

# Preparation of Starch-based Polyurethane Films and Their Mechanical Properties

Dae-Hyun Kim, Oh-Jin Kwon, Seong-Ryul Yang, and Jong-Shin Park\*

Department of Biosystems and Biomaterials Science and Engineering, Seoul National University, Seoul 151-742, Korea  
Intelligent Textile System Research Center, Seoul 151-742, Korea  
Research Institute for Agriculture and Life Sciences, Seoul 151-742, Korea  
(Received February 13, 2007; Revised April 27, 2007; Accepted May 7, 2007)

**Abstract:** In this study, polyurethane films were prepared using starch as the main polyol component, and the mechanical properties of these films were investigated. The starch content of the polyols was 30-50 wt%. To confirm the formation of a urethane linkage between the -OH of starch and -NCO of toluene 2,4-diisocyanate, Fourier transform infrared (FT-IR) spectroscopic analysis was performed. Differential scanning calorimetry (DSC) thermograms of the polyurethanes resulted in two endothermic peaks, which shifted to higher temperatures with increasing starch content and -NCO/-OH molar ratio. Due to the melting behavior of polyurethane, films could be prepared by hot pressing at an appropriate temperature. Polyurethane films were prepared with various polyol starch content and -NCO/-OH molar ratios. Tensile testing indicated that the breaking stress and elastic modulus increased significantly with starch content and -NCO/-OH molar ratio. In addition, bending tests indicated an increase in breaking stress and bending modulus with starch content and -NCO/-OH molar ratio and decreased breaking strain. The strain rate in both tensile and bending tests had a significant effect on the mechanical properties.

**Keywords:** Polyurethane film, Starch, Tensile property, Bending property, DSC

## Introduction

Environment-friendly polymeric materials are classified into two categories: degradable synthetic polymers (polycaprolactone, polylactide, polyvinyl alcohol, and polyesteramide) and renewable natural polymers (chitin, chitosan, pectin, starch, and cellulose). Among these, starch is the most attractive candidate because it exists abundantly in nature and is very inexpensive. For these reasons, starch has been used widely in the food, textile, and paper industries [1].

Starch-based biodegradable plastic materials can be prepared by various methods: embedding granular or gelatinized starch in synthetic polymeric matrices such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride [2-6]; blending starch with a hydrophilic polymer [7]; foaming starch within an extruder [8]; and preparing thermoplastic starch by melting under high temperature and pressure [9]. When incorporated with a synthetic polymer, the synthetic polymer will remain in an undegraded state even after the starch is biodegraded. When blended with other polymeric materials, phase separation may occur, causing reduction of mechanical properties [10]. In addition, there are disadvantages when starch is used as a major component, such as inferior mechanical properties due to brittleness and limitation of usage due to the hydrophilicity [11].

Polyurethanes are polymeric materials with urethane linkages along the backbone, and they are prepared by polyaddition polymerization between polyisocyanates and polyols. Polyurethanes with various chemical, mechanical, and degradation properties can be prepared in molded article, film, fiber, foam, and emulsion forms according to the nature of the

polyisocyanates and polyols used [12]. Polyurethanes have been widely used in industry as fibers, elastomers, adhesives, and coatings. In particular, polyurethane foams are used widely in many fields as structural, cushioning, insulational, electrical, flotation, and packaging materials. In general, toluene 2,4-diisocyanate (2,4-TDI), hexamethylene diisocyanate (HDI), and diphenylmethane diisocyanate (MDI) are often used as diisocyanates, while low molecular weight materials (ethylene glycol, glycerin, and butanediol), as well as polymeric materials (polyether, polyester polyols, and natural materials such as castor oil, sucrose, and sorbitol) are used as polyols [13-21]. Starch has often been used as either a polyol or a crosslinker in preparation of the polyurethane, because it has more than two hydroxyl groups per repeating anhydroglucose unit, allowing for efficient reaction with diisocyanate [22-24]. In such cases, however, starch has been used only as an auxiliary component or an additive to improve the rigidity of flexible polyurethane foam.

In the previous study [25], the structural, thermal, and mechanical properties of polyurethane foams were investigated. In this study, polyurethane films using starch as a main polyol component were prepared. Poly(ethylene glycol) (PEG) was used as the other polyol component, and 2,4-TDI was the diisocyanate. The thermal and mechanical properties of the polyurethane film were investigated by Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), tensile and bending tests.

## Experimental

### Materials

Native corn starch (Samyang Co., Korea), PEG (#200, Shinyo

\*Corresponding author: jongshin@snu.ac.kr

Pure Chemicals Co., Ltd., Japan), and glycerol (Shingyo Pure Chemicals Co., Ltd., Japan) were vacuum-dried at 120 °C for 24 h and used as polyols. 2,4-TDI (Sigma-Aldrich Co.) was used as a diisocyanate without further purification. Double distilled water was used as a foaming agent.

### Preparation of the Polyurethane Film

The predetermined amounts of starch, PEG, and glycerol were mixed and heated to 95 °C. The mixture was stirred for one hour until homogenous and cooled to 40 °C. Water was added as a foaming agent and the mixture was stirred vigorously for one min, followed by addition of the 2,4-TDI. The mixture was vigorously stirred for 30 sec, poured into a mold (width × length × height = 12 cm × 12 cm × 10 cm) and then stored in an auto-desiccator (Sanpla Dry Keeper, Sanplatec Corp., Japan) at 15 % R.H. and 20 °C for 24 h. The resulting polyurethane foam was ground to a powder using a milling machine (IKA<sup>®</sup>-WERKE, GmbH & Co. KG, Germany) and pressed using a hot press (Carver 2699, Carver Inc., USA) at 1000 psi and at a temperature predetermined from the DSC thermograms. The prepared polyurethane films were stored in an auto-desiccator at 15 % R.H. and 20 °C. The -NCO/-OH molar ratio ( $R_{-NCO/-OH}$ ) was calculated using equation (1).

$$R_{-NCO/-OH} = \frac{\frac{\text{TDI(g)}}{87}}{\frac{\text{H}_2\text{O(g)}}{9} + \frac{\text{Starch(g)} \times 3}{162} + \frac{\text{PEG(g)}}{4409} + \frac{\text{Glycerol(g)} \times 3}{92}} \quad (1)$$

The compositions of the ingredients and molding temperatures for the polyurethanes are shown in Tables 1 and 2. As can be seen in the last column of Table 1, the foam compositions varied.

### FT-IR Spectroscopy

FT-IR spectroscopy (M series, Midac Co., USA) was used to confirm reaction between 2,4-TDI and starch. After being

**Table 2.** Thermal analysis results and molding temperature for polyurethane

Sample	Endothermic peaks		Molding temperature	Formation of film
	First (sharp)	Second (broad)		
TS5-11	91 °C	203 °C~	220 °C	No
TS5-09	72 °C	180 °C~	220 °C	No
TS5-07	63 °C	80~174 °C	180 °C	No
TS5-05	59 °C	78~157 °C	160 °C	Yes
TS4-11	70 °C	79~178 °C	180 °C	Yes
TS4-09	60 °C	81~185 °C	190 °C	Yes
TS4-07	56 °C	67~142 °C	150 °C	Yes
TS3-11	78 °C	~184 °C	190 °C	Yes
TS3-09	59 °C	70~136 °C	140 °C	Yes

ground to the powder, polyurethane specimens were prepared in the form of KBr pellets. FT-IR spectra between 400 and 4000  $\text{cm}^{-1}$  were analyzed with a 4  $\text{cm}^{-1}$  resolution.

### Thermal Analysis

The thermal behavior of the polyurethane was investigated using DSC (TA 2910, TA Instruments, USA). A hermetic aluminum pan was used and the heating rate was 10 °C/min.

### Tensile and Bending Tests

The tensile test for each polyurethane film (length × width × thickness = 20 × 7 × 0.7-1.2 mm) was performed according to ASTM D638 with a MiniMat 2000 (Rheometric Scientific, Inc., USA) at strain rates of 5, 10, and 20 mm/min. Following ASTM D790, three-point bending was performed with a MiniMat 2000 in bending mode with parameters shown in Table 3. The stress at maximum or break ( $S$ ) and bending elastic modulus ( $E_b$ ) were obtained using equations (2) and (3). Five specimens were used for each test.

$$S = \frac{3PL}{2bd^2} \left[ 1 + 6 \left( \frac{D}{L} \right)^2 - 4 \left( \frac{d}{L} \right) \left( \frac{D}{L} \right) \right] \quad (2)$$

**Table 1.** Compositions of the ingredients for the preparation of polyurethane

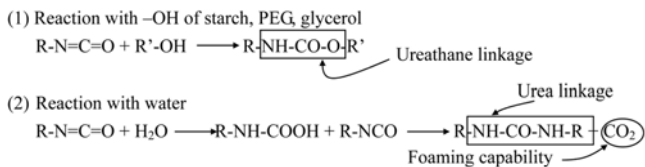
Sample	PEG/glycerol/starch (g)	Water (g)	2,4-TDI (g)	-NCO/-OH molar ratio	Formation of foam
TS5-11	56.4/3.6/60	0.48	124.6	1.1	Yes
TS5-09	56.4/3.6/60	0.48	98.5	0.9	Yes
TS5-07	56.4/3.6/60	0.48	76.6	0.7	Yes
TS5-05	56.4/3.6/60	0.48	54.7	0.5	Yes
TS4-11	67.7/4.3/48	0.48	105.7	1.1	Yes
TS4-09	67.7/4.3/48	0.48	83.1	0.9	Yes
TS4-07	67.7/4.3/48	0.48	64.9	0.7	Yes
TS4-05	67.7/4.3/48	0.48	46.4	0.5	No
TS3-11	78.9/5.04/36	0.48	86.8	1.1	Yes
TS3-09	78.9/5.04/36	0.48	71.1	0.9	Yes
TS3-07	78.9/5.04/36	0.48	55.2	0.7	No
TS3-05	78.9/5.04/36	0.48	39.5	0.5	No

**Table 3.** Parameters for the three-point bending test

Parameters	Values
Support length, $L$ (mm)	20
Crosshead speed, $R$ (mm/min)	1, 10
Specimen dimension	
Length (mm)	30
Width, $b$ (mm)	5
Thickness, $d$ (mm)	0.7-1.2

$$E_b = \frac{L^3 m}{4bd^3} \quad (3)$$

$S$ : stress at maximum or break ( $N/m^2$ )  
 $E_b$ : bending elastic modulus ( $N/m^2$ )  
 $P$ : load at maximum or break (N)  
 $L$ : support length (mm)  
 $b$ : sample width (mm)  
 $d$ : sample thickness (mm)



**Figure 1.** Expected reaction schemes between 2,4-TDI and polyols.

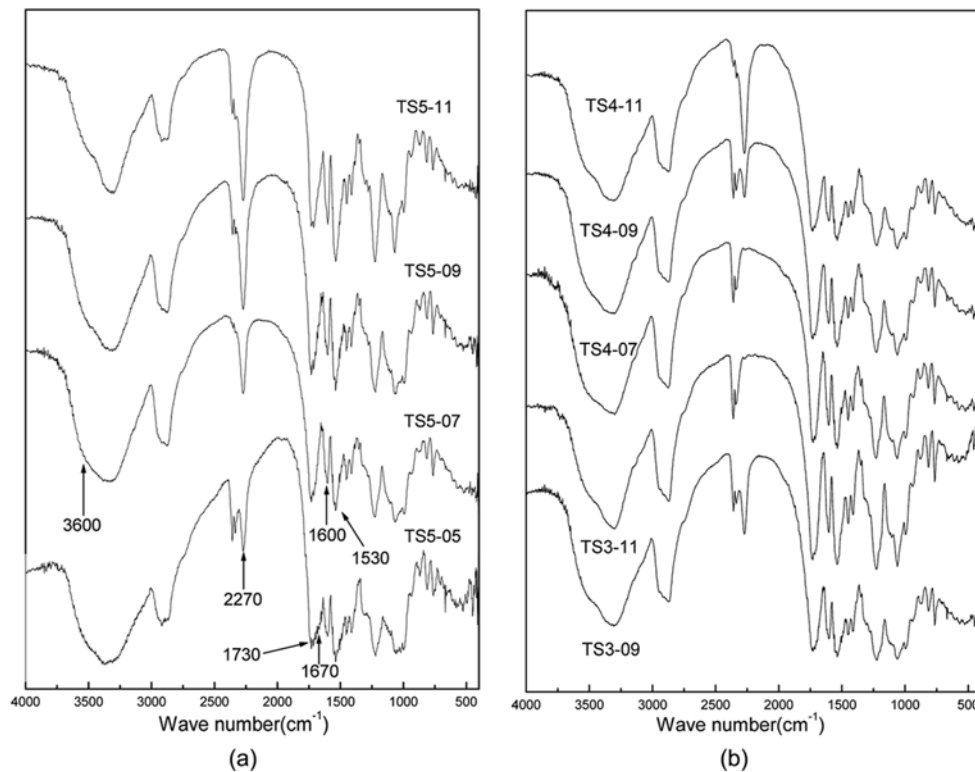
$D$ : deflection at maximum or break (mm)  
 $m$ : initial slope of load-deflection curve

### Results and Discussion

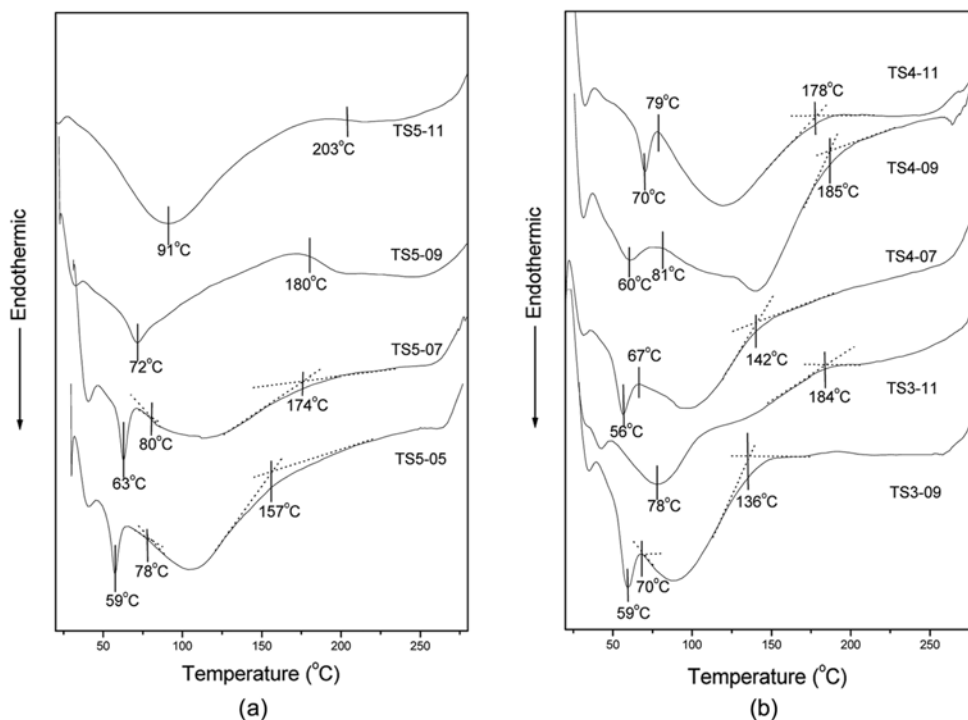
#### FT-IR Spectroscopic Analysis

The urethane linkage forms by the reaction between the isocyanate of 2,4-TDI and polyols. Carbon dioxide gas, which is known to have foaming capability, may be a reaction product of 2,4-TDI and water. The expected reactions are shown in Figure 1. Upon reaction and vigorous mixing of 2,4-TDI and the polyols, the reaction was exothermic. As shown in the last column of Table 1, foams did not develop for some compositions. Samples with low starch content as well as low -NCO/-OH molar ratio (ex. TS4-05, TS3-07, and TS3-05) could not be foamed. Starch, which is known to act as a hard segment, played a significant role in maintaining the foamed structure. The reaction between 2,4-TDI and starch was not fully completed at low -NCO/-OH molar ratios.

FT-IR results (Figure 2) confirmed the reaction between 2,4-TDI and polyols. FT-IR spectrum of each polyurethane composition showed characteristic peaks at  $1730\text{ cm}^{-1}$  (C=O of urethane) and  $1530\text{ cm}^{-1}$  (N-H of urethane), which are attributed to the urethane linkage formation between diisocyanates of 2,4-TDI and hydroxyl groups of the polyol. The intensity of the characteristic peaks increased with the -NCO/-OH molar ratio due to more reaction between 2,4-



**Figure 2.** FT-IR spectra of (a) TS5 and (b) TS4, TS3 polyurethane.



**Figure 3.** DSC thermograms of (a) TS5 and (b) TS4, TS3 polyurethanes.

TDI and the polyol. The intensity of the peak at  $1600\text{ cm}^{-1}$  (aromatic C-H of 2,4-TDI) also increased with -NCO/-OH molar ratio due to the increased amounts of 2,4-TDI in the mixture. The peak at  $1670\text{ cm}^{-1}$  (C=O of urea) is attributed to the formation of a urea linkage by the reaction between 2,4-TDI and water, which proves that the polyurethane was foamed by the  $\text{CO}_2$  byproduct. However, the intensity the  $1670\text{ cm}^{-1}$  peak decreased with -NCO/-OH molar ratio, contrary to the increasing  $1730\text{ cm}^{-1}$  peak. There may be some limitations of the reaction between 2,4-TDI and water due to the limited amounts of water added. Therefore, the difference in peak intensity between  $1730$  and  $1670\text{ cm}^{-1}$  increased with -NCO/-OH molar ratio. The peak at  $3600\text{ cm}^{-1}$ , which is attributed to the hydrogen bonding between -OH groups of water and starch, decreased with the -NCO/-OH molar ratio. To this end, the water content and hydrophilicity of polyurethane decreased significantly. Additionally, the peak at  $2270\text{ cm}^{-1}$ , which is attributed to excess and unreacted -NCO, increased with the -NCO/-OH molar ratio, suggesting the internal hydroxyl groups of the granular starch did not react completely with 2,4-TDI.

### Thermal Behaviors of Polyurethane

Two endothermic peaks were observed from DSC analysis (Figure 3 and Table 2). The sharp peak at a lower temperature is due to the melting of low-molecular weight polyurethane formed between PEG and 2,4-TDI. The broad peak at a higher temperature is due to the typical melting of starch.

Both melting peaks shifted to higher temperatures with increasing starch content and -NCO/-OH molar ratio.

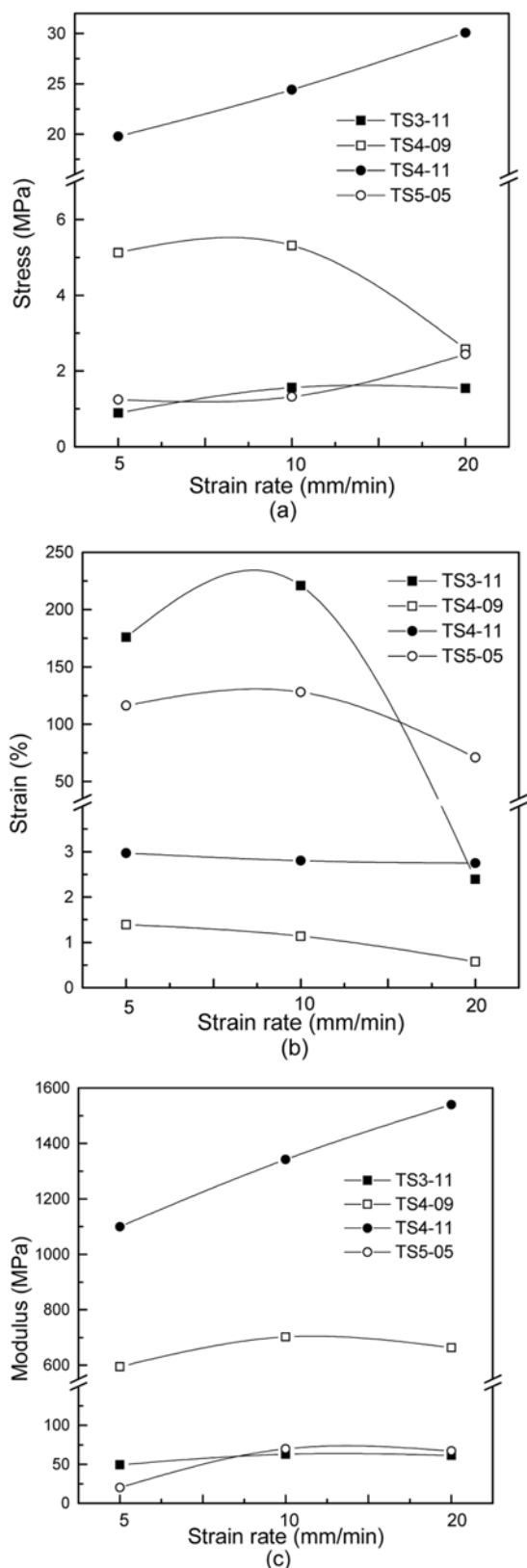
### Mechanical Properties of Polyurethane Films

As shown in Figure 3, the prepared polyurethane exhibited melting behavior. Therefore, polyurethane films could be prepared by hot pressing the ground polyurethane at the proper temperature, as shown in Table 2. However, TS5-07, TS5-

**Table 4.** Tensile test results of polyurethane films

Samples	Stress at break (MPa)	Strain at break (%)	Initial modulus (MPa)	Work of rupture ( $\text{Nm/m}^3$ )
TS5-05-05 <sup>1)</sup>	1.2 (1.6) <sup>2)</sup>	116.3 (25.2)	20.1	$1.3 \times 10^6$
TS5-05-10	1.3 (2.4)	128.1 (15.4)	69.6	$1.8 \times 10^6$
TS5-05-20	2.4 (3.5)	70.1 (10.0)	67.0	$1.1 \times 10^6$
TS4-11-05	19.8	3.0	1099.5	$2.1 \times 10^5$
TS4-11-10	24.4	2.8	1342.2	$3.3 \times 10^5$
TS4-11-20	30.1	2.8	1539.6	$2.6 \times 10^5$
TS4-09-05	5.1	1.4	594.6	$2.2 \times 10^4$
TS4-09-10	5.3	1.1	702.0	$4.2 \times 10^3$
TS4-09-20	2.6	0.6	663.7	$6.3 \times 10^3$
TS3-11-05	0.9 (1.9)	175.8 (9.2)	49.4	$2.5 \times 10^6$
TS3-11-10	1.6 (3.1)	220.8 (17.9)	62.9	$4.1 \times 10^6$
TS3-11-20	1.5	2.4	61.4	$3.7 \times 10^4$

<sup>1)</sup>TS5-05-05 means TS5-05 was strained at 5 mm/min, <sup>2)</sup>( ): stress and strain at maximum.



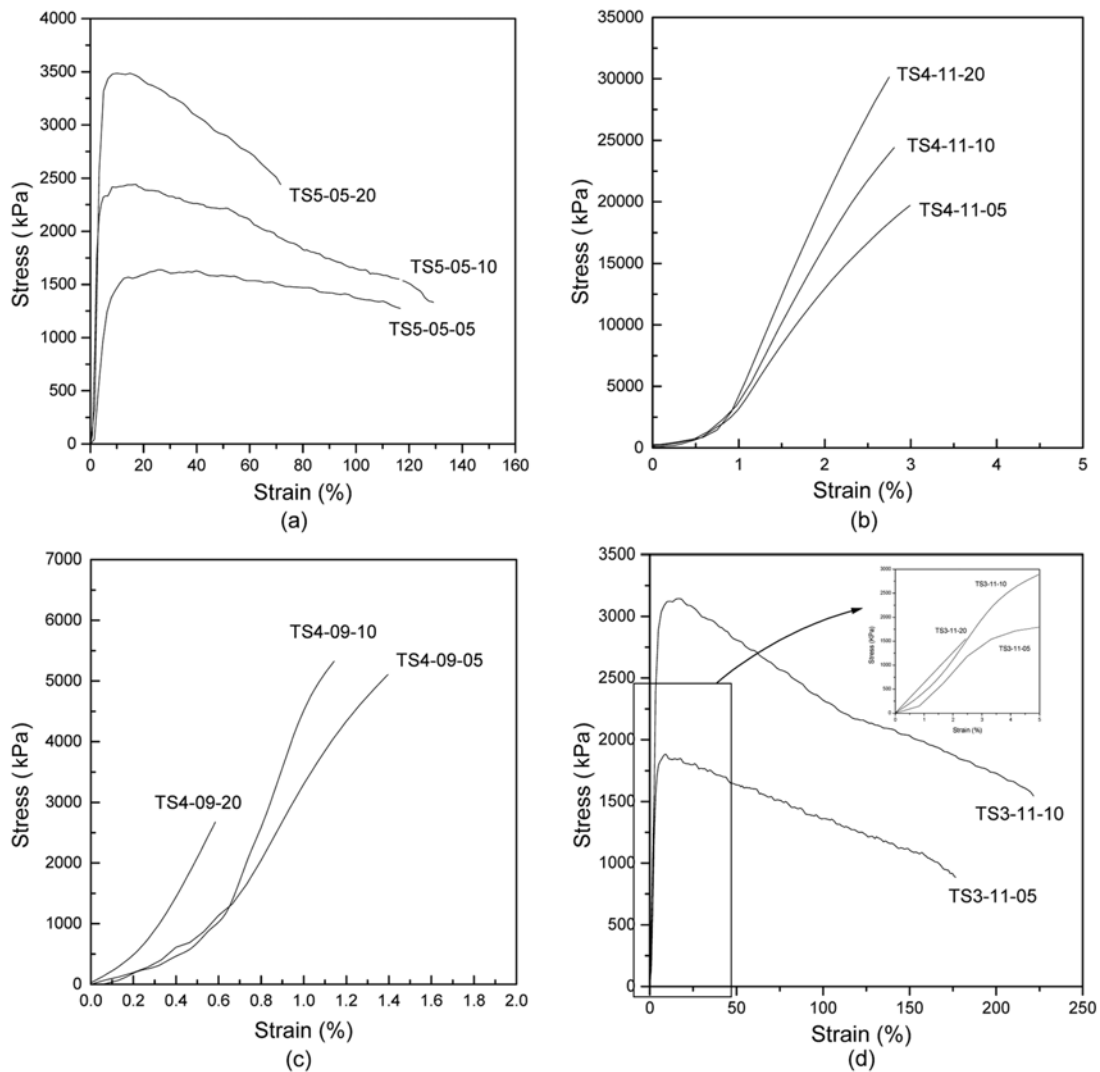
**Figure 4.** Tensile properties of polyurethane films as a function of strain rate; (a) stress, (b) strain, and (c) modulus.

09, and TS5-11 did not melt sufficiently at the predetermined temperature and began to degrade at higher temperatures, preventing film formation. TS4-07 and TS3-09 formed films, however they were not solidified enough to be tested at ambient temperature. To this end, mechanical testing of TS5-05, TS4-11, TS4-09, and TS3-11 films was performed.

The results of tensile tests for the polyurethane films are shown in Table 4 and Figure 4. The stress at break and modulus increased significantly with starch content and -NCO/-OH molar ratio, however, strain at break shows various trends among samples. The strain at break of TS4-11 (2.8-3.0 %) was higher than that of TS4-09 (0.6-1.4 %) and much smaller than that of TS3-11 (2.4-220.8 %). The strain at break of TS5-05 (70.1-128.1 %) was also very high. In addition, TS5-05 and TS3-11 had the highest stress and strain at yield.

As shown in Table 4 and Figure 4, the strain rate had a significant effect on the tensile properties of polyurethane films. Generally, the stress at break and modulus increased with strain rate and strain at break decreased with strain rate. The stress at break increased from 1.2 to 2.4 MPa in TS5-05 and from 19.8 to 30.1 MPa in TS4-11. The stress at break of TS4-09 and TS3-11 increased with increasing strain rate, however stress at break with 20 mm/min was lower than that with 10 mm/min because the films fractured at a much lower strain. Specifically, the strain at break of TS3-11 decreased significantly with a strain rate of 20 mm/min. The above-mentioned stress-strain behaviors of polyurethane films are shown in Figure 5.

The results of the bending tests of the polyurethane films are shown in Table 5 and Figure 6. The stress at break and the bending modulus increased with starch content and -NCO/-OH molar ratio and the deflection at break decreased. Similarly to the tensile test results, the strain rate of the bending test had a significant effect on the bending properties. Using a 1-mm/min crosshead speed, the stress at break of TS4-11 (14.5 MPa) was higher than those of TS4-09 (2.5 MPa) and TS3-11 (2.1 MPa). The bending modulus of TS4-11 (467.1 MPa) was also higher than those of TS4-09 (83.4 MPa) and TS3-11 (155.4 MPa), however the deflection at break of TS4-11 (0.9 mm) was lower than those of TS4-09 (1.0 mm) and TS3-11 (5.0 mm). TS5-05 had the highest stress at break (23.3 MPa) and bending modulus (467.1 MPa). Using a 10-mm/min crosshead speed, the bending modulus of TS4-11 (559.8 MPa) was higher than those of TS4-09 (298.2 MPa) and TS3-11 (404.8 MPa), and TS5-05 had the highest value (570.5 MPa) of bending modulus. The deflection at break of TS4-11 (0.5 mm) was lower than those of TS4-09 (0.7 mm) and TS3-11 (0.9 mm), however the stress at break of each sample did not exhibit regularity. Generally, the bending modulus at 10 mm/min was higher than that at 1 mm/min and the deflection at break was lower, however the stress at break for most of the samples at 10 mm/min, except for TS3-11, was lower than that at 1 mm/min.



**Figure 5.** Stress-strain curves of (a) TS5-05, (b) TS4-11, (c) TS4-09, and (d) TS3-11 polyurethane films.

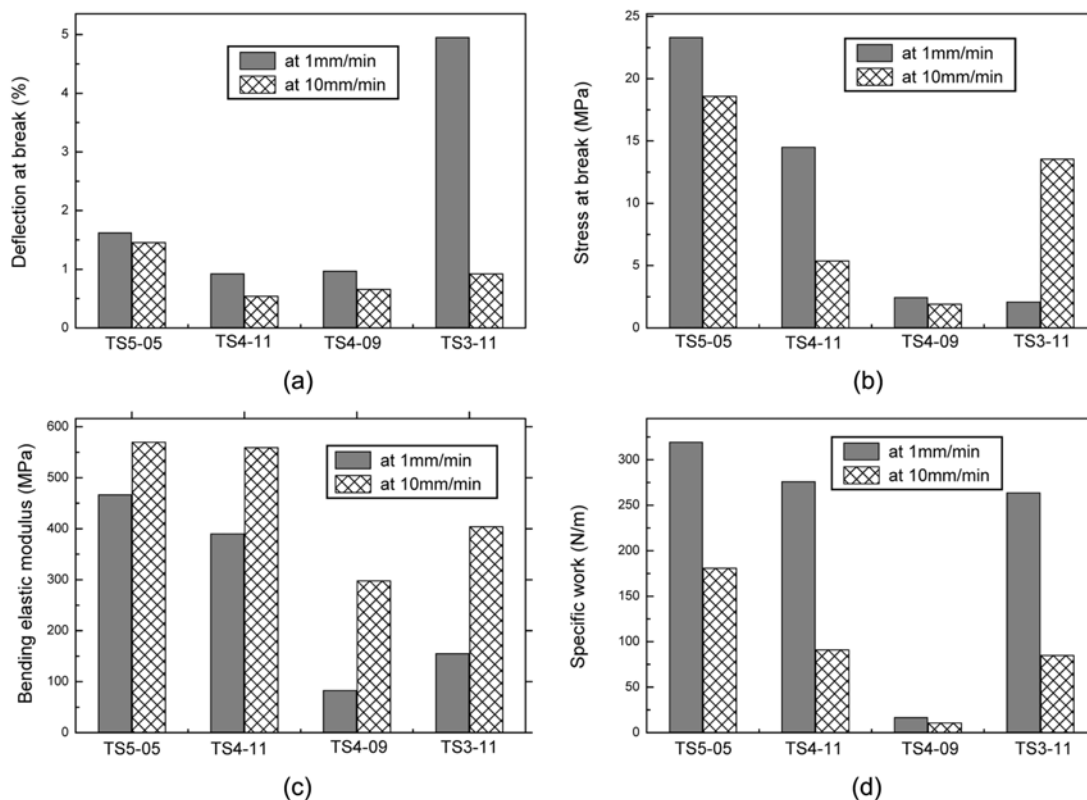
**Table 5.** Bending test results of polyurethane films

Samples	Deflection at break (mm)	Stress at break (MPa)	Bending elastic modulus (MPa)	Specific work (N/m)
TS5-05-01 <sup>1)</sup>	1.6	23.3	467.1	319.7
TS5-05-10	1.5	18.6	570.5	181.1
TS4-11-01	0.9	14.5	390.5	276.2
TS4-11-10	0.5	5.4	559.8	91.4
TS4-09-01	1.0	2.5	83.4	16.9
TS4-09-10	0.7	1.9	298.2	11.0
TS3-11-01	5.0 (2.0)	2.1 (2.8)	155.4	263.8
TS3-11-10	1.0	13.6	404.8	85.2

<sup>1)</sup>TS5-05-01 means TS5-05 was bended at 1 mm/min, <sup>2)</sup>( ): deflection and stress at maximum.

## Conclusion

In this study, polyurethane films with starch as the main polyol component were prepared and their mechanical properties were investigated. Due to the melting behavior of polyurethane, films could be prepared by hot pressing at an appropriate temperature. The formation of urethane and urea linkages was confirmed by FT-IR analysis. Two endothermic peaks were observed by DSC analysis. From tensile testing, the stress at break and modulus were observed to increase significantly with starch content and -NCO/-OH molar ratio. From the bending tests, the stress at break and the bending modulus were observed to increase with starch content and -NCO/-OH molar ratio while deflection at break decreased. In addition, the strain rate in both the tensile and bending tests had a significant effect on mechanical properties.



**Figure 6.** Bending properties of polyurethane films; (a) deflection at break, (b) stress at break, (c) bending modulus, and (d) specific work.

### Acknowledgements

This work was supported by the SRC/ERC program of MOST/KOSEF (R11-2005-065).

### References

- R. P. Ellis, M. P. Cochrane, M. F. P. Dale, C. M. Duffus, A. Lynn, I. M. Morrison, R. D. M. Prentice, J. S. Swanston, and S. A. Tiller, *J. Sci. Food. Agr.*, **77**, 289 (1998).
- I. Arvanitoyannis, C. G. Biliaderis, H. Ogawa, and N. Kawasaki, *Carbohydr. Polym.*, **36**, 89 (1998).
- P. B. Shah, S. Bandopadhyay, and J. R. Bellare, *Polym. Degrad. Stabil.*, **47**, 165 (1995).
- Z. Yang, M. Bhattacharya, and U. R. Vaidya, *Polymer*, **37**, 2137 (1996).
- N. S. Pierra, B. D. Favis, B. A. Ramsay, and J. A. Ramsay, *Polymer*, **38**, 647 (1997).
- D. Zuchowska, R. Steller, and W. Meissner, *Polym. Degrad. Stabil.*, **60**, 471 (1998).
- B. T. Nwufu, *J. Appl. Polym. Sci.*, **23**, 2023 (1985).
- A. S. Sokhey, A. N. Kollengode, and M. A. Hanna, *J. Food Sci.*, **59**, 895 (1994).
- N. L. Lacourse and P. A. Altieri, *U.S. Patent*, 4863655 (1989).
- D. Bikiaris, J. Prinios, and C. Panayiotou, *Polym. Degrad. Stabil.*, **56**, 1 (1997).
- S. C. Warburton and A. M. Donald, *J. Mater. Sci.*, **25**, 4001 (1990).
- G. Oertel, "Polyurethane Handbook", Hanser Publishers, Munich, 1985.
- S. K. Ha and H. C. Broecker, *Polymer*, **43**, 5227 (2002).
- S. D. Desai, J. V. Patel, and V. K. Sinha, *Int. J. Adhes. Ades.*, **23**, 393 (2003).
- Y. Yao, M. Yoshioka, and N. Shiraishi, *J. Appl. Polym. Sci.*, **60**, 1939 (1996).
- X. Cao, L. Zhang, J. Huang, G. Yang, and Y. Wang, *J. Appl. Polym. Sci.*, **90**, 3325 (2003).
- R. Garcon, C. Clerk, J. P. Gesson, J. Bordado, T. Nunes, S. Caroco, P. T. Gomes, M. E. M. D. Piedade, and A. P. Rauter, *Carbohydr. Polym.*, **45**, 123 (2001).
- S. Ryabov, N. Kotelnikova, Y. Kercha, S. Laptiy, R. Gaiduk, L. Kosenko, and Yakovenko, *Macromol. Symp.*, **164**, 421 (2001).
- R. L. Cunningham, M. E. Carr, and E. B. Bagley, *J. Appl. Polym. Sci.*, **44**, 1477 (1992).
- J. Ge, W. Zhong, Z. Guo, W. Li, and K. Sakai, *J. Appl. Polym. Sci.*, **77**, 2575 (2000).
- S. H. Lee, Y. Teramoto, and N. Shiraishi, *J. Appl. Polym. Sci.*, **83**, 1482 (2002).

22. B. K. K. Swamy and Siddaramaiah, *J. Appl. Polym. Sci.*, **90**, 2945 (2003).
23. S. K. Ha and H. C. Broecker, *Macromol. Mater. Eng.*, **288**, 569 (2003).
24. R. L. Cunningham, M. E. Carr, E. B. Bagley, S. H. Gordon, and R. V. Greene, *J. Appl. Polym. Sci.*, **51**, 1311 (1994).
25. D. H. Kim, O. J. Kwon, S. R. Yang, J. S. Park, and B. C. Chun, *Fibers and Polymers*, **8**, 155 (2007).