Characterization of Polyurethane Foam Prepared by Using Starch as Polyol

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ABSTRACT: Polyurethane foams were prepared using starch as a main component of polyols and their structural, mechanical, and absorbing properties for organic solvents were investigated. Fourier transform infrared spectra showed that urethane linkage was formed by the reactions between —NCO of diisocyanates and —OH of polyols. When polyurethane foams were prepared at high molar ratio of —NCO/—OH, the unreacted —NCO groups were detected. Also, urea linkage was formed by the reaction between diisocyanate and water, which was used as the foaming agent. The micrographs showed that the polyurethane foams had closed-cell structure, of which the cell size increased with —NCO/—OH molar ratio. The density of polyurethane foams increased with molecular weight of polyethylene glycol. The compressive moduli of polyurethane foams increased with —NCO/—OH molar ratio. Polyurethane foams prepared using toluene-2,4-diisocyanate as diisocyanate had the highest modulus, while those prepared using hexamethylene diisocyanate had the lowest modulus. In case of the absorbency for the organic solvents, the polyurethane foams prepared at —NCO/—OH molar ratio of 0.8 had the maximum absorbency. Among several organic solvents, the absorbency for dimethyl sulfoxide was the highest, while the absorbency for tetrahydrofuran was the lowest. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1544–1553, 2007

Key words: starch; polyurethane; absorbency; density; FTIR

INTRODUCTION

The environmental pollution problems related with petrochemicals have been recognized as serious problems for long years. Therefore the regulations on the consumption of plastic goods and bags are restricted more and more in the world. There are several disposition methods for the plastic waste: incineration, filling-up in landfill, recycling, and so on. However, the incineration and filling-up can induce additional environmental pollution, and in case of recycling, the difficulty of collecting the waste plastics and economic problems arise.

One of the efforts to resolve the environmental pollution is the development of environment-friendly biodegradable plastics.[1] The environment-friendly plastic polymers include synthetic polymer, biosynthetic polymer utilizing microorganisms, and natural polymers. The synthetic polymer is a polymer containing the microorganism-susceptible functional groups such as ester group. This polymer includes polycaprolacton, polylactide, polyvinyl acetate (PVA), polyester-amide, etc.[2,3] The biosynthetic polymer is a polymer that is produced by microorganism for their nutriments. This polymer includes polyhydroxyalkanoate (PHA), which is biodegraded completely. The problem in production on a large scale is yet to be solved.[4] The natural polymer is the inherently biodegradable polymer that exists in the nature abundantly. This polymer includes starch and cellulose.[5]

The urethane is the general name for polymer having the urethane linkage in their chain, and has various shapes and properties according to the polymerization methods. Because of its versatility, the urethane has been applied to many areas in our living environment. Among them, polyurethane foam has been watched as an oil-absorbent material to remove the spilled oil.[6–9]

However, because of the limited biodegradability, the problem arises in the disposal after being used as oil-absorbent. On the other hand, starch is the inherently biodegradable polymer existing abundantly in the nature. Therefore the starch has been recognized as substitutive materials for synthetic polymer for long years. The starch has —OH groups abundantly in their polymer chain, so it can be utilized as polyol for polyurethane. Thus, the preparation of polyurethane foams using starch can not only improve the biodegradability but also reduce the cost of polyurethane foams.[10]

TABLE I
Nomenclature of the Samples Made from Three Kinds of Diisocyanate

| Sample code[a] | Diisocyanate | Polyols (100 wt %) | | | | Water (w/w %)[c] | DBTDL (w/w %)[c] | −NCO/−OH molar ratio | Molecular weight of PEG |
		Starch (w/w %)	PEG (w/w %)[b]	Glycerol (w/w %)[b]	Butanediol (w/w %)[b]				
T-30-0.6-200	TDI	30	56	7	7	1	1	0.6	200
T-30-0.6-1000		30	56	7	7	1	1	0.6	1000
T-30-0.7-200		30	56	7	7	1	1	0.7	200
T-30-0.7-1000		30	56	7	7	1	1	0.7	1000
T-30-0.8-200		30	56	7	7	1	1	0.8	200
T-30-0.8-1000		30	56	7	7	1	1	0.8	1000
T-30-0.9-200		30	56	7	7	1	1	0.9	200
T-30-0.9-1000		30	56	7	7	1	1	0.9	1000
T-40-0.6-200		40	48	6	6	1	1	0.6	200
T-40-0.6-1000		40	48	6	6	1	1	0.6	1000
T-40-0.7-200		40	48	6	6	1	1	0.7	200
T-40-0.7-1000		40	48	6	6	1	1	0.7	1000
T-40-0.8-200		40	48	6	6	1	1	0.8	200
T-40-0.8-1000		40	48	6	6	1	1	0.8	1000
T-40-0.8-4000		40	48	6	6	1	1	0.8	4000
T-40-0.9-200		40	48	6	6	1	1	0.9	200
T-40-0.9-1000		40	48	6	6	1	1	0.9	1000
M-30-0.6-200	MDI	30	56	7	7	1	1	0.6	200
M-30-0.6-1000		30	56	7	7	1	1	0.6	1000
M-30-0.7-200		30	56	7	7	1	1	0.7	200
M-30-0.8-200		30	56	7	7	1	1	0.8	200
M-30-0.8-1000		30	56	7	7	1	1	0.8	1000
M-30-0.9-200		30	56	7	7	1	1	0.9	200
M-40-0.6-200		40	48	6	6	1	1	0.6	200
M-40-0.6-1000		40	48	6	6	1	1	0.6	1000
M-40-0.6-4000		40	48	6	6	1	1	0.6	4000
M-40-0.7-200		40	48	6	6	1	1	0.7	200
M-40-0.8-200		40	48	6	6	1	1	0.8	200
M-40-0.9-200		40	48	6	6	1	1	0.9	200
H-30-0.6-200	HDI	30	56	7	7	1	1	0.6	200
H-30-0.7-200		30	56	7	7	1	1	0.7	200
H-30-0.8-200		30	56	7	7	1	1	0.8	200
H-30-0.9-200		30	56	7	7	1	1	0.9	200
H-40-0.6-200		40	48	6	6	1	1	0.6	200
H-40-0.7-200		40	48	6	6	1	1	0.7	200
H-40-0.8-200		40	48	6	6	1	1	0.8	200
H-40-0.8-1000		40	48	6	6	1	1	0.8	1000
H-40-0.9-200		40	48	6	6	1	1	0.9	200

[a] Sample Code (A-B-C-D): A, kind of diisocyanate (T, M, H); B, wt % of starch (30%, 40%); C, −NCO/−OH molar ratio (0.6, 0.7, 0.8, 0.9); D, molecular weight of PEG (200, 1000, 4000). For example, T-30-0.6-200 means the sample that was prepared using TDI as diisocyanate, 30 w/w % of starch, 0.6 molar ratio of −NCO/−OH, and 200 molecular weight of PEG.
[b] The content ratio of PEG : glycerol : butanediol was fixed at 8 : 1 : 1 in all samples.
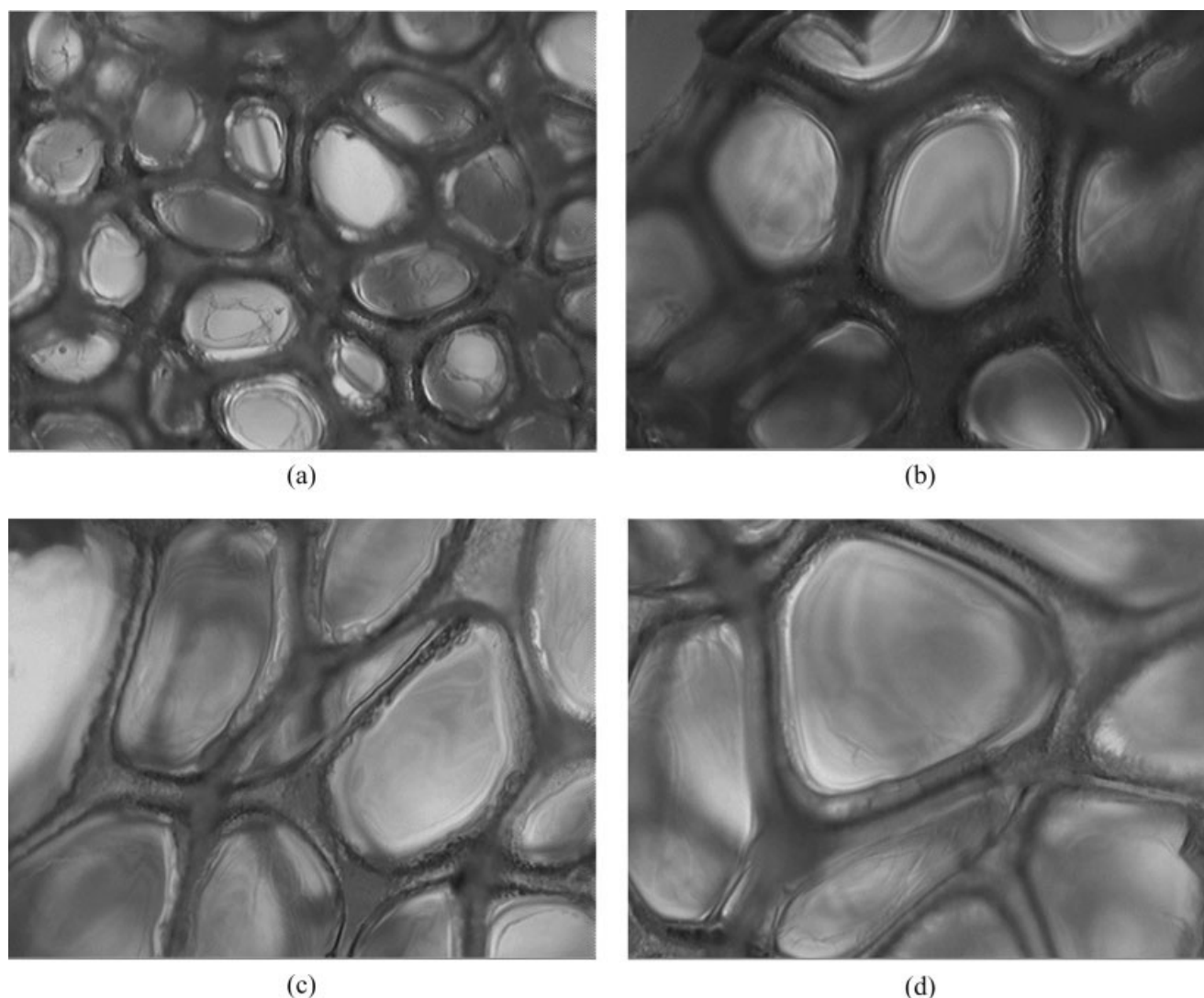[c] The w/w % of both water/polyol and DBTDL/polyol are fixed at 1%.

Figure 1 Optical micrographs of polyurethane foams as a function of —NCO/—OH molar ratio (×40); (a) 0.6 (T-30-0.6-200), (b) 0.7 (T-30-0.7-200), (c) 0.8 (T-30-0.8-200), and (d) 0.9 (T-30-0.9-200).

In this work, we prepared the polyurethane foams using starch as polyol, and studied the physical and chemical properties of foams prepared at various processing conditions, and also investigated the absorption properties of organic solvents, which could induce the environmental pollution when it flows out.

EXPERIMENTAL

Materials

The corn-starch was supplied by Samyang, Korea as powder containing amylase of 25–30 wt %. As polyol, starch, polyethylene glycol (PEG), glycerol, and 1,4-butanediol were used. Tolyene-2,4-diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI), and 4,4-diphenylmethane diisocyanate (MDI) were used as diisocyanates. Besides, distilled water was used as foaming agent, and dibutyltin dilaurate (DBTDL) was used as catalyst. PEG was supplied by Yakuri Pure Chemicals,

Japan, and was used as three types of molecular weight (200, 1000, and 4000). Glycerol that acts as crosslinking agent was supplied by Shinyo Pure Chemicals, Japan. 1,4-Butanediol that acts as chain extender was supplied by Daejung Chemicals and Metals, Korea. TDI and MDI were supplied by Kanto Chemical, Japan, and HDI was supplied by Wako Pure Chemical Industries, Japan. DBTDL was supplied by Lancaster, UK. All agents were used without purifying process.

Dimethlyformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) were organic solvents used for absorbency test of polyurethane foams, and all of them were supplied by Daejung Chemicals and Metals, Korea.

Preparation of polyurethane foams

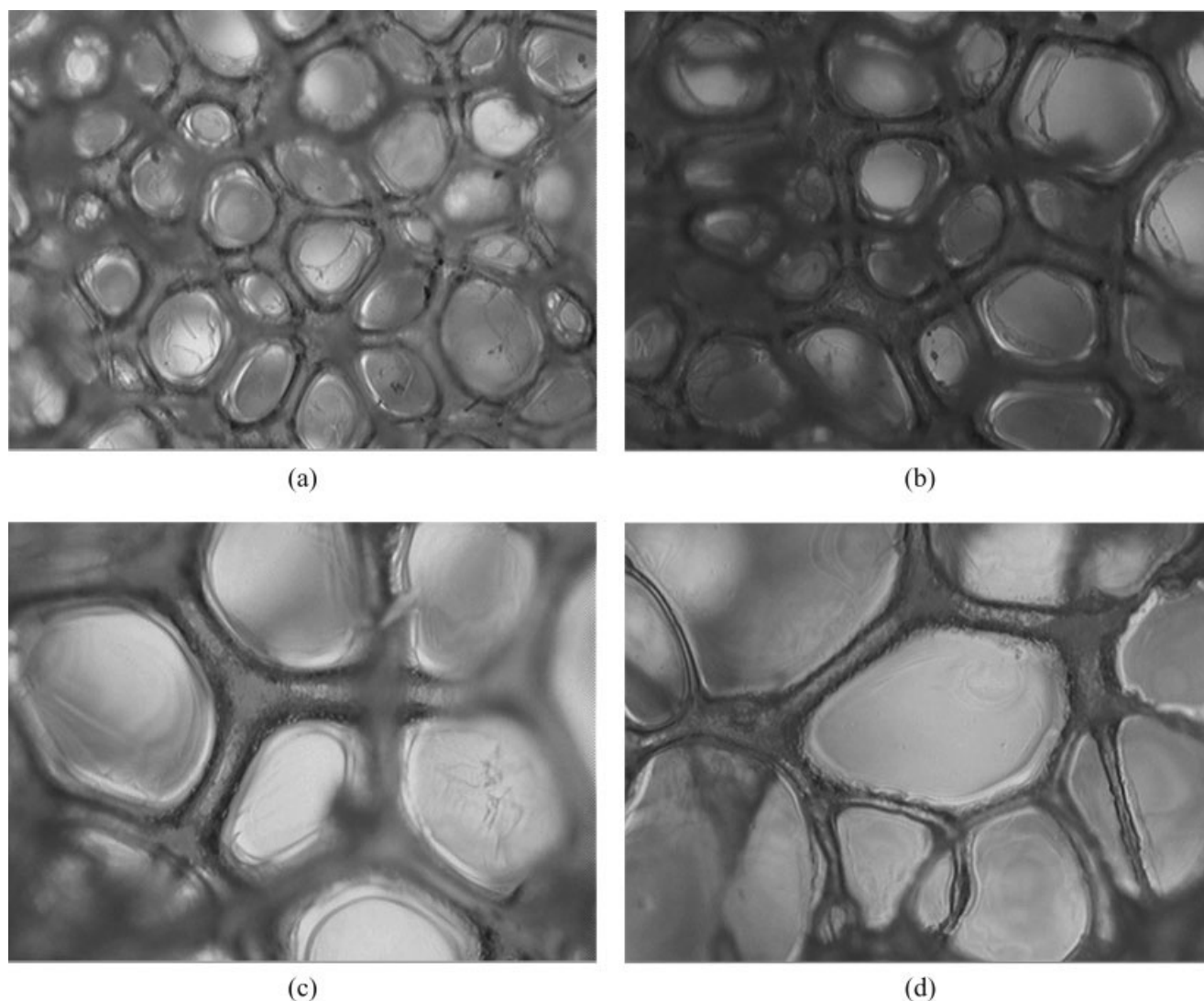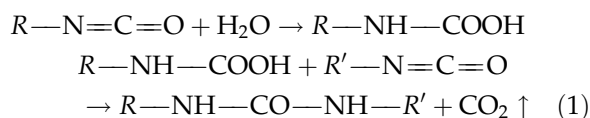A fixed weight ratio of polyols (starch, PEG, glycerol, and 1,4-butanediol) was mixed strongly in reactor with

Figure 2 Optical micrographs of polyurethane foams as a function of —NCO/—OH molar ratio (×40); (a) 0.6 (H-30-0.6-200), (b) 0.7 (H-30-0.7-200), (c) 0.8 (H-30-0.8-200), and (d) 0.9 (H-30-0.9-200).

a four-winged impeller at 100°C for 1 h for the starch to be fully gelatinized. After the mixture was cooled to 40°C with continuous stirring, a small quantity of DBTDL and distilled water were added as catalyst and foaming agent, respectively. The mixture was stirred vigorously for 1 min, and then diisocyanate (TDI, HDI, or MDI) was added. After being stirred vigorously for 30 s, the final mixture was poured into the mold (width × length × height = 12 cm × 12 cm × 10 cm). The reaction between water and diisocyanate is shown in eq. (1). Because of the carbon dioxide (CO_2) generated by this reaction, the polyurethane can form the foam.

$$R\text{—}N\text{=}C\text{=}O + H_2O \rightarrow R\text{—}NH\text{—}COOH$$
$$R\text{—}NH\text{—}COOH + R'\text{—}N\text{=}C\text{=}O$$
$$\rightarrow R\text{—}NH\text{—}CO\text{—}NH\text{—}R' + CO_2 \uparrow \quad (1)$$

The —NCO/—OH molar ratio ($R_{-NCO/-OH}$) was calculated by the following eq. (2). The compositions of the ingredients for the preparation of the polyur-

ethane foam are shown in Table I. The varied factors in the polymerization of the polyurethane foam were weight/weight percentage (w/w %) of starch/polyol,
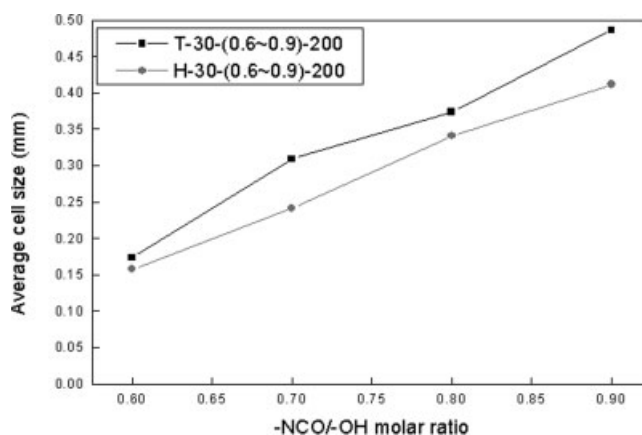

Figure 3 The average cell size of polyurethane foams as a function of —NCO/—OH molar ratio.
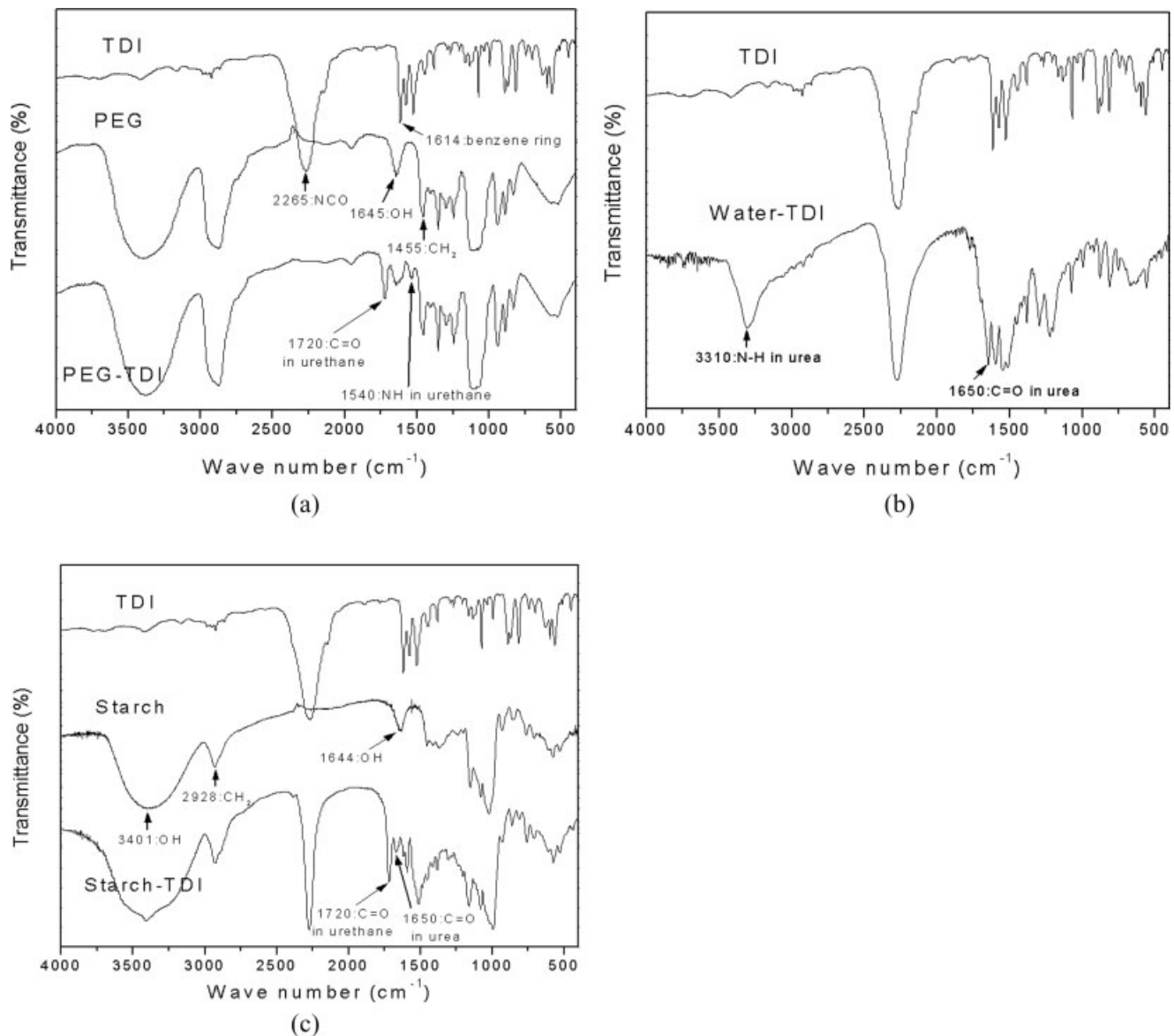
Figure 4 FTIR spectra of reaction products between (a) TDI and PEG, (b) TDI and water, and (c) TDI and starch.

PEG molecular weight, species of diisocyanate, and —NCO/—OH molar ratio.

$$R_{-NCO/-OH}$$

$$= \frac{\frac{TDI\ (g) \times 2}{M_{diisocyanate}}}{\frac{Starch\ (g) \times 3}{162} + \frac{PEG\ (g) \times 2}{M_{PEG}} + \frac{Glycerol\ (g) \times 3}{92} + \frac{Butanediol \times 2}{90}} \quad (2)$$

where $M_{diisocyanate}$ is the molecular weight of diisocyanate used and M_{PEG} is the molecular weight of PEG used.

Structure of polyurethane foams

To observe the cell structure of polyurethane foams, the optical microscope (CSB-HP5, SamWon, Korea) and charge-coupled device camera (CCD camera,

WAT-202B, Watec, Japan) were used at the magnification of 40. Because the shape of the cell was mostly elliptical, the diameter of major axes of the cell was measured and averaged to give the average cell size. The diameters were measured by using image analysis software (Image-Pro Plus Version 2.0) from the photomicrographs taken by CCD camera. Eight different pore sizes from each sample were measured and averaged to give the average cell size.

Fourier transform infrared spectroscopy

FTIR spectrometer (Nicolet Magna 550 series II, Midac, USA) was used to confirm the reaction between isocyanate group of various diisocyanates and hydroxyl group of various polyols. The specimens were prepared in the form of KBr pellets. Before the preparation of the speci-
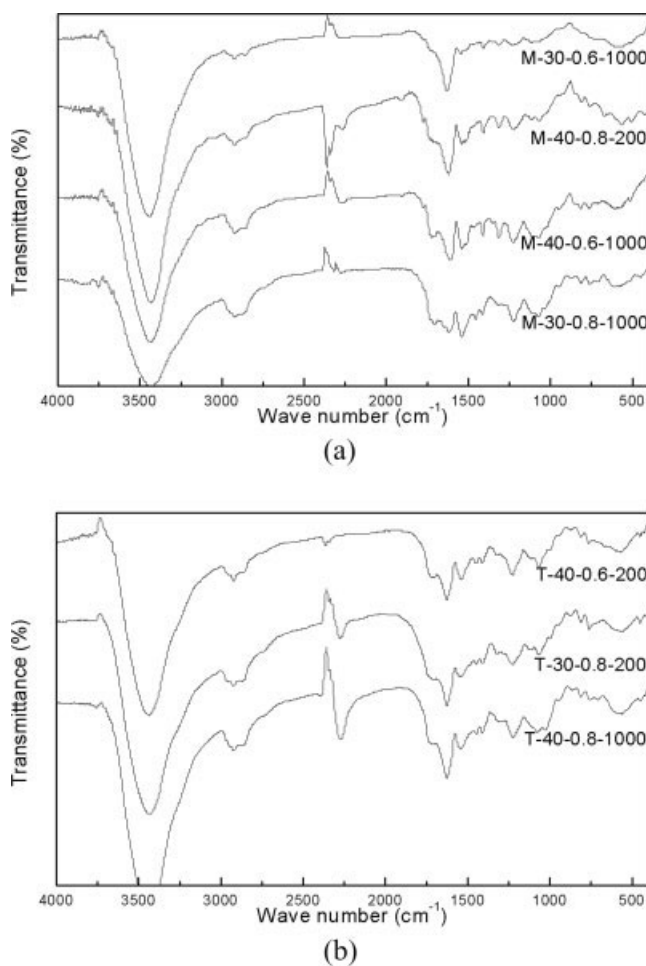
Figure 5 FTIR spectra of polyurethane foams made at various conditions.

mens, polyurethane foams were dried in a vacuum oven for 20 h. Operated with 4 cm^{-1} resolution, FTIR spectra between 400 and 4000 cm^{-1} were obtained.

Density of polyurethane foams

The densities of polyurethane foams were measured according to ASTM D3574. At first, polyurethane foams were cut into the specimens with the dimension of 10 mm × 10 mm × 10 mm (width × length × height). After being dried in an auto-desiccator (Sanpla Dry Keeper, SanplaTec, Japan) for 24 h at 15% R.H. and at 20°C, the specimens were weighed with precision. Dividing the dried weight of the specimen by the calculated volume gave the density in the unit of gram per cubic centimeter.

Compression test

The compressive properties of polyurethane foams were investigated by the compression test using the MiniMat2000 (Rheometric Scientific, USA) according to ASTM D695. The polyurethane foams were cut into

specimens with the dimension of 25 mm × 25 mm × 50 mm (width × thickness × length). Before being tested, the specimens were conditioned at the ambient atmosphere of (20 ± 2)°C and (50 ± 5)% R.H. for 24 h. The test rate was fixed at 1 mm/min.

Absorbency for organic solvents

Absorption properties of polyurethane foams for water and organic solvents were tested according to ASTM F726 and the absorbency was calculated by following eq. (3).

$$\text{Absorbency} = \frac{S_{ST} - S_0}{S_0} \qquad (3)$$

where S_{ST} is the weight of samples after absorption and S_0 is the initial weight of dried sample.

RESULTS AND DISCUSSIONS

Cell structures

The cell structure of polyurethane foam was observed using the optical microscope at a magnification of 40. Figures 1 and 2 show the cell surface of T-30-(0.6–0.9)-200 and H-30-(0.6–0.9)-200 respectively. As seen in the figures, the closed cells having various cell sizes were formed. Generally, in the case of application of polyurethane foams as oil-absorbent, the ratio of open cell acts as very an important factor.[6] Because spilled oil can permeate through open cell more easily than closed cell, the cell must be opened for higher efficiency of oil-absorbent. To make open cell structure, the silicone-surfactant was sometimes added in preparing the polyurethane foams. But if the target of absorption is not oil but organic solvent, the ratio of open cell does not influence absorbency much. Because the permeability of organic solvents for polyurethane foam is superior to that
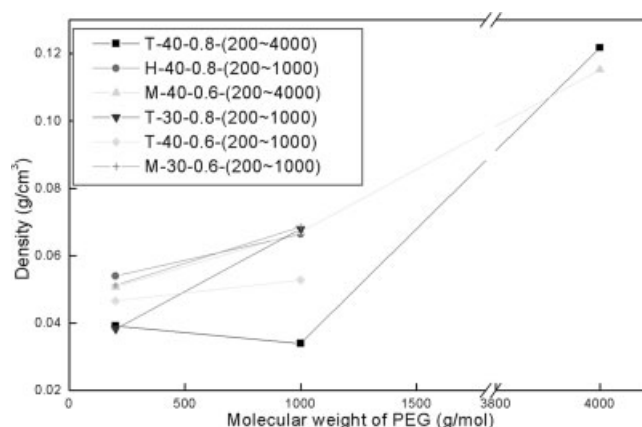

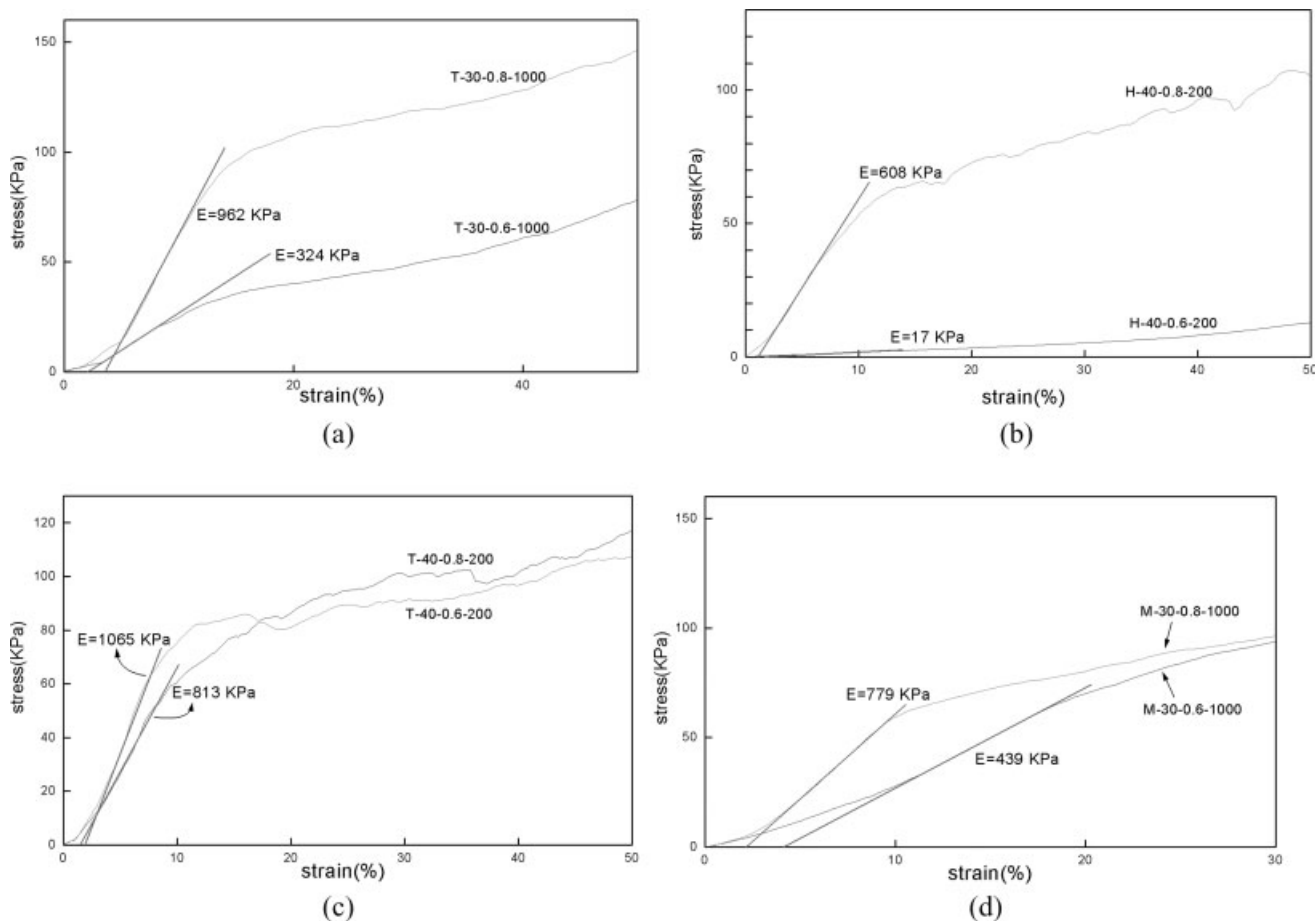**Figure 6** Densities of polyurethane foams as a function of molecular weight of PEG.

Figure 7 Compressive stress–strain curves of polyurethane foams at two different —NCO/—OH molar ratio; (a) T-30-0.6-1000 and T-30-0.8-1000, (b) H-40-0.6-200 and H-40-0.8-200, (c) T-40-0.6-200 and T-40-0.8-200, and (d) M-30-0.6-200 and M-30-0.8-200.

of oil, the organic solvents can permeate into foam even if the cells were closed. Therefore, in case of organic solvent, the efficiency of absorbent is higher when the cells are closed because once penetrated organic solvents cannot flow out of the foam easily.

Figure 3 shows the average cell size of foams as a function of —NCO/—OH molar ratio. As shown in this figure, the higher the —NCO/—OH molar ratio, the higher the average cell sizes of foams were found. This phenomenon could be the result of the more active generation of CO_2. Because —NCO groups in diisocyanate can react with —OH groups in foaming agent (water) more easily at higher content of —NCO/—OH molar ratio in processing, the generation of CO_2 becomes more active.

FTIR spectroscopies

Figures 4 and 5 show the FTIR spectra of 400–4000 cm^{-1} wavelength of polyurethane foam. Figure 4 shows the FTIR spectra of products that were reacted between TDI and —OH-containing materials. In Figure 4(a), the peak around 2265 cm^{-1} caused by

—NCO group in TDI disappeared due to the reaction between TDI and PEG. It means that all —NCO groups were reacted in urethane reaction. The peak around 1720 cm^{-1} due to C=O of the urethane group (—NH—CO—O—) was generated newly after the reaction. Figure 4(b) shows the FTIR spectra of reaction product between TDI and water. When —NCO groups in diisocyanate react with water, not only urethane groups but also urea groups (—NH—CO—NH—) were generated.[11] Therefore, two peaks around 1650 and 3310 cm^{-1} due to C=O and N—H of urea respectively, were generated. Figure 4(c) shows the result of reaction between TDI and starch. As in Figure 4(a), the new urethane peak was observed, but —NCO group peak did not disappear. This result could be due to the granule structure of starch that was not gelled completely during processing. Because the —OH group in granule could not react with the —NCO group easily, the peak of unreacted —NCO group appeared. At the same time, the urea peak around 1650 cm^{-1} appeared and this result could be due to the reaction between the —NCO group of diisocyanate and moisture in the starch.
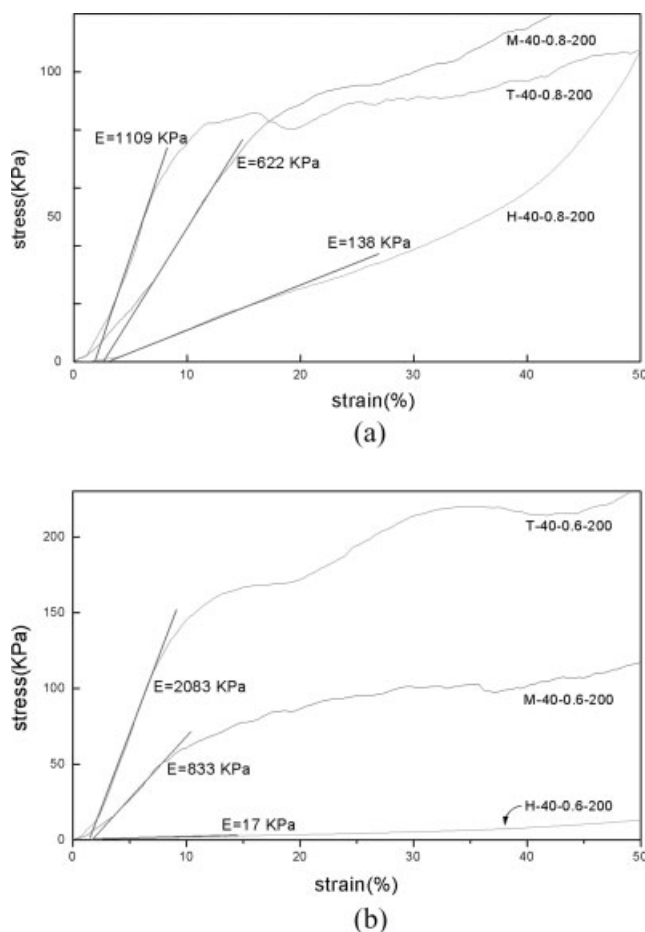
Figure 8 Compressive stress–strain curves of polyurethane foams made using three different kinds of diisocyanates; (a) T-40-0.8-200, M-40-0.8-200, and H-40-0.8-200 and (b) T-40-0.6-200, M-40-0.6-200, and H-40-0.6-200.

Figure 5 shows the FTIR spectra of polyurethane foams using starch. Because urethane and urea peak around 1720 and 1650 cm^{-1} respectively, could be observed in all samples, it is concluded that the starch could be used as polyol in polyurethane foams. Meanwhile, the peak of —OH group around 3400 cm^{-1} in starch was observed obviously in all samples. As stated above, this result is also due to the unreacted —OH groups in the granule of starch. It means that the gelling process of starch was not accomplished completely. Therefore, the unreacted —NCO groups could exist in samples considerably even if the —NCO/—OH molar ratio was lower than 1.0. Conclusively, the —NCO/—OH molar ratio must be between 0.6 and 0.8 for the complete reaction of —NCO groups.

Densities

When the foams are utilized for absorbent materials, the density of foam is very important factor. In absorb-

ing oil or organic solvents, the foam does not swell in itself and maintain its shape and volume. Therefore, not the swelling ratio of foam but the porosity of foam is the most important factor in the absorbency.

Figure 6 shows densities as a function of molecular weight of PEG. As seen in Figure 6, the higher the molecular weight of PEG, the higher the density of polyurethane foam observed. This may be due to the fact that the mobility of PEG molecules decreased with the viscosity, which was increased by the increased molecular weight.[8]

Compressive properties

Figure 7(a–d) show the compressive stress–strain curves of samples as a function of —NCO/—OH molar ratio. The slope of the tangential line to the curve means the Young's modulus. When the —NCO/—OH molar ratio was higher, the Young's modulus was higher. This phenomenon was the same regardless of diisocyanate species. The molecular structure of polyurethane is known to have both soft-segment and hard-segment. The urethane group (—NH—CO—O—) belongs to hard-segment. If the —NCO/—OH molar ratio is increased, the number of urethane group would be increased. The increased number of urethane group would make the polyurethane foam more rigid. That is why the Young's modulus increased with —NCO/—OH molar ratio.

Figure 8(a,b) show the Young's modulus of polyurethane foam when several different kinds of diisocyanate were used. When TDI was used as diisocyanate, the Young's modulus showed the highest value. The Young's modulus showed the lowest value in the case of HDI. This can also be explained by the influence of hard-segment and soft-segment. While TDI and MDI have the hard segment like aromatic groups, HDI has only soft segment like aliphatic groups.
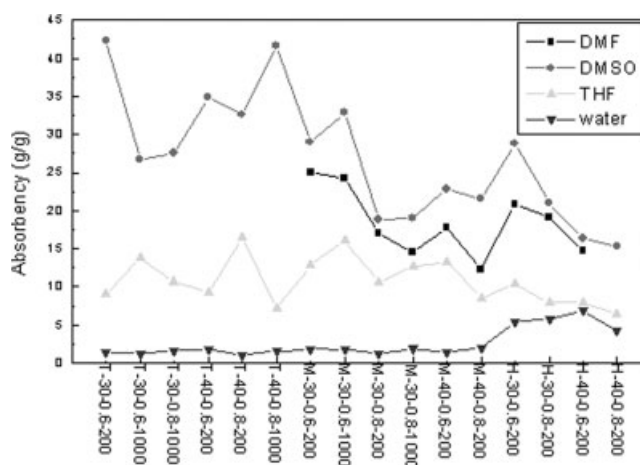

Figure 9 Absorbency of polyurethane foams for water and several organic solvents.
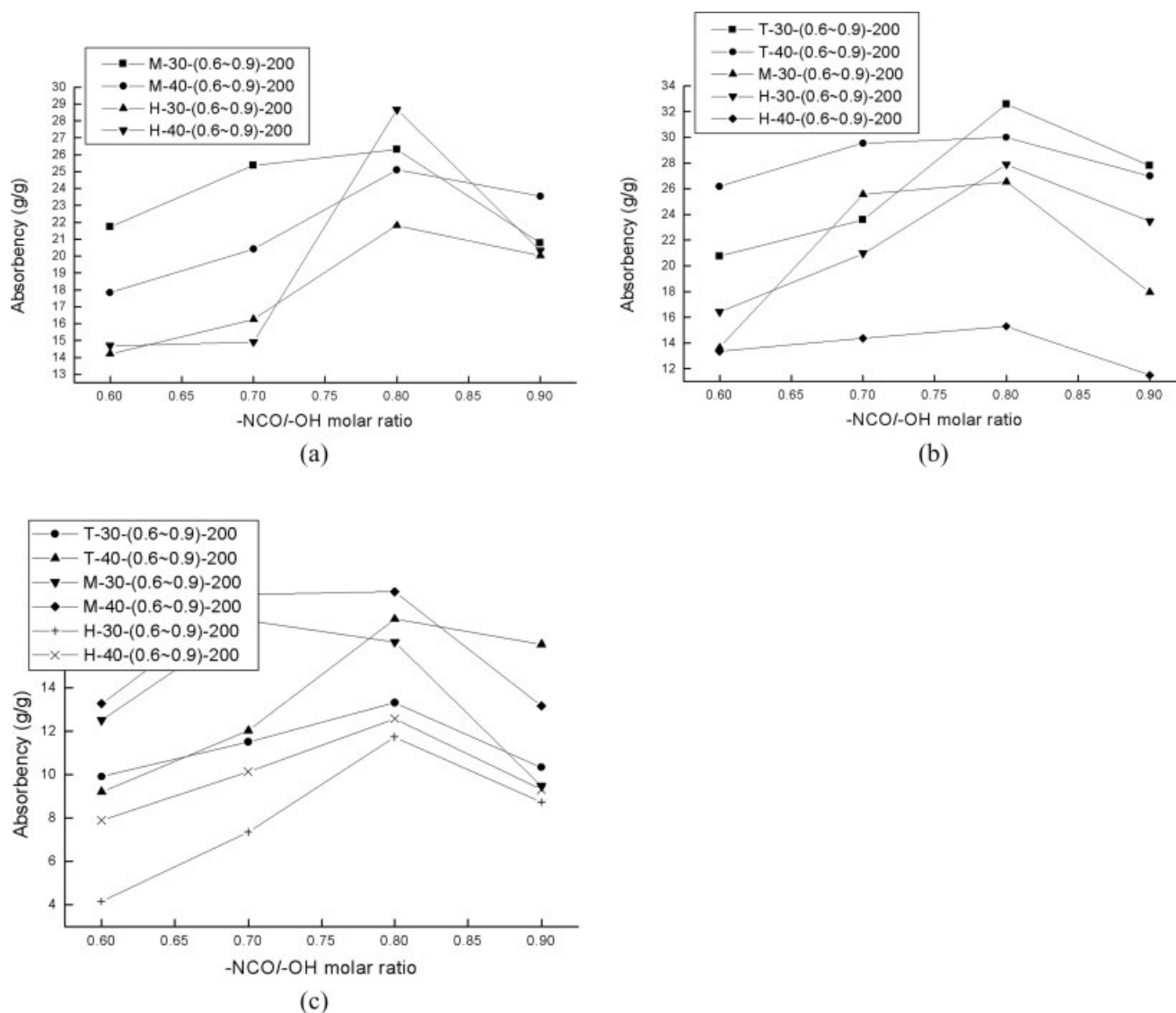
Figure 10 Absorbency of polyurethane foams as a function of —NCO/—OH molar ratio for organic solvents; (a) DMF, (b) DMSO, and (c) THF.

Absorption properties

Figure 9 shows the absorbency (g/g) of polyurethane foams for organic solvents. The absorbency for organic solvents was higher than that for water in all samples. While the absorbency for DMSO showed the highest values, the absorbency for THF showed the lowest values. Absorbency data for TDI in DMF are missing because the samples are completely dissolved in DMF. When TDI or MDI was used, the absorbency value for water was lower than 2. This is probably due to the fact that most of water molecules are adsorbed only on the surface of sample. This was confirmed by another test, which shows no difference in density between before and after immersion of sample in water. The absorbency for organic solvents varied from 10 to 40 according to the solvent type. When the HDI was used as diisocyanate, the absorbency for

water ranged from 6 to 10, which is much higher than TDI or MDI. But the absorbency for organic solvents ranged from 5 to 15, which is lower than TDI or MDI. This result could be explained by either hydrophilic or hydrophobic properties of samples. While the TDI and MDI have the aromatic ring, which is hydrophobic, the HDI does not have one. That is why the absorbency for water is higher in the case of HDI.

Figure 10 shows the absorbency of polyurethane foams for organic solvents as a function of —NCO/—OH molar ratio. The absorbency increased with —NCO/—OH molar ratio initially and showed the maximum value at —NCO/—OH molar ratio of 0.8 and then decreased. This tendency is the same in all types of samples in organic solvents. This tendency could be partly explained by the cell size effect (Fig. 3). The cell size of foams increased with —NCO/—OH molar ratio. When the cell size becomes larger,

organic solvent molecules can penetrate into foams more easily. Therefore, the absorbency increased with the cell size initially. But if the cell size is larger than a certain critical value, the once penetrated solvent molecules comes out of the cell easily due to the gravitational force.[6] That is why the absorbency decreased after a certain value of —NCO/—OH molar ratio.

CONCLUSIONS

Polyurethane foams were prepared using starch as a main component of polyols and their structural, mechanical, and absorption properties for organic solvents were studied. From FTIR spectra, it was confirmed that urethane linkage was formed between —NCO groups and —OH groups. The cell size of the foams increased with —NCO/—OH molar ratio. The density of polyurethane foams increased with molecular weight of PEG. The compressive modulus of foams increased with —NCO/—OH molar ratio, and the modulus was the highest when TDI was used as diisocyanate. The absorbency for organic solvents shows the maximum at —NCO/—OH molar ratio of 0.8. The absorbency for DMSO was the highest among organic solvents used.

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