ELSEVIER

Polymer 43 (2002) 5227–5234

polymer

www.elsevier.com/locate/polymer

Characteristics of polyurethanes incorporating starch granules

Seung-kyu Ha, H.C. Broecker*

Chemie und Chemietechnik, Universität Paderborn FB 13, 33098 Paderborn, Germany

Received 21 August 2001; received in revised form 27 May 2002; accepted 29 May 2002

Abstract

Polyurethanes containing different starch contents were synthesized in a one-step reaction by suspending starch granules in polycaprolactone diol, MDI and 1,4 butane diol in a bulk phase at 175 °C. The products were characterized by FTIR spectroscopy, SEM, DSC, and swelling behavior. Their mechanical properties, e.g. tensile strength and elongation, were measured for different starch contents. The starch dispersed well as a grafted state in the polyurethane phase. The grafted percentage of polyurethane to starch granules increased with the starch content to a maximum point (about 20 wt%) and then decreased due to gapping between the two phases and probably the homo-polymerization tendency of the polyurethane. The DSC indicated that T_g increased with the starch content due to the decreased average molecular weight of the homo-polyurethane. Three endothermic transitions at 60–70 °C (I), ~150 °C (II), 190–210 °C (III) were observed. Transition I was not changed by the starch content, whereas transition II appeared only for the psb2m3 series (32–48 wt% hard segment) at the lower range of 26 wt% of starch content. The temperature of transition III, which is related to the melting point of the hard segments, increased with the starch content despite a decrease in the molecular weight of the homo-polyurethane. The tensile strength and the elongation of the polymers slightly increased or were constant up to about 20 wt% of starch, and then decreased rapidly because of phase separation (gapping) between the starch granules and the polyurethane phase and division of the starch granules.

Keywords: Starch; Grafting; Polyurethane

---

1. Introduction

World production of native starch is high and inexpensive; This leads to enormous interest in studying its uses. Studies carried out concerning the use of starch, hitherto, are related to the blending of synthetic polymers with starch. The blending of starch granules with synthetic polymers generally results in a filler effect on the polymer properties [1–3].

When the starch content in a polymer is increased, elongation to break and tensile strength decrease [4,5], but the modulus increases [6] due to the stiffening effect of the starch granule. The main reason for the lowering of the mechanical properties of the starch polymer blends could be explained by different properties of the starch and the synthetic polymers such as hydrophilic starch and hydrophobic synthetic polymer. Therefore, many researchers have tried to modify the surface of the starch granule [7–10] and also used the de-structured starch [11–13], introducing the compatible component by grafting with starch.

In this study, without any modification to increase the compatibility of the starch, we directly utilized the hydroxyl group of the starch granule surface for the urethane reaction in the polymerization process with the polyurethane. Polycaprolactone diol ($M_n = 2000$), MDI and 1,4 butane diol as reactants could produce linear thermoplastic polymers, but as starch has a large granule having polyol and sphere-like granule, could be imagined a 3D network structure of the products. Furthermore, we adapted a high temperature bulk reaction at 175 °C bearing in mind reactive polymerization in an extruder. The purpose of the study is to understand the structure and properties of such a polyurethane system incorporated with starch granules.

2. Experimental

2.1. Materials

The basic materials used in this research were 1.4-butane diol and polycaprolacton diol ($M_n \cong 2000$) and 4,4-diphenylmethane diisocyanate (MDI, 98%) from Aldrich Chemical Company. Merck supplied dibutyltin dilaurate

---

* Corresponding author. Tel.: +49-5251-603616; fax: +49-5251-603244.

E-mail address: mbroe1@tc.uni-paderborn.de (H.C. Broecker).

0032-3861/01/$ - see front matter
PII: S0032-3861(02)00344-0

Table 1
Potato starch description

Description	
Protein content	$<0.13\%$
Starch total	
Polarimetric ewers procedure	$>98\%$
Megazyme procedure	$>98\%$
Amylose content	~30–34%
Particle size	~37 μm
Lipid content	No lipid
Hydroxyl number of the granule surface	41.7
Ash content	$<0.63\%$

(DBTDL) used as a catalyst. All the chemicals were used as such without further purification. Potato starch was kindly supported by the Institute for Cereal, Potato and Starch Technology (in Detmold, Germany). Tables 1 and 2 show the specifications of the potato starch and chemicals used.

2.2. Synthesis

Polycaprolactone diol and 1.4-butane diol were added to a 2 l reaction flask equipped with a heating mantel, stirrer, thermometer, and vacuum inlet. Each diol was heated to 100 °C and degassed for 1 h to remove moisture and dissolved gases. The temperature of the diol was then increased to 175 °C while degassing was continued under vacuum. The pre-measured hydroxyl (–OH) value of potato starch was poured into the reactor in order to have longer pre-mixing with polycaprolactone diols and dried again under vacuum at 175 °C. After this pre-blending of the diols, the dibutyltin dilaurate (DBTDL) catalyst and 4,4-diphenylmethane diisocyanate (MDI) were added. The mixture was stirred vigorously for about 1 min, degassed for 30 min and transferred to an aluminum tray that had previously been treated at 100 °C with a silicon release agent. It was then placed in an oven and cured at 120 °C for 4 h. After removal from the oven, the samples were removed from the mold and post-cured at room temperature for one week before further characterization.

2.3. Characterizations

2.3.1. Scanning electron microscopy (SEM)

The specimens were mounted on aluminum stubs using double-sided carbon tape and were coated with gold–palladium to a thickness of about 2 μm in a sputter coater. The coated specimens were observed in a SEM (Hitachi H301U). An accelerating potential of 10 kV was used for the analysis of samples. The micrographs of representative areas of the samples were taken at various magnifications.

2.3.2. Differential scanning calorimetry (DSC)

The transition behavior of the polyurethane incorporating starch was characterized using differential scanning calorimetry (Mettler TC 10A/TC 15, TA controller). The samples were quenched using liquid N_2 to the required temperature and then scanned at a rate of 10 °C/min in a dynamic nitrogen atmosphere with a flow rate of 6 cm^3/min. The sample size was 30 ± 1 mg. The temperature scale was calibrated with an indium standard before the experiments. Indium has a melting temperature of 156.6 °C and a heat of fusion of 28.45 J/g. The glass transition temperature (T_g) was measured at the point of intersection between tangents drawn at the point of inflection of transition and at the flat part of the curve before transition.

2.3.3. Fourier transformation infrared spectroscopy (FTIR)

The sample was fully dissolved in dimethylsulfoxide and dropped onto a NaCl salt plate. The dried extracted polyurethane was recorded in the transmittance mode. FTIR spectra were obtained using a Nicolet 510 P FTIR spectrometer at a range of 4000–400 cm^{-1} and resolution was maintained at 2 cm^{-1}.

2.3.4. Grafted percentage

Polyurethane incorporating starch was extracted with a mixed solvent (DMF (95%) + THF (5%)) to remove the homo-polymer of polyurethane in the sample. One gram of the blended samples was thinly sliced and stored in 25 ml of solvent for 24 h at room temperature. It was then washed by decanting four times in 25 ml of fresh solvent. The washed blends were dried at 100 °C in a vacuum for three days. In this study, we defined the polyurethane grafted to starch as follows:

$$\text{Grafted (\%)} = \frac{\text{weight of PU remaining after extraction}}{\text{weight of PU before extraction}} \times 100 \qquad (1)$$

2.3.5. Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution were measured using a GPC equipped with a Waters 515 HPLC pump/717 auto-sampler/410 differential Refractometer

Table 2
Chemicals used for the synthesis of polyurethane

Materials	Description	Source
Polycaprolactone diol (M_n 2000)	Molecular weight: 2000, softening temperature: 50 °C	Aldrich
4,4-Diphenylmethane diisocyanate (MDI, 98%)	$F_p = 42–44$ °C	Aldrich
1.4-Butane diol	$B_p = 230$ °C	Aldrich
Dibutyl tin dilaurate (DBTDL, 98%)	–	Merck

and Styragel HR 4 (MW 5000–600 000) column. The mobile phase was tetrahydrofuran (THF) at a rate of 1.0 ml/min and the column temperature was maintained at 35 °C. Polystyrenes with six different molecular weights were used as standards. All samples were prepared in DMF and THF at a concentration of 0.01 (w/v). Number-average (M_n), weight average (M_w), and polydispersity (M_w/M_n) were calculated using Waters Chromatography Millennium software.

2.3.6. Polymer mechanical properties

Specimens for tensile testing were compression molded in a Lauffer und Butscher compression molder at 200 kg/cm^2. The detailed dimension of test specimen bars was in the form of dumbbells according to DIN (EN ISO 527-2). Tensile specimens were dried in a vacuum drying oven at 10 mm Hg at 100 °C for 5 h. The tensile mechanical properties of the polyurethanes incorporating with starch were measured using a Zwick (Material prüfung 1446) machine. The specimens were fixed using a grip with a tensiometer. A crosshead speed of 50 mm/min with a 0.1 N/mm^2 load cell was used at room temperature.

3. Results and discussion

3.1. Characterization

3.1.1. Scanning electron microscopy

Polyurethane incorporating starch. The dispersion of the starch in the continuous polyurethane phase and the adhesion between them were confirmed by SEM. Fig. 1 shows the SEM micrographs of p7s3b2m3. The surface of the sample for the SEM was prepared by breaking the samples at liquid nitrogen temperature. As shown in Fig. 1, the starch granules are well dispersed in the polyurethane phase without any aggregation. The scanned surface reveals that some starch granules were broken into two parts and others were completely coated by a tightly adhering polyurethane layer. Some gaps were found between the starch and polyurethane phases in which stretched polyurethane threads connect the two phases. This also confirms the strong adhesion between the polyurethane and the surface of the starch granules. This phenomenon as evidence of grafting between the starch and polyurethane, as shown in Fig. 2, is supported in previous reports in which Suh et al. [14] also confirmed such an adhesion between polyethylene terephthalate and low-density polyethylene blends with isocyanate. The SEM micrographs show that the potato starch has a relatively large granule size that is not de-structured during the reactions.

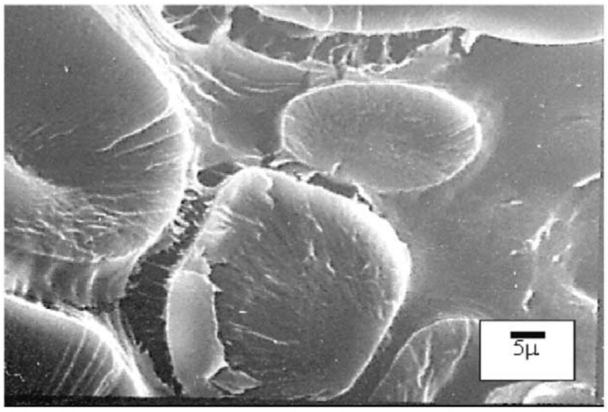


Fig. 1. Cryogenically fractured SEM micrograph for p7s3b2m3 (25.7 wt% of starch) (magnification: × 1000).

Polyurethane-extracted starch. The evidence of starch grafted with a polyurethane phase was also confirmed directly by comparing SEM micrographs of homo-polymer-extracted starch with pure starch granules. Extraction was carried out with a mixed solvent, DMF(95%) + THF(5%), at ambient temperature for 5 days. The surface of pure starch is clean and in its original shape (Fig. 2(a)). The sample after extraction with the mixed solvent (Fig. 2(b)) shows a layered polyurethane phase on the surface of the starch granule.

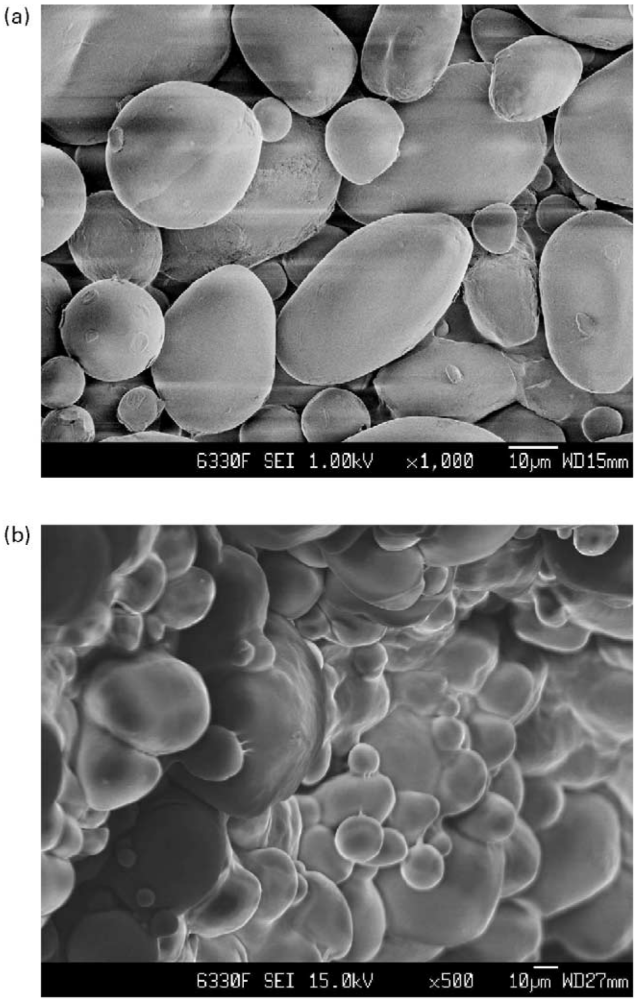


Fig. 2. SEM micrographs for (a) pure potato starch and (b) homo-polymer-extracted starch (p5s5b2m3).

3.1.2. Infrared spectroscopy

IR spectrograms for the polyurethane incorporating starch (p9s1b4m5 (7.31 wt% starch) and p7s3b4m5 (21.1 wt% starch)) are shown in Fig. 3. Fig. 3 shows the broad OH and NH bands due to un-reacted –OH. There is a band at ~3440 cm^{-1} that can be contributed to the bonded NH band of the polyurethane over the broad OH band. A bonded carbonyl band ~1703–1732 cm^{-1} can also be observed. These two bands also confirm the grafting between the starch and polyurethane phase.

3.1.3. Differential scanning calorimetry

In this study, one glass transition T_g and three endothermic transitions associated with the hard segments of the polyurethane phase were observed at 40–70 °C (endotherm I), 120–190 °C (endotherm II) and above 200 °C (endotherm III) as shown in Fig. 4. The three endothermic peaks were associated with different morphologies of the hard segments of the polyurethane phase. Yoon and Han [15] indicated that these endotherms are quite sensitive concerning the thermal processing history and annealing conditions. Therefore, the phase transitions of polyurethane in our samples also had to be changed by starch addition because of crosslinking between the starch and polyurethane. Furthermore, starch is a polyol that can produce a complicated and crosslinked network of samples.

The glass transition temperature T_g increased with the starch content due to increased hard segment concentration for the psb2m3 series. However, for the psb4m5 series that has a higher hard segment concentration than the psb2m3 series, T_g transition did not clearly appear and also disappeared at a high starch content level. Transition I can be attributed to the morphology of short-range hard segments [16,17] which are randomly distributed and decrease with starch content without a temperature change for the transition in both series of samples. Transition II can be attributed to dissociation of long-range ordering in the hard microphase and increases with the starch content up to 25.71 wt% (p7s3b2m3) for the psb2m3 series. At even higher starch contents, transition III appeared and the transition temperature increased with starch content despite decreased molecular weight, as shown in Table 3, and decreased space of the polyurethane phase. Therefore, the increase of crystalline melting transition III, due to the starch content, could be explained by the grafted polyurethane with the starch and crosslinking between starch granules, which enhanced the hard segment arrangement due to the stretching behavior between two starch granules. The changes of T_g, T_m and ΔH_f for the psb2m3 and psb2m3 series are shown in Table 4 in which the hard segment

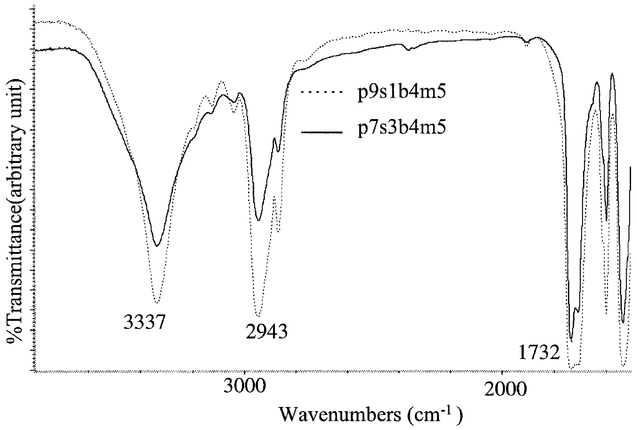
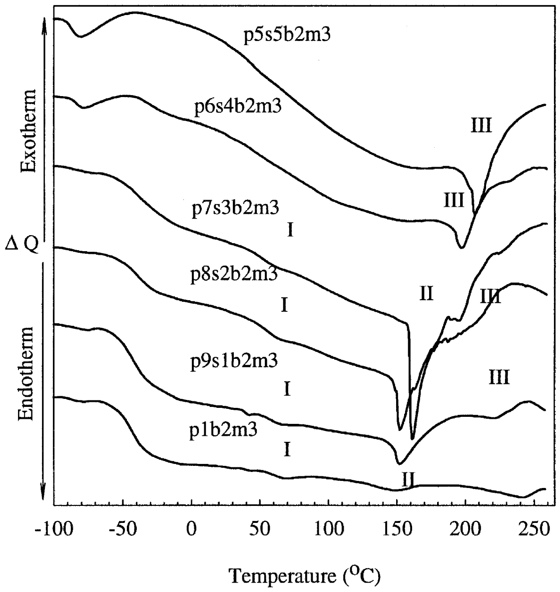
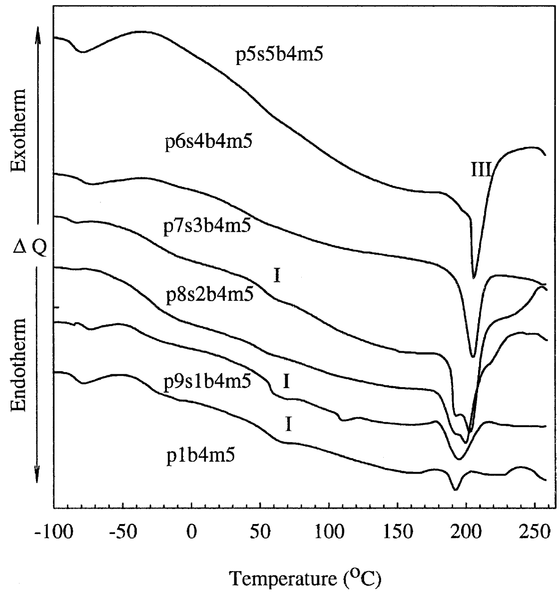


Fig. 3. IR spectra of (a) p9s1b4m5 (7.3 wt% starch) and (b) p7s3b4m5 (21.1 wt% starch) after solvent extraction.



(a) psb2m3



(b) psb4m5

Fig. 4. DSC thermograms of rapidly cooled compression-molded psb2m3 and (b) psb4m5 series. Heating rate, 10 °C/min.

Table 3
Average molecular weights of homo-polymers separated from polyurethane incorporated with starch in psb2m3 and psb4m5 series

psb2m3 Series	M_n	M_w	M_w/M_n	psb4m5 Series	M_n	M_w	M_w/M_n
p1b2m3	116 900	266 110	2.27	p1b4m5	127 680	258 641	2.02
p9s1b2m3	136 878	260 584	1.90	p9s1b4m5	79 141	149 139	1.88
p8s2b2m3	102 439	192 829	1.88	p8s2b4m5	55 515	89 087	1.60
p7s3b2m3	49 979	75 613	1.51	p7s3b4m5	47 568	71 385	1.50
p6s4b2m3	55 751	93 753	1.68	p6s4b4m5	32 767	44 751	1.36
p5s5b2m3	32 254	42 795	1.32	p5s5b4m5	31 073	42 063	1.35

concentrations in the polyurethane phase increased as indicated in Table 5 (31.7 → 48.19 wt% for psb2m3, 44.6 → 61.69 wt% for psb4m5). In the case of the psb4m5 series, endotherm peaks III clearly appeared because of higher hard-segment concentrations.

The total heat of fusion related to transitions I–III increased with the starch content up to 20–25 wt%. This trend agrees with change of mechanical properties as shown in Fig. 7. As shown in Fig. 1, it is suggested that the grafted polyurethane phase aligned from the starch granule surface to polyurethane phase in a stretched form, which may increase the transition temperature.

Grafted percentage of polyurethane for various starch contents. The percent of grafting was defined as the weight of the polyurethane remaining on the starch after solvent extraction in relation to the weight of polyurethane with starch before extraction. Therefore, if there is crosslinking between polyurethane chains, this grafted percentage will be larger in comparison to the non-crosslinked fraction. However, we used this percentage as a parameter of grafting. The grafted weight percent was measured at various starch contents. As shown in Fig. 5, the grafted % increased up to 20–25% of starch and then decreased.

The decrease in the percentage of grafting at a higher content of starch may be ascribed to the gapping (phase separation) between the polyurethane phase and starch granule probably due to the homo-polymerization tendency of the polyurethane phase as indicated in the grafting of polypropylene [18]. It is believed that the appeared gap in SEM micrographs, as shown in Fig. 10, at high starch contents confirms this.

3.1.4. Swelling behavior

To identify the crosslink-density of the polymers, a swelling test was carried out with THF solvent for two series of the samples. As expected Fig. 6 shows that, swelling decreases with the starch content due to the increased crosslinking of the polymers. Even in the samples of the non-starch p1b2m3 and p1b4m5, the solvent uptakes were measured without the solution of the polyurethane.

3.1.5. Average molecular weight of polyurethane homo-polymer

All the polyurethane phase was separated from the starch granules by using a strong mixed solvent (DMF (95%) + THF (5%)), long agitation (12–48 h) and a high temperature (70–80 °C). Table 3 shows the results for two series of the samples psb2m3 and psb4m5. As expected, the average molecular weight of homo-polyurethane decreased with the starch content. This decrease could be explained by the decrease of pre-polymer content in the reactant as well as a decrease in the space of the polyurethane phase between starch-granules. It could be shown that the average molecular weights were high possibly due to the cross-linking between polyurethane-chains, which may have increased the molecular weight.

Table 4
Soft segment T_g, hard segment T_m and heats of fusion for two series of sample

Samples	T_g (°C)	T_m (°C)			ΔH_f (J/g)			$\Delta H_{f,total}$ (J/g)
		I	II	III	I	II	III	
p1b2m3	−45.09	67.86	147.36	242.42	0.98	2.81	3.27	7.06
p9s1b2m3	−45	65.54	152.36	222.75	0.88	7.4	2.07	10.35
p8s2b2m3	−42.43	64.30	152.44	206.53	1.13	8.6	3.38	13.11
p7s3b2m3	−42.75		161.52, 196.39			17.02, 2.15		19.17
p6s4b2m3	−30.19		198.32			9.48		9.48
p5s5b2m3	−8.32			207.14			11.74	11.74
p1b4m5	−35.26	64.19	192.48	228.29	1.55	1.97	1.35	4.87
p9s1b4m5	−38.11	63.36	109.74, 194.86		1.11	0.46, 7.95		9.52
p8s2b4m5	−41.70	56.91		200.13	0.64		16.28	16.92
p7s3b4m5	−22.18			205.56			13.80	13.80
p6s4b4m5	−38.59			208.85			9.88	9.88
p5s5b4m5	−48.18			211.39			11.47	11.47

Table 5
Molar ratios in the synthesis of polyurethane incorporating starch (OH/NCO mole ratio = 1)

Sample	Starch–OH	PCL–OH	1,4-Butane diol	MDI	Hard segment (wt% in polyurethane phase)	Starch (wt%)
p1b2m3	0.0	1.0	2	3	31.74	0.0
p9s1b2m3	0.1	0.9	2	3	34.07	8.96
p8s2b2m3	0.2	0.8	2	3	36.76	17.53
p7s3b2m3	0.3	0.7	2	3	39.91	25.71
p6s4b2m3	0.4	0.6	2	3	43.66	33.55
p5s5b2m3	0.5	0.5	2	3	48.19	41.05
p1b4m5	0.0	1.0	4	5	44.60	0.0
p9s1b4m5	0.1	0.9	4	5	47.21	7.31
p8s2b4m5	0.2	0.8	4	5	50.16	14.35
p7s3b4m5	0.3	0.7	4	5	53.49	21.13
p6s4b4m5	0.4	0.6	4	5	57.30	27.67
p5s5b4m5	0.5	0.5	4	5	61.69	33.96

3.1.6. Mechanical properties

The results for the tensile strength and elongation percent for two series are presented in Fig. 7(a) and (b). As shown in the figures, the tensile strength and elongation percent are either improved or not changed for the lower range of starch contents. As shown above, at low starch contents for the psb2m3, the average molecular weights of homo-polyurethane are similar to one another and the grafted weight increased as shown in Fig. 5. The slight increase or non-change in the tensile strength and elongation at a lower starch content could be caused by several parameters such as the molecular weight of homo-polyurethane, grafted percentage, degree of crosslinking and the development of the hard-segment formation in the polyurethane phase. The heat of fusions appearing in Table 4 could also be related to the tensile strength. However, we cannot correlate them with these parameters. We plotted the mechanical properties with swelling uptake as crosslinking parameter in Figs. 8 and 9.

As shown in the figures, elongation is constant or slightly increased with the decrease of solvent uptake up to 1.5 or 2 and then rapidly decreases. For the tensile strength, although the data were scattered, at the higher range of the solvent uptake they slightly increased with the uptake, but they decreased rapidly for the high range of crosslinking.

Fracturing of the starch granules and/or gapping between two phases, which define the limit of the tensile strength of the samples, may cause the rapid decrease of tensile strength and the elongation in the range of high starch content. Fig. 10 shows the fractured surface of a tensile bar of p5s5b4m5 (starch ~ 34 wt%). Phase separation between starch granule and polyurethane phase, and division of the starch granules into two parts can be seen on the SEM micrograph. The hole appearing in the figure is small compared to the mean size of the starch granules, which indicates a small area of the starch granule was stripped when the bar was broken.

4. Conclusions

The polyurethane was synthesized with a pre-polymer of

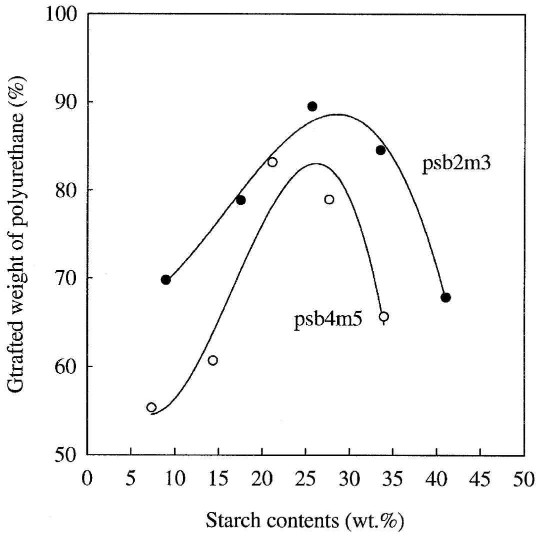


Fig. 5. Grafted wt% of starch for two series of the sample.

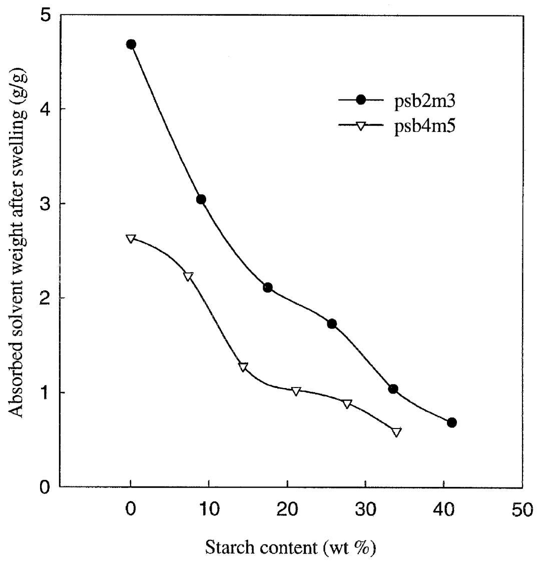


Fig. 6. Swelling behavior of polyurethane incorporating starch for two series of samples, psb2m3 and psb4m5.

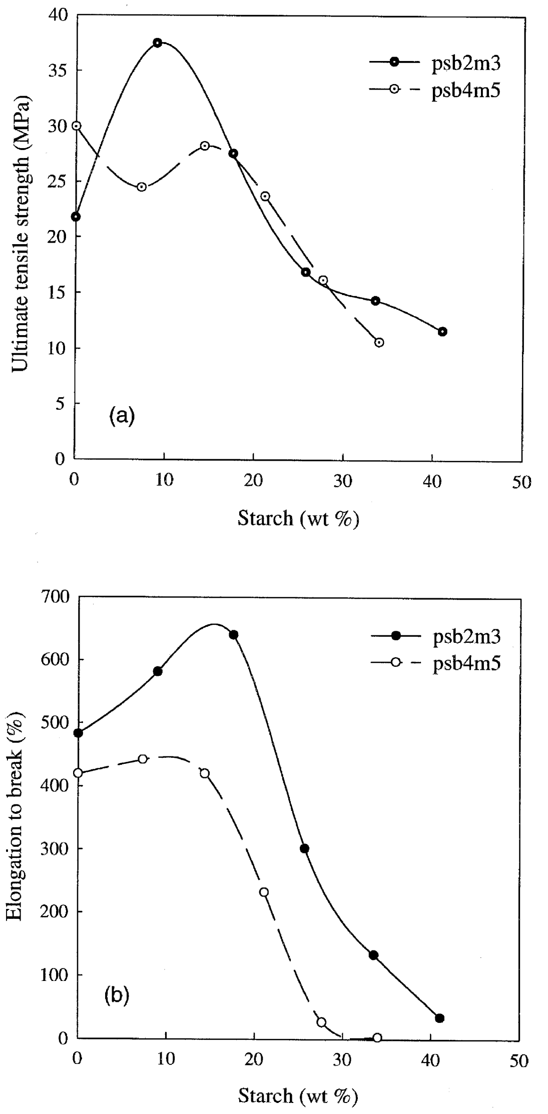


Fig. 7. Tensile strength (a) and elongation (b) as a function of starch content for psb2m3 and psb4m5 series.

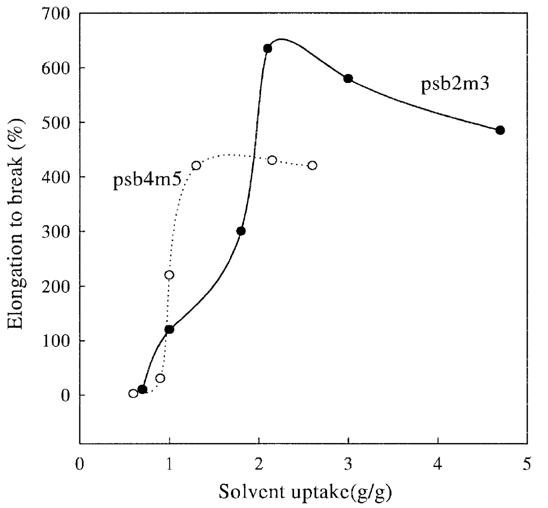


Fig. 8. Elongations to break as a function of solvent uptake (crosslinking parameter) for two series of sample.

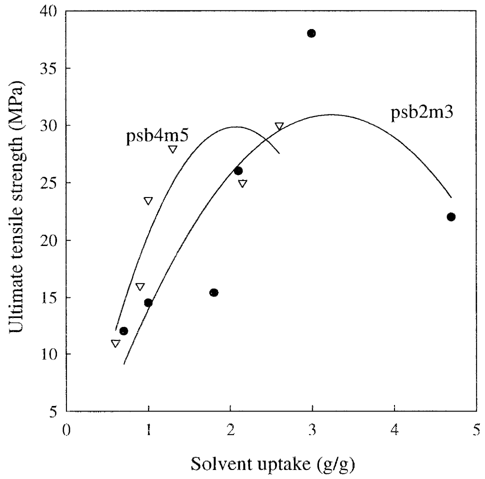


Fig. 9. Tensile strengths as a function of solvent uptake for two series of sample.

polycaprolactone diol ($M_n = 2000$), MDI, and 1,4 butane diol in the presence of starch granules (polyol) in a bulk phase at 175 °C to understand their characteristics for the use of starch as a raw material in a polyurethane system. The starch granules were well dispersed without shape modification of the granule in the continuous polyurethane phase and there was crosslinking between the starch granules and between the polyurethane chains. The grafted percentage increased to about 20 wt% and then decreased in the range of high starch content due to the homo-polymerization tendency of polyurethane at the higher starch content, which produced phase separation between the two phases. The average molecular weight of the homo-polymer separated from the samples decreased with the starch content due to the diminishing of pre-polymer concentration of polycaprolactone as well as the limited space between starch grains. The incorporation of polyurethane with starch granules improved the tensile strength and elongation of the samples at the lower starch content up to about 20 wt%, but these properties decreased rapidly for the higher range

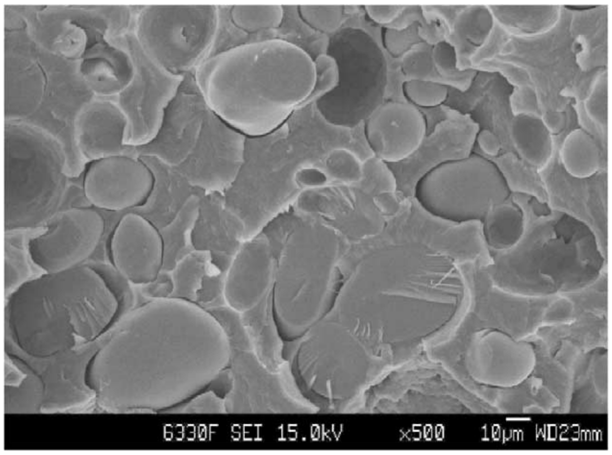


Fig. 10. SEM-image of the fractured surface of a tensile bar of p5s5b4m5 at ambient temperature after tensile test.

of starch content due to phase separation between the starch granules and polyurethane phase causing lowering of the grafting and fracturing of the starch granules. Therefore, it is considered that polyurethane incorporating starch granules could be used without loss of mechanical properties up to 20 wt% of the starch granule.

References

[1] Evangelista RL, Nikolov ZL, Sung W, Jane J, Gelina RJ. Ind Engng Chem Res 1991;30:1841.

[2] Breslin VT, Li BJ. J Appl Polym Sci 1993;1:127.

[3] Willett JL. J Appl Polym Sci 1994;54:1685.

[4] St-Pierre N, Favis BD, Ramsay BA, Ramsay JA, Verhoogt H. Polymer 1997;38:647.

[5] Lim S-T, lin JJ, Rajagopalan S, Seib PA. Biotechnol Prog 1992;8:51.

[6] Vaidya UR, Bhattacharya M, Zhang D. Polymer 1995;36:1179.

[7] Athawale VD, Rathi SC. J Appl Polym Sci 1997;66:1399.

[8] Abo-Shosha MH, Ibrahim NA. Starch/Stärke 1992;44:296.

[9] Bayazeed A, Elzairy MR, Hebeish A. Starch/Stärke 1986;41:233.

[10] Pfannemuller VB, Emmerling WN. Starch/Stärke 1983;35:298.

[11] Yoon KJ, Carr ME, Bagley EB. J Appl Polym Sci 1992;45:1093.

[12] Cunningham RL, Carr ME, Bagley EB. J Appl Polym Sci 1992;44:1477.

[13] Desai S, Thakore IM, Sarawade BD, Devi S. Polym Engng Sci 2000;40:1200.

[14] Park SH, Park KY, Suh KD. J Polym Sci, Part B 1998;36:447.

[15] Yoon PY, Han CD. Macromolecules 2000;33:2171.

[16] Hesketh TR, Van Bogart JWC, Cooper SL. Polym Engng Sci 1980;20:190.

[17] Seymour RW, Cooper SL. Macromolecules 1973;6:48.

[18] Yaz'ddani-Pedram M, Vega H, Quijada R. Macromol Rapid Commun 1996;17:577.