

Smart temperature-controlled water vapor permeable polyurethane film

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Abstract

Aim of this study was to develop a temperature-controlled polyurethane (PU) film for the application in film coated clothes. The PU film should be a smart one that can control its water vapor permeability (WVP) through temperature change. The study was carried out by increasing the water vapor permeability of various breathable/waterproof PU films through variations of their hard-to-soft-segment ratio, PEG content, and isocyanate index; the thermal properties and morphologies were investigated using Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). It was found that the WVP of the PU film (MDI/PEG/PBA/1,4-BD = 3:0.6:0.4:2) can control its WVP by temperature change by itself. The WVP of the PU film started to rise obviously at 18 °C which is near the material's glass transition temperature (23.88 °C). The result also showed that the PEG content affected the WVP dramatically; higher water permeabilities occurred at higher percentages of PEG in the main chain, but with concomitant decreases in the mechanical strengths. The most permeable PU film had a WVP of 6745 g/m²/day, a tensile strength of 29.38 MPa, and a tear strength of 112 kg/cm.

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1. Introduction

Research on water vapor permeability of polyurethane (PU) film was carried out over different formulation sets by varying hard segment concentrations, isocyanate indexes, and different ratios of PEG/PBA. Also, polyurethane film water vapor permeability near T_g at different humidity is studied in this paper.

PU comprises a class of materials whose properties vary widely: from rubbery to glassy, and from linear thermoplastic polymers to thermosetting polymers. This versatility can be exploited in conjunction with various processing and composition techniques to fulfill a vast variety of product requirements [1–3]. If the component compounds contain isocyanate groups or active hydrogen atoms (e.g., polyethers or polyesters), the processing conditions can be tailored to produce PU molecular structures that have desirable physical properties [4]. The PU main chain includes both soft (with low glass transition temper-

ature (T_g)) and rigid segments. The soft segments, which arise from high-molecular-weight polyols, provide rubbery properties. The hard segments, which provide crosslinking agents and crystalline chains for PU, are composed of isocyanate and low-molecular-weight diols [5]. Kim and Kim [6] found that the mechanical properties of PU were enhanced at higher polyester-type polyol (PTAd) contents, prepared using IPDI and PTAd/PPG as the hard and soft segments, respectively [7]. Xiu et al. [8], who utilized ester-type PTAd and ether-type PPG as polyols to synthesize PU, discovered that better mechanical properties arose from the ester-type polyol PU. Yen and Kuo [9] studied the effects of various kinds of soft segments (PCL, PEG, PCL/PEG blending, and triblock PCL–PEG–PCL) on the properties of PU; the best properties were observed for the single ester-type PU, followed by PCL–PEG–PCL PU, as a result of conformational and the inter-molecule hydrogen bonding phenomena [10]. Among these systems, the ester–ether PU exhibits the highest water vapor permeability (WVP). Because of macro phase separation among the soft segments of the PU, higher water vapor permeability is obtained at higher PEG contents. Yen and Kuo [11] also modified the soft segment composition

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of PCL–PEG–PCL triblock PU polyol and found that a higher WVP, lower mechanical properties, and obvious macro phase separation could be obtained upon increasing the EG ratio in the soft segment [12]. Yen and Kuo [13] discovered that irrespective of the nature of the PCL–PEG–PCL triblock or of the blending of the PCL/PEG soft segments, the mechanical properties increased upon increasing the NCO-to-OH ratio. The WVP increases at higher percentages of 2,2-bis(hydroxyl methyl) propionic acid (DMPA) and greater NCO-to-OH ratios. In terms of the thermal properties, the value of T_g increases upon increasing the NCO-to-OH ratio. Jeong et al. [14] discovered that the PEG and DMPA forms of PU have lower mechanical properties, and higher values of WVP can be obtained from lower values of T_g . Cho et al. [15] found that the WVP decreased upon increasing the percentage of the PU hard segment or by using a concentrated PU solution.

The specific focus of this study was to determine the water vapor permeability near the values of T_g , using the PEG/PBA blended polyols as soft segments of the polyurethane film. Herein, we also discuss the mechanical strength and tear strength of the resulting PU films.

2. Experimental

2.1. Chemicals

4,4-Diphenylmethane diisocyanate (MDI; TCI Chem. Co.), ethanol (99.5%; Acros Co.), 1,4-butanediol (1,4-BD, >99%; Acros Co.), and *N,N*-dimethylformamide (DMF; Acros Co.) were used as received. Polybutyleneadipate (PBA, M.W. 700) was supplied by U-Conn Technology, Taiwan. Poly(ethylene oxide glycol) (PEG) samples (M.W. 600 and 2000) were supplied by Sino Chem., Japan. The PBA and PEG samples were degassed at 60 °C under vacuum overnight prior to use.

2.2. Preparation of polyurethane films

MDI/polyol samples, dissolved in DMF at various mixing ratios (2:1, 3:1, 4:1), were placed in four-neck reactors and stirred at 5 Hz (300 rpm) and 70 °C. The changes in the appearance of the signal for the isocyanate (NCO) group (2270 cm^{-1}) were monitored using FTIR spectroscopy.

The PU solution was poured onto a mold having a Teflon coating; the thickness was controlled to within 0.01–0.05 mm. The sample was then placed in a hood for 48 h to remove the DMF solvent, resulting in a PU film.

2.3. Testing methods

The water vapor permeability experiment is carried out according to JIS-1099 A1 method, which an upright cup covered with the polyurethane sample film and filled with fixed amount of calcium chloride inside, is placed in a controlled chamber at fixed temperatures and humidity at 90%. WVP values were calculated by the gained weight of desiccant and divided by the fixed surface area of the polyurethane film and the time inside the controlled chamber. The mechanical

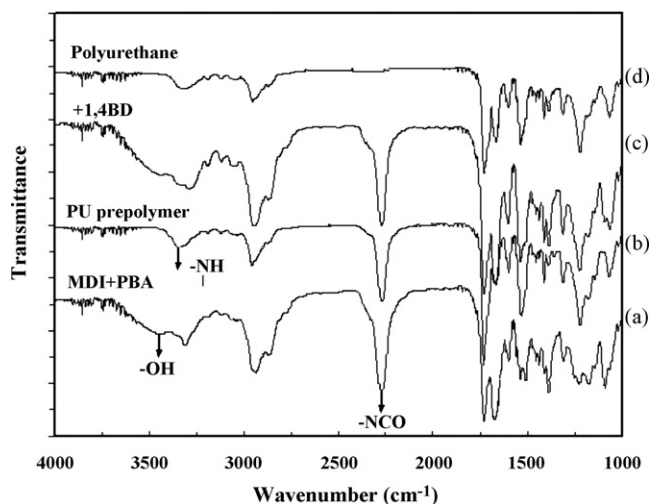


Fig. 1. FTIR spectra recorded at four reaction states: (a) 2MDI + PBA; (b) PU prepolymer; (c) PU prepolymer + 1,4BD; (d) polyurethane.

properties were measured according to ASTM D412 (tensile strength) and ASTM 62C (tear strength). The thermal properties were measured using differential scanning calorimetry (DSC, Mettler–Toledo DSC–821^e, USA). A heating rate of 10 °C/min was employed over the temperature range from –60 to +200 °C.

3. Results and discussion

3.1. Reaction

The FTIR spectra in Fig. 1(a) indicate that the signals for the hydroxyl (OH, 3400 cm^{-1}) and NCO (2270 cm^{-1}) groups coexisted in the initial reaction state. In the intermediate state (Fig. 1(b)), the signal for the OH groups disappeared, that of the NCO groups reduced to half of its original intensity, and a signal for NH units appeared at 3300 cm^{-1} , suggesting that the PU prepolymer had been formed. In the final step, the chain extender (1,4-BD) was added; Fig. 1(c) indicates that the peak intensity of the residual NCO units (2270 cm^{-1}) eventually disappeared. The changes in the intensity of the signal of the carbonyl groups (C=O) of urethane linkages (at 1740 cm^{-1}) indicate the chemical reactions of the diisocyanate and the polyol and of the diisocyanate and 1,4-BD.

3.2. Thermal properties

Table 1 presents the thermal properties of various samples. The value of T_g increased upon increasing the content of the hard segment in the PU, presumably because of the rigidity resulting from the larger number of aromatic rings in the TPU main chain and the greater number of hydrogen bonds formed between NH and C=O groups.

In Table 1, we observe that increasing the soft segment ratio, which enhanced the flexibility of the PU chains, also decreased the value of T_g . These results are consistent with those described previously.

Table 1
Designation and thermal properties of PU samples at various sample ratios

MDI/PEG/PBA/1,4-BD	Designation	Isocyanate index	T_g (°C)
2/0.4/0.6/1	PU1	1.00	-9.96
3/0.4/0.6/2	PU2	1.00	12.86
4/0.4/0.6/3	PU3	1.00	28.03
4/0.6/0.4/3	PU4	1.00	26.35
4/0.8/0.2/3	PU5	1.00	13.38
4/1/0/3	PU6	1.00	10.21
3/0.6/0.4/2	PU7	1.00	6.09
3/0.6/0.4/2	PU8	1.10	13.37
3/0.6/0.4/2	PU9	1.20	23.88

3.3. Mechanical properties

Fig. 2 displays the tensile strengths and tear strengths for polymers at various hard/soft segment ratios. The mechanical strength and the tear strength both increased with increasing hard segment content in the PU chain, presumably because of the increased rigidity and strength resulting from the hydrogen bonds formed between the NH and C=O groups.

Fig. 3 displays the tensile strengths and tear strengths for samples containing various PEG contents in the polyol, but at the same hard/soft segment ratio. Both the tensile strength and the tear strength decreased upon increasing the soft segment PEG/PBA ratio. The higher flexibility of the PEG units relative to that of PBA meant that it could diffuse more readily into the hard segments and reduce the crystallinity. In addition, the ester-type PBA presents carbonyl groups along the PU main chain, which readily interact with the hard segments.

Fig. 4 presents the tensile strengths and tear strengths as a function of various isocyanate indexes. Both the tensile strength and the tear strength increased upon increasing the isocyanate index because of the increasing number of hard segments. Furthermore, the presence of too many hard segments, which enhance the phase separation domains dispersed into PU molecule, will also increase the mechanical properties.

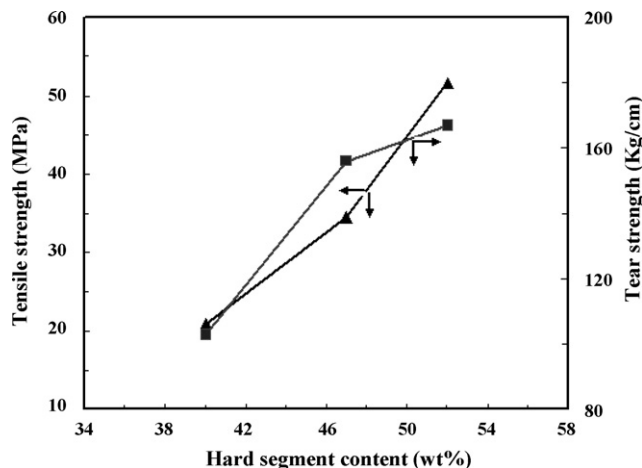


Fig. 2. Tensile strength and tear strength plotted as functions of the hard/soft segment ratio of the PUs.

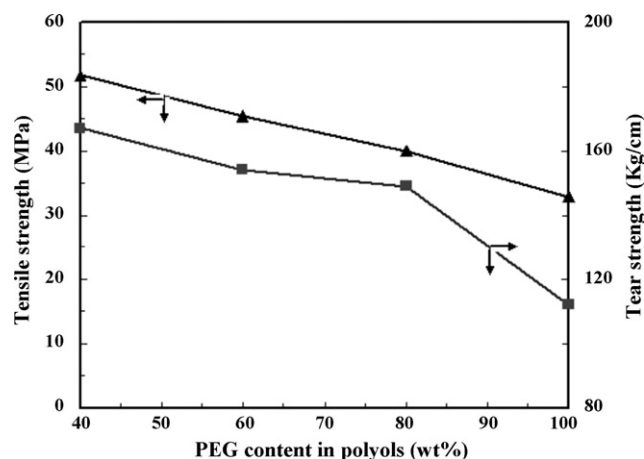


Fig. 3. Tensile strength and tear strength plotted as functions of the PEG content in the polyols at a constant MDI/polyol/1,4-BD molar ratio (4:1:3).

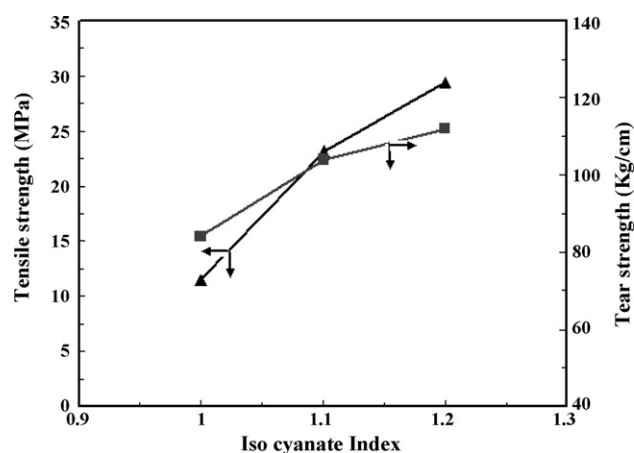


Fig. 4. Tensile strength and tear strength plotted as functions of the isocyanate index of PU at an MDI/polyol/1,4-BD molar ratio of 3:1:2.

3.4. Water vapor permeability

Table 2 presents the results of WVP analyses of various samples. The WVP decreased with increasing hard segments along the PU chain, comparing PU1, PU2, PU3, presumably more rigid hard segments surround the soft segments prohibiting water permeation [16,17]. In Table 2, comparing PU3, PU4, PU5, PU6,

Table 2
Mechanical properties and WVP of PU samples at various sample ratios

Samples	Mechanical properties		WVP (g/m ² day)
	Tensile strength (MPa)	Tear strength (kg/cm)	
PU1	20.92	103	1257
PU2	34.53	156	984
PU3	51.65	167	813
PU4	45.37	154	1742
PU5	39.84	149	4648
PU6	32.90	121	10729
PU7	11.47	84	2484
PU8	23.17	104	3744
PU9	29.38	112	6745

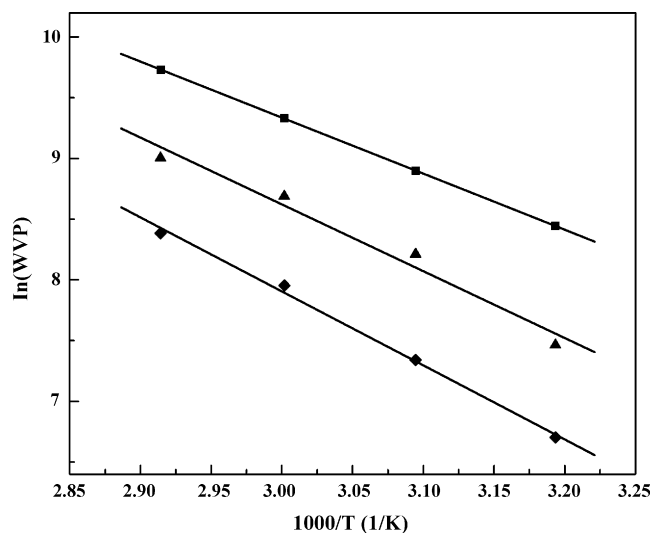


Fig. 5. Natural log of water vapor permeability plotted as a function of inverse temperature and the PEG content in the polyol at an MDI/polyol/1,4-BD molar ratio of 4:1:3 (■) 80 wt.% PEG in soft segment; (▲) 60 wt.% PEG in soft segment; (◆) 40 wt.% PEG in soft segment).

we observe that the WVP also increased greatly upon increasing the PEG/PBA ratio of the soft segments. In comparison with PBA, PEG is more hydrophilic, water soluble, and flexible.

Although, in theory, the WVP should decrease upon increasing the isocyanate index, in Table 2, comparing PU7, PU8, PU9, we observe the opposite behavior, presumably because of the many well-dispersed small domains within the PU microstructure that arose through hydrogen bond formation between the NH and C=O groups.

Temperature dependence of gas permeability coefficient in polymer can be described by Arrhenius type equation [18]:

$$P = P_0 \exp\left(\frac{-E\pi}{PT}\right)$$

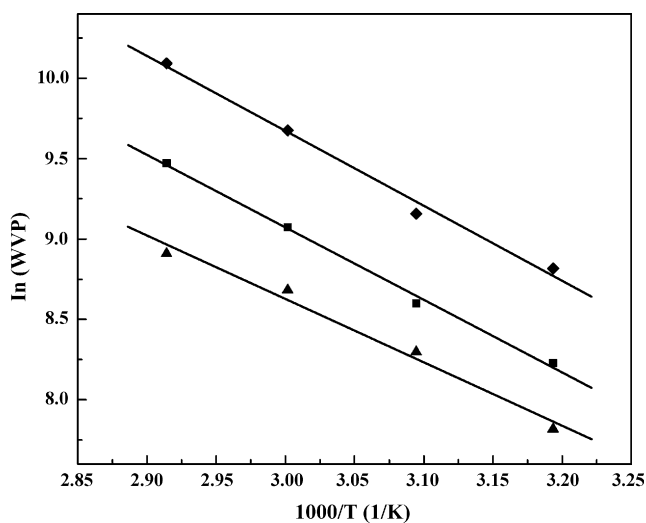


Fig. 6. Natural log of water vapor permeability plotted as a function of inverse temperature and the isocyanate index at an MDI/polyol/1,4-BD molar ratio of 3:1:2 (▲) isocyanate index = 1; (■) isocyanate index = 1.1; (◆) isocyanate index = 1.2).

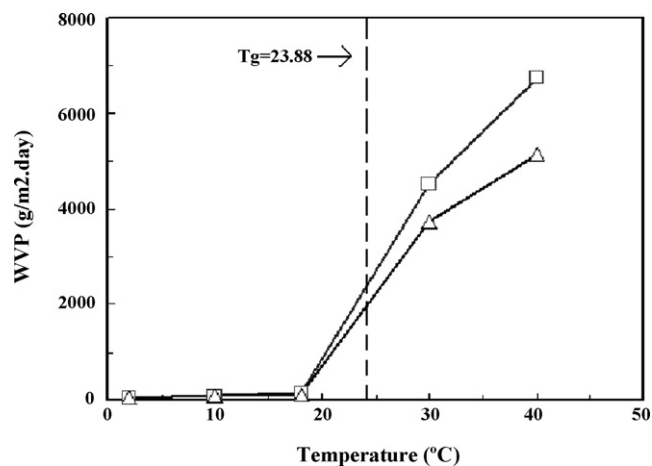


Fig. 7. Water vapor permeabilities of PU specimens (MDI/PEG/PBA/1,4-BD=3:0.6:0.4:2) plotted as a function of the temperature and the relative humidity (□) RH=90; (△) RH=70).

where P_0 is the pre-exponential factor and E_p is the apparent activation energy of permeation. From the equation above, it is known that $\ln(WVP)$ and $(1/T)$ is a linear relation. In Figs. 5 and 6, we mention that obvious variations in the WVP were obtained at different temperatures. It is observed that the relationship between the natural log WVP and the inverse absolute temperature is linear dependence. Indeed, a higher temperature causes the soft segments to become more flexible such that the water vapor molecule can pass through more readily.

3.5. Water vapor permeability analysis near the glass transition temperature

Fig. 7 indicates that the WVP of the PU film (MDI/PEG/PBA/1,4-BD=3:0.6:0.4:2) is affected dramatically by temperature changes near to the material's value of T_g (ca. 23.88 °C). The result showed that the PU film can control the

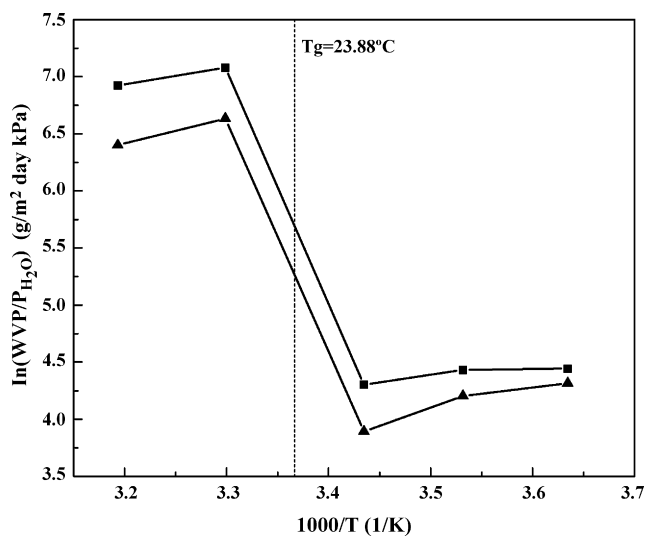
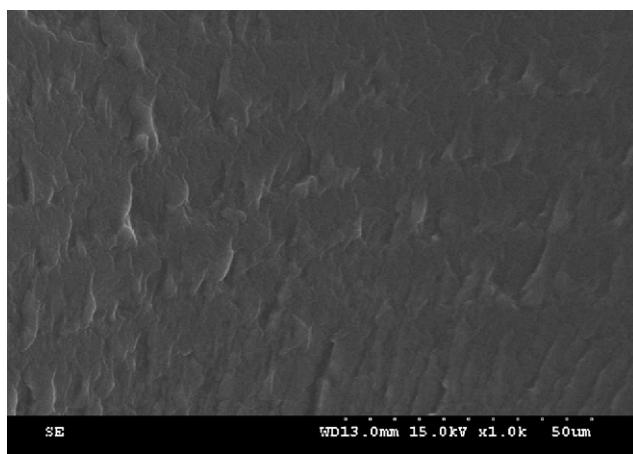
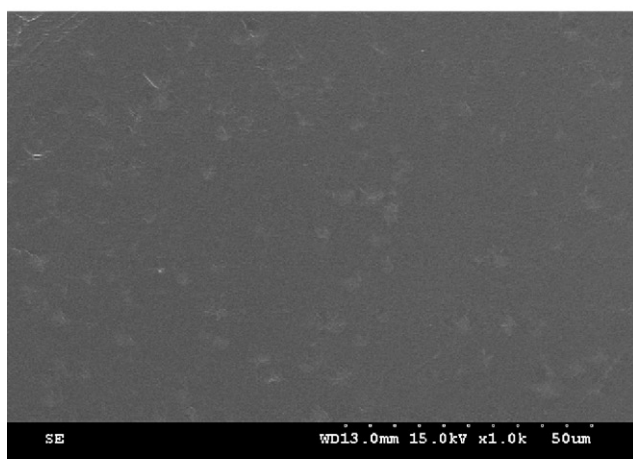


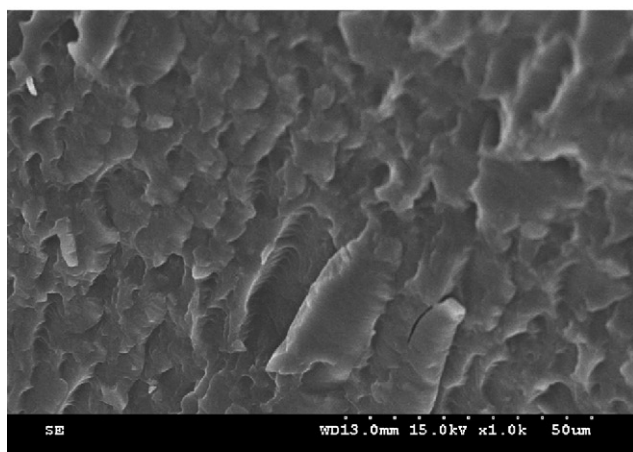
Fig. 8. Natural log of (water vapor permeability divided by partial water pressure) plotted as function of inverse temperature of (MDI/PEG/PBA/1,4-BD=3:0.6:0.4:2) and the relative humidity (■) RH=90; (▲) RH=70).



(a)



(b)



(c)

Fig. 9. Morphologies of PU samples at various MDI/PEG/PBA/1,4-BD ratios. (a) PU(MDI/PEG/PBA/1,4-BD = 2:0.4:0.6:1), (b) PU(MDI/PEG/PBA/1,4-BD = 3:0.4:0.6:2) and (c) PU(MDI/PEG/PBA/1,4-BD = 4:0.4:0.6:3).

WVP which stays low until the temperature is higher than 18 °C and starts to rise dramatically. In order to ignore the affection from the water partial pressure driving force which is changing exponentially with temperature in a similar manner to the WVP, the WVP was divided by the water partial pressure driving force

and plotted as log-plot versus inverse temperature in Fig. 8. From Fig. 8, it is also observed that WVP/P_{H_2O} still rises dramatically at temperature near materials' T_g .

At temperatures below T_g , the PU film exists in a glassy state that is very rigid. The WVP of PU film is provided by the non-crystalline part, which exists in a rubber-like state; this phase can move when the temperature is between the glass transition temperature and the crystalline temperature. Therefore, the WVP is low when the temperature is below the T_g , but it increases when the temperature is above the T_g .

3.6. Cross-sectional surface morphologies

Fig. 9 displays the different morphologies observed at various percentages of hard segments in the PU. An excess of hard segments caused more wrinkles to appear on the PU film surface; these wrinkles arose through micro phase separation of the hard and soft segments.

4. Conclusions

The utilization of PEG/PBA multiple-polyol system presented better WVP than PBA system of PU films. The result showed that the WVP of the PU film (MDI/PEG/PBA/1,4-BD = 3:0.6:0.4:2) stayed low until the temperature was higher than 18 °C. Then the WVP started to rise obviously. The WVP of PU films increased upon increasing the hard segment ratio, the temperature, or the isocyanate index, but it decreased when the temperature was decreased to below the T_g . The glass transition temperature of PU films increased upon increasing the percentage of hard segments or decreasing the soft segment PEG/PBA ratio. The mechanical strength and the tear strength both increased upon (a) increasing the percentage of hard segment, (b) decreasing the soft segment PEG/PBA ratio, or (c) increasing the isocyanate index.

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