongation, and modulus are significantly influenced by the hard-segment content.

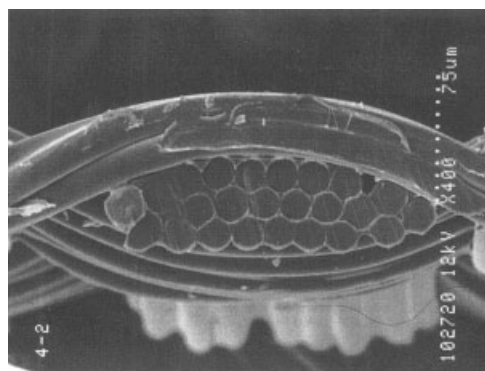
Shape recovery measured at 20°C above the glass-transition temperature of PU samples is also shown in Table II. It increases from 83% (with a hard-segment content of 30%) to 95% (with a hard-segment content of 40%) because of the increase of physical crosslink formation. At a hard-segment content of 50 wt %, a permanent deformation in the hard domain appears without any shape recovery, which is attributed to reduction of the soft segment that absorbs the stress, and the increased number of aromatic rings of MDI, thus weakening the overall shock-absorption ability and recovery of its original shape. These results indicate that the PUs with hard-segment contents of 30 and 40% are preferable in the application of shape-memory effect.

Water vapor permeability (WVP) was measured for PU-coated fabrics as a function of hard-segment content together with different levels of PU. As the PU hard-segment content increases, WVP tends to slightly decrease, as shown in Figure 1.<sup>17</sup> However, it is strongly influenced by PU coating concentration, suggesting that the permeation can be more easily controlled by the concentration of coating solution rather than by hard-segment content. That is, the permeabil-

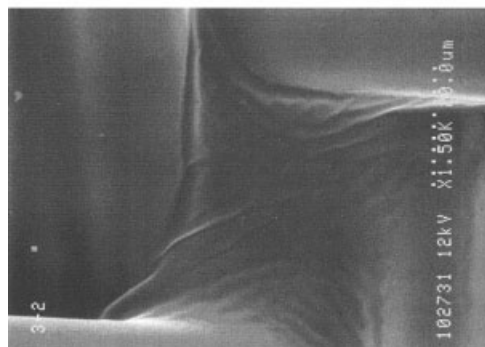
ity of PU-coated fabrics is primarily dependent on the concentration or viscous property of the coating solution. The above result emphasizes the importance of density rather than thickness of the PU layer formed in fabric coating; that is, density of the PU layer formed in the fabric increases, if a concentrated viscous coating solution is used, with a resultant decrease of permeability. Meanwhile, A diluted PU coating solution can penetrate deeply into the fabric, forming a less-dense PU layer and leading to high WVP.

Figure 2 shows the micrographs of both the surface and cross section of PU-coated fabrics obtained from SEM observation: the nonporous PU layer is formed continuously over the surface of the coated fabric, judging from the cross-sectional view of the fabric. The presence of a nonporous PU layer suggests that WVP of coated fabrics originates from the coated PU itself, and thus the mobility of PU at above its glass-transition temperature is important in permeation of water vapor. Such a characteristic is useful in preparing smart breathable fabrics that can control moisture evaporation rate depending on the surrounding temperature.

Figure 3 shows the stress–strain relationship of uncoated and PU-coated fabrics at different levels of

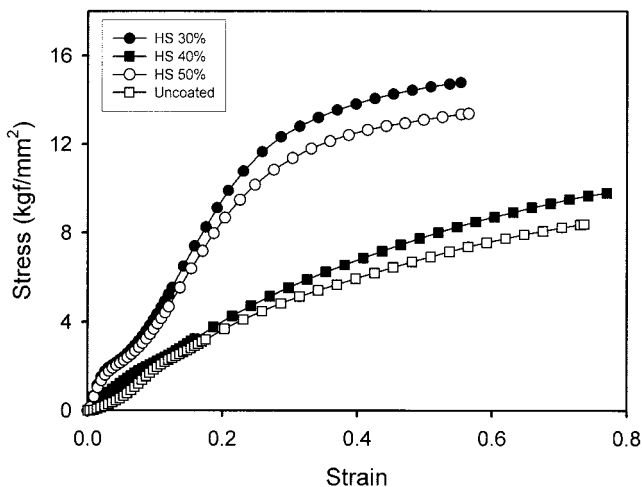


(a)



(b)

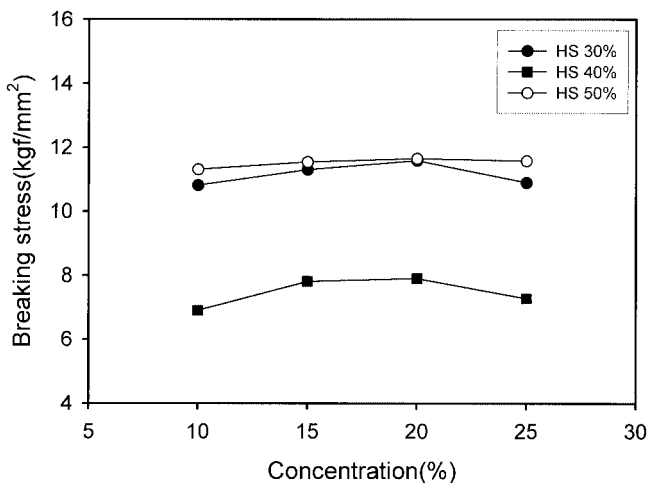
**Figure 2** SEM micrographs of coated fabrics prepared from 20% of solution concentration and hard-segment content of 40%: (a) surface; (b) cross section.



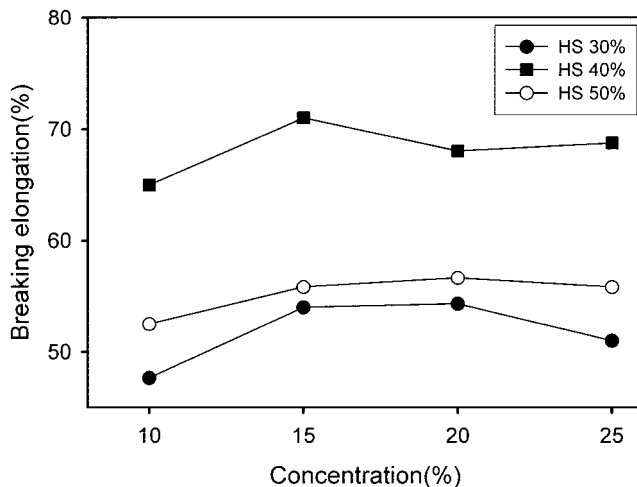
**Figure 3** Stress–strain curves of uncoated and coated fabrics at different PU hard-segment contents (20% solution concentration).

hard-segment content and concentration of coating solution. It can be clearly seen that the tensile properties of coated samples are dependent on PU hard-segment content. Breaking stress and breaking elongation of coated fabrics vary with hard-segment content, and in particular, stress behavior at the initial strain region changes substantially. Breaking stress against the concentration of PU solution is shown in Figure 4. The influence of solution concentration on breaking stress does not change as significantly as in the case of permeability. Breaking stress of samples coated with 40% of hard-segment PU, the lowest one among the samples, is close to that of the uncoated fabric.

Figures 5 and 6 show breaking elongation and modulus of coated samples against PU hard-segment con-



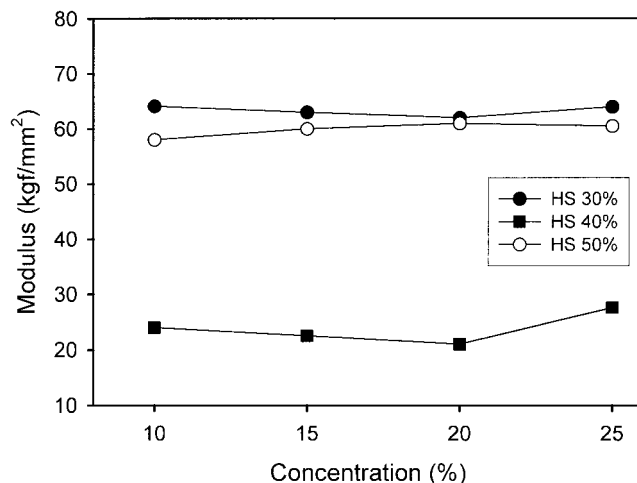
**Figure 4** Breaking stress of coated fabrics versus the polymer concentration at different PU hard-segment contents.



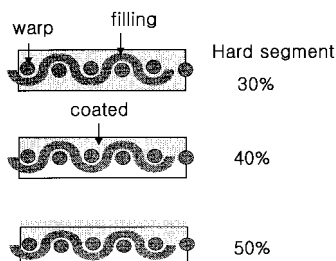
**Figure 5** Breaking elongation of coated fabrics versus the coating concentration at different PU hard-segment contents.

tent, respectively. However, breaking elongation and modulus of coated samples, which significantly depend on hard-segment content, are not changed by the PU concentration in spite of some scattering of data. The coated sample with 40% hard-segment content has the highest breaking elongation and the lowest modulus. Overall, the above results indicate that a relatively flexible fabric can be prepared by choosing the optimum hard-segment content in coating PU.

Elucidation of which factors determine such mechanical properties is the focus of the following discussion. The tensile behavior of coated fabrics cannot be explained just by the mechanical properties of PU itself. We must also take into consideration the contribution of viscosity of the coating solution and geometrical structure of the woven fabric composed of warp



**Figure 6** Modulus of coated fabrics versus coating concentration at different PU hard-segment contents.



**Figure 7** Geometrical structure of coated fabrics at different PU hard-segment contents of 30, 40, and 50%.

and filling. Because the modulus of PU increases with high hard-segment content, PU-coated fabric with 50% hard segment also shows higher modulus than fabrics with 30 and 40% hard-segment PU. In addition, as the PU hard-segment content increases, the viscosity of the coating solution increases and thus the thickness of the coated PU layer decreases. Comparison of the mechanical properties of coated fabrics is shown in Figure 7. With the fabric coated with 50% hard-segment PU, penetration of the coating solution into the fabric is reduced because of its relatively high viscosity,<sup>18,19</sup> which results in a high modulus fabric coated with a PU layer of low thickness and high stiffness.<sup>20</sup> However, for the fabric coated with 30% hard-segment PU, the coating solution can penetrate deeper inside of the fabric by its low viscosity and thus prohibit, even when the fabric is elongated, the deformation of fabric or decrimping of constituent yarns. As a result, the coated fabric with 30% hard-segment PU is not easy to elongate because of the moderate modulus. However, the mechanical properties of the coated fabric with 40% hard-segment PU are different from those of the previous samples, which can be explained by the fact that the coating solution cannot easily penetrate into fabric, such as that with 30% hard-segment PU solution, and the modulus of PU was not high compared with 50% hard-segment PU. Overall, fabric coated with 50% hard-segment PU has a modulus value closest to that of uncoated fabric.

Such results suggest that the proper choice of PU may lead to attainment of exceptional mechanical properties. Consequently, it was found that the mechanical properties of coated fabrics are influenced by both mobility of the coating solution and mechanical properties of PU.

## CONCLUSIONS

Water vapor permeability of PU-coated fabrics was influenced primarily by concentration of the coating solution and less by PU hard-segment content, and decreased with increasing concentration of coating solution. A nonporous PU layer was formed on the coating and good water permeability control could be achieved because of the smart characteristics of PU. Mechanical properties of coated fabrics were dependent on PU hard-segment content, whereas the effect of coating concentration was negligible. The sample coated with 40% hard-segment PU had the lowest values in breaking stress and modulus, and the highest in breaking elongation, which could be interpreted in terms of the dependency of mechanical properties on PU hard-segment content, mobility of fabric, and penetrating degree of coating solution into the fabric.

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