

Effect of Polymer Glycols on Micro-Aggregation Structure and Mechanical Properties of Spherulite Size Graded Polyurethane Elastomers

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Received 21 May 2008; accepted 27 December 2008

DOI 10.1002/app.30047

Published online 14 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Spherulite size graded polyurethane elastomers (PUEs) were prepared using a mold with a temperature gradient from different polymer glycols, 4,4'-diphenylmethane diisocyanate (MDI) and a mixture of 1,4-butanediol (BD), and 1,1,1-trimethylol propane (TMP) as a curing agent by a prepolymer method. The used polymer glycols were poly(oxytetramethylene)glycol (PTMG, $M_n = 2000$), poly(ethylene adipate)glycol (PEA, $M_n = 2000$), and poly(hexamethylene adipate)glycol (PHA, $M_n = 2000$). The effect of polyether and polyester glycols and the temperature gradient on the micro-aggregation structure and mechanical properties were studied by polarized optical microscopy, differential scanning calorimetry, Fourier transform infrared spectroscopy, micro-hardness test, pulsed nuclear magnetic resonance spectroscopy, and tensile test. The prepared PUEs had spherulite size graded super-structure. Spherulite sizes of the PUEs depended significantly on the temperature gradient of the mold. Spherulite of the PUEs in contact with the mold at low tem-

perature was significantly smaller and more dense than that contacting the mold at high temperature. The spherulite diameter of PTMG-, PEA-, and PHA-PUEs changed from 12.6 to 16.3 μm , 8.4 to 15.6 μm , and 10.4 to 16.0 μm , respectively from the lower temperature side (LTS) toward the higher temperature side. In contrast, the number of spherulites became sparser toward the higher one. The glass transition temperature (T_g) of PTMG-, PEA-, and PHA-based PUEs elevated from -55.3°C , -19.0°C and -33.8°C at the LTS to -48.6°C , -17.8°C and -32.8°C at the HTS, respectively. T_g of all PUEs exhibited elevation from the LTS toward the higher one. This result associated with the strong microphase separation of the LTS. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1454–1461, 2009

Key words: polyurethane elastomers; temperature gradient molding; graded spherulite size; micro-aggregation; functional graded Elastomers; mechanical properties; micro-structure; morphology; polyurethanes

INTRODUCTION

Polyurethane elastomers (PUEs) have excellent mechanical properties compared with the general-purpose elastomers. These characteristics are utilized in many kinds of industrial products such as industrial parts, building materials, sport goods, medical fields, and daily life products. These properties are strongly dependent on the chemical structures and super-structures of PUEs. The super-structures of PUEs are varied with raw materials, recipes, preparation conditions, molding condition, and so on. Therefore, control of morphology of PUEs is required to obtain high performance PUEs.^{1–4}

In recent years, investigation of multi-component polymers with graded micro-domain structures has

been conducted. Okinaka et al. studied the binary polymer mixtures undergoing phase separation induced by a temperature gradient.^{5,6} Liu et al. designed the epoxy resin (EP)/polyurethane (PU) functionally graded material by microwave irradiation and reported that the temperature and thermal stress distribution decreased along the graded direction of these functionally graded materials.⁷ Okazaki et al. designed polyether-based PUE with graded micro-domain structures by using mold with different temperatures. They found that the mechanical properties were changed continuously with variation of micro-domain structure at mold temperature of 130°C .^{8–10} Furukawa et al. found that the higher BD content and molecular weight of polymer glycol exhibited stronger phase separation on the temperature gradient of FGPEs.¹¹ However, structures and mechanical properties of functionally graded PUEs have not been studied in spite of important research to develop novel functional materials.

In this study, PUEs with graded micro-domain structures were prepared from various polymer

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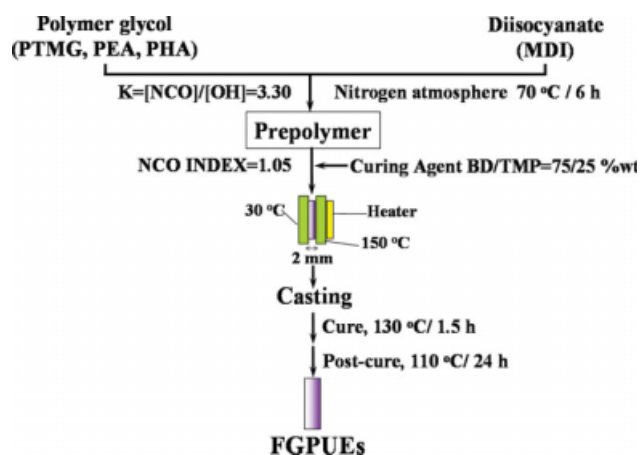


Figure 1 Synthetic scheme of PUE with spherulite size graded structure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

glycols using a mold with temperature gradient. The effect of polyether and polyester glycols on the micro-aggregation structure and mechanical properties of the PUEs were studied by differential scanning calorimetry (DSC), polarizing optical microscopy, pulse NMR, micro-hardness test, and tensile test.

EXPERIMENTAL

Raw materials

Poly(oxytetramethylene)glycol (PTMG: $M_n = 2000$, Nippon Polyurethane, Japan), poly(ethylene adipate)glycol (PEA: $M_n = 2000$, Mitsui Takeda Chemical, Japan), and poly(hexamethylene adipate)glycol (PHA: $M_n = 2000$, Nippon Polyurethane, Japan) were used as a polymer glycol. The polymer glycols were dried by bubbling dried nitrogen gas under reduced pressure at 80°C before preparing polyurethanes. 4,4-Diphenylmethane diisocyanate (MDI, Nippon Polyurethane, Japan) was used as received after the determination of isocyanate content. 1,4-Butanediol (BD, Wako Chemical, Japan) and 1,1,1-trimethylol propane (TMP, Wako Pure Chemical, Japan) as a cur-

ing agent were used by purification with vacuum distillation and recrystallization, respectively.

Preparation of spherulite size graded PUEs

The PUEs were prepared from each polymer glycol, MDI and a mixture of BD and TMP as a curing agent by a prepolymer method. The blend ratio of curing agent (BD/TMP) was with weight ratio of 75/25. Synthetic scheme of the spherulite size graded PUEs is shown in Figure 1. The prepolymer was prepared from each polymer glycol and MDI with a ratio of $[NCO]/[OH] = 3.30$ at 70°C for 6 h under a nitrogen atmosphere. The curing agents were added to the prepolymers with $NCO\ INDEX = [NCO]_{pre}/[OH] = 1.05$ and stirred for 3 min, where $[NCO]_{pre}$ is the concentration of NCO groups in the prepolymer. The viscous product was then poured into a mold constructed with a spacer 2 mm thick. Two aluminum plates were heated at 30 and 150°C prior to use, respectively. When the casting was initiated, the temperatures of low- and high-temperature mold plates transformed to 60 and 130°C, respectively. The sample was cured for 1.5 h at 130°C. Then, a sheet of 2 mm thickness was demolded, and the sheet was post-cured at 110°C for 24 h under an air atmosphere. PTMG-based PUE, PEA-based PUE, and PHA-based PUE were denoted as PTMG-PUE, PEA-PUE, and PHA-PUE, respectively.

Characterization of PUEs

The PUEs of 2 mm thickness were sliced up to five pieces (about 0.4 mm thickness) by a microtome (Yamato Koki, ROM-380 model, Japan). These obtained sheets are used for the following tests.

Density was measured by the weight of polyurethane in air and the weight of polyurethane in water.

The gel fraction (g) of the PUEs was determined from the original weight and the weight of the dried

TABLE I
The density, Gel Fraction and Degree of Swelling for the Lower and higher Temperature Side and the Middle Part of PTMG-, PEA-, and PHA-PUEs

PUE	Position	Density (kg/m^3) $\times 10^3$	Gel fraction (%)		Degree of swelling	
			Toluene	DMA	Toluene	DMA
PTMG-PUE	LTS	1.05	98.3	97.7	1.54	2.39
	Middle	1.06	98.5	97.9	1.62	2.41
	HTS	1.05	98.3	98.8	1.79	2.58
PEA-PUE	LTS	1.20	97.2	98.6	1.32	5.02
	Middle	1.21	98.0	98.9	1.31	5.14
	HTS	1.21	98.5	99.2	1.38	5.22
PHA-PUE	LTS	1.15	98.3	95.3	1.81	4.18
	Middle	1.15	98.1	96.2	1.81	4.20
	HTS	1.15	98.9	97.6	1.84	4.34

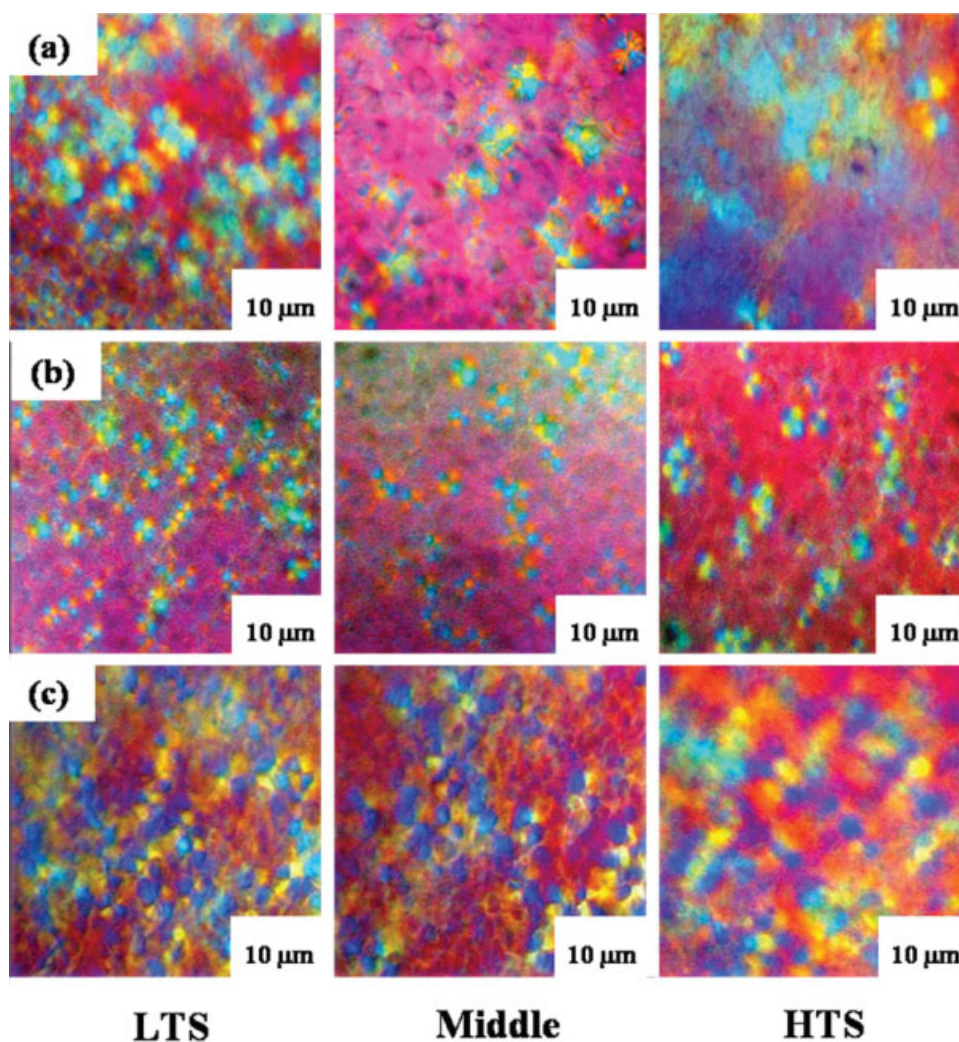


Figure 2 Polarized optical micrographs at each part in PTMG-PUE (a), PEA-PUE (b), and PHA-UE (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polyurethane after swelling to an equilibrium state in toluene and *N,N*-dimethyl acetamide (DMA) at 60°C, using the following formula: $g = W_b/W$, where W_b is the weight of the sample that was dried after equilibrium swelling and W is the original weight. The degree of swelling of the PUEs was determined from the weights before and after equilibrium swelling with toluene and DMA. The degree of swelling (q) was calculated as shown in equations (1) and (2).

$$q = 1 + Q \quad (1)$$

$$Q = \left[\frac{(W_a - W_b)/d_s}{W_b/d_p} \right] \quad (2)$$

where Q , W_a , d_s , and d_p are respectively the volume ratio of solvent in the swollen state to gel in the unswollen state, the weight of a sample swollen to the equilibrium state, the density of the solvent and the density of a sample.

The spherulite structures were observed by polarized optical microscopy (POM, Optiphotp2-Pol, Nikon, Japan). A sensitive color plate with wavelength of 530 nm was used for birefringence analysis.

DSC measurements were performed to determine the thermal behavior of PUEs. Thermograms of PUEs were recorded with DSC (DSC8230HT, Rigaku Denki, Japan) at heating rate of 10°C/min from -140°C to 250°C under a nitrogen atmosphere.

Fourier transfer infrared (FTIR) spectra of PUEs were recorded by Fourier transform infrared spectroscopy spectrometer (Bio-Rad FTS 3000, Nippon Bio-Rad Laboratories, Japan) in the ATR mode at the wavelength range between 4000 and 500 cm^{-1} . The sensitivity, the resolution and the number of scanning were 1, 4 cm^{-1} and 32 times, respectively.

Pulsed nuclear magnetic resonance spectrometer (NMR; JNM-MU25AH model, JEOL, Japan) in the solid echo mode at 25°C was used to determine the

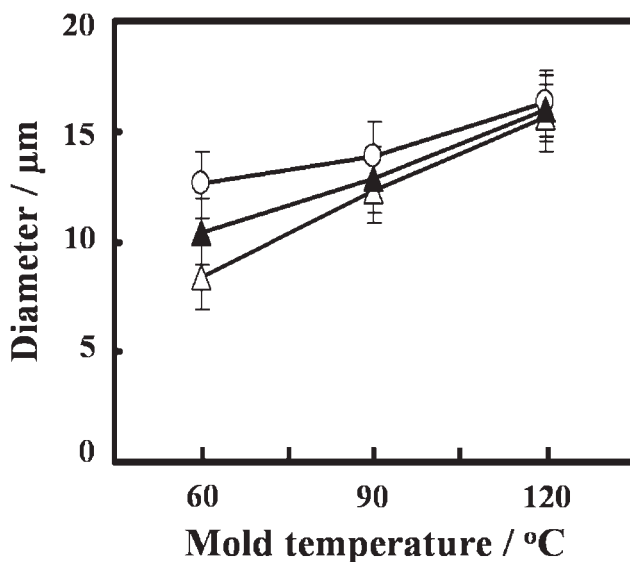


Figure 3 Relationship between the diameter of spherulite and molding temperature of PTMG-, PEA-, and PHA-PUEs. ○PTMG-PUE, △PEA-PUE, and ▲PHA-PUE.

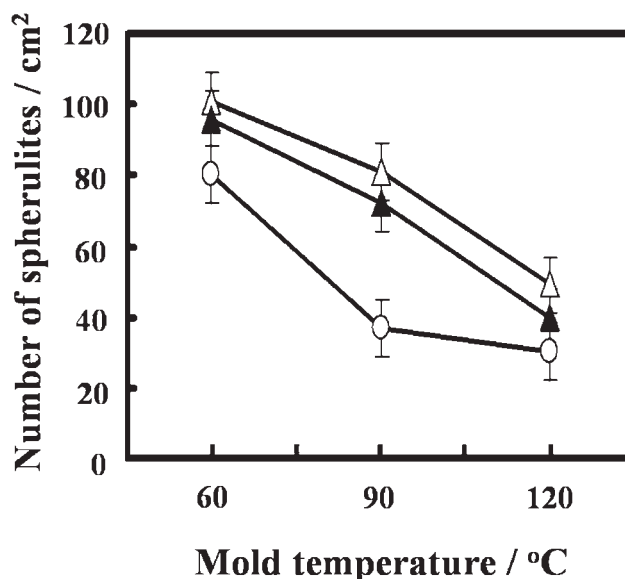


Figure 4 Relationship between the number of spherulite and molding temperature of PTMG-, PEA-, and PHA-PUEs. Symbols are same as in Figure 3.

mobility of hard segment or soft segment chains. Samples were cut into small pieces and densely added into the sample glass tube.

The changes of micro-hardness due to the temperature gradient were measured by micro-hardness test. This test was performed for each 100 μm of cross section from one surface to the other surface by using micro-durometer (Asker, MD-1 model, Japan) based on JIS K 6253. The micro-hardness was determined as the International Rubber Hardness.

Tensile test was performed by means of the Instron type tensile tester (U-4410 model, Orientec, Japan) at ambient temperature. Specimen size was 60.0 mm × 5.0 mm × 0.4 mm. The initial length and

elongation rate were set to be 30 mm and 10 mm/min, respectively.

RESULTS AND DISCUSSION

Table I shows the density, gel fraction, and degree of swelling for the lower-, higher-temperature side (HTS) and the middle part of PTMG-, PEA-, and PHA-PUEs. The samples obtained from the lower, middle, and HTSs of all PUEs were abbreviated as LTS, Middle, and HTS, respectively. Density of each position of PTMG-, PEA-, and PHA-PUEs was quite similar about $1.05 \times 10^3 \text{ kg/m}^3$, $1.21 \times 10^3 \text{ kg/m}^3$, and $1.15 \times 10^3 \text{ kg/m}^3$, respectively. These results

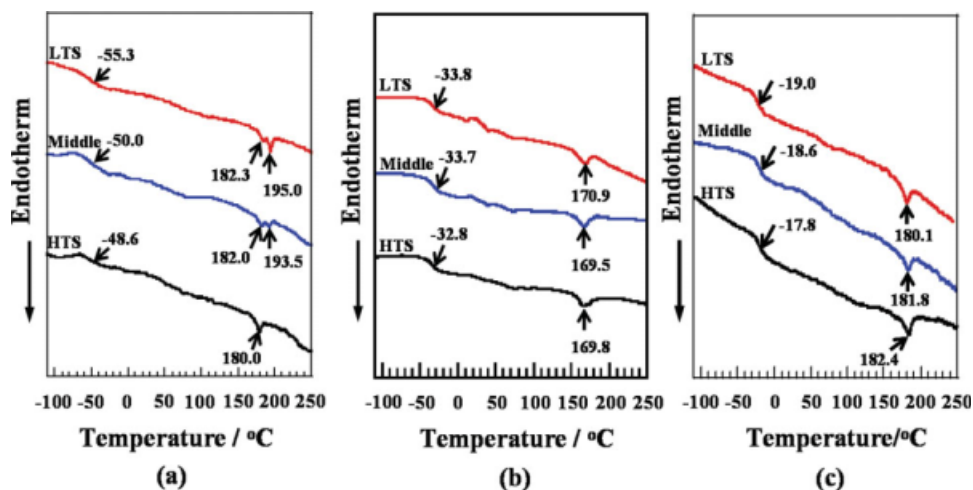


Figure 5 DSC thermograms at each part of PTMG-PUE (a), PEA-PUE (b), and PHA-PUE (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

clearly suggest that the density of each series of the PUEs was dependent on soft segment structure but independent on molding temperature. The gel fractions in both solvents of all three PUEs were over 97%. The gel fraction of the all UEs at low temperature side (LTS) was smaller than that at HTS. The degree of swelling in toluene and DMA differed with structure of the polymer glycols, and that of all PUEs slightly increased from LT to HT. The results suggest that the morphology at each position of each PUEs are different and the morphology of PUEs with the different polymer glycols are also different.

Figure 2 shows the polarizing micrographs taken at each part in PTMG-, PEA-, and PHA-PUEs. The PUEs in contact at low temperature mold plate had many small pherulites. On the other hand, the opposite phenomena occurred with PUEs in contact at high temperature mold plate. Additionally, the spherulite size of PTMG-PUE was higher than that of PEA- and PHA-PUEs. These spherulites were the negative spherulites; that is, the molecule oriented perpendicular to the radial direction. It is known that the spherulites are composed of a small amount of soft segment component and a lot of hard segment component.⁹ Thus, it can be suggested that the carbonyl group in polyester polyol interrupt the aggregation of the hard segments to form spherulites.

The effects of molding temperature on the spherulite diameter and the number of spherulites were shown in Figures 3 and 4, respectively. All PUEs in contact with lower temperature mold had large number of spherulites. These spherulites grew to 12.6–16.3 μm diameter in PTMG-PUE, to 8.4–15.6 μm diameter in PEA-PUE and to 10.4–16.0 μm diameter in PHA-PUEs from the LTS toward the HTS. The number of spherulites decreased and the size increased gradually toward the HTS. The spherulite size of PEA- and PHA-based PUEs (polyester-based PUEs) was smaller than those of PTMG-based PUE (polyether-based PUE) at each position. The continuous changes of spherulite size depending on the temperature gradient and type of polymer glycols were explained as follows. The spherulites grew outwards from the nucleation points but could not grow out radially in all direction either contacted at low temperature or when the spherulites met each other. Generally, the growth rate is extremely temperature sensitive and control by the nucleation. The nucleus growth in the HTS was very slow, resulting in the formation of larger spherulite. The growth of spherulite in the polyester-based PUE was lower than polyether-based PUE because the spherulites of polyester-based PUE composed of a lot of hard segment components and a small amount of soft segment components. Moreover, the effect of carbonyl in the ester group of polyester-based PUEs could have induced the hydrogen bonding between hard

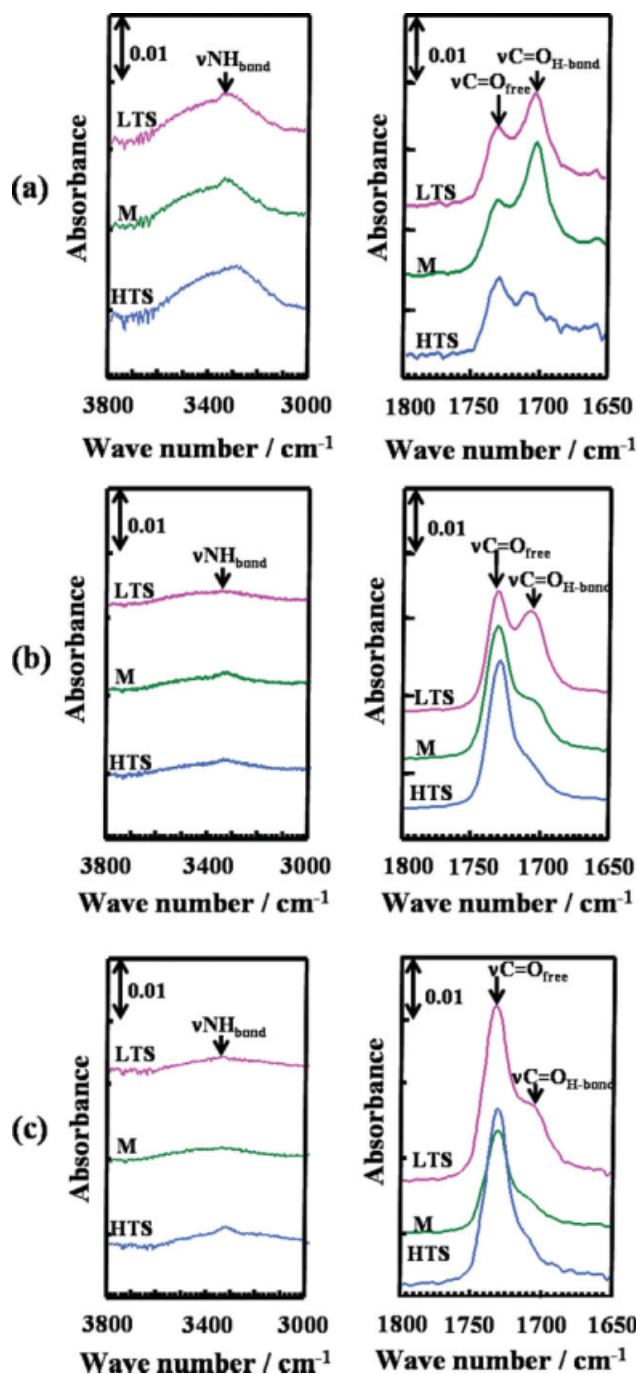


Figure 6 FTIR spectra at each part of at each part of PTMG-PUE (a), PEA-PUE (b), and PHA-PUE (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and hard segments and also hard and soft segments of other chain. In contrast, the hydrogen bonding of polyether-based PUE is mainly formed between hard and hard segments, but slightly formed between hard and soft segments. It is conceivable that the polyester chains had higher molecular interaction than that of in polyether chains. Thus, the hard segments domain components for spherulite

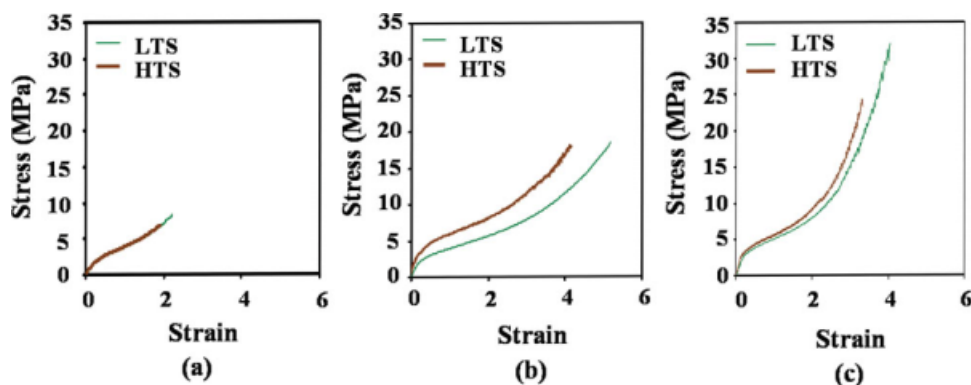


Figure 7 Stress–strain curves at each part of PTMG-PUE (a), PEA-PUE (b), and PHA-PUE (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

growth in the polyester-based PUEs was less than that in polyether-based PUEs.

Figure 5 shows the DSC thermograms of each part of PTMG-, PEA-, and PHA-PUEs. The glass transition temperature (T_g) of PTMG-, PHA-, and PEA-PUEs increased from -55.3°C , -33.8°C , and -19.0°C at the LTS to -48.6°C , -32.8°C , and -17.8°C at the HTS, respectively. The endothermic peaks due to the melting of hard segment domains ($T_{m,H}$) of all samples were about 169 – 195°C . The trend of T_g of all PUEs increased and melting point of hard domains decreased from the LTS to the HTS. The results can conclude that the microphase separation became weaker toward the HTS. In addition, the crystallization due to the rearrangement and melting of the crystals of soft segments were not observed in these PUEs. T_g of soft segment of PTMG-PUE was the lowest and those of PEA-PUE was the highest at the same positions. $T_{m,H}$ of PTMG-PUE exhibited higher than that of PEA- and PHA-PUEs at every positions, resulting in high crystallizability in PTMG-PUE. On the other hand, in PEA- and PHA-PUEs, the intermolecular interaction was very strong. Thus, crystallizability of the hard segment is quite low. Therefore, the degree of microphase separation of polyester-based PUE was weaker than that of polyether-based PUE. In case of polyester-based PUEs, the ester group along the chain of polyester induced force to hold the chains. Hence, the PHA-PUE with long methylene chain showed the greater microphase separation than the PEA-PUE with short methylene chain.

Figure 6 shows FTIR spectra at the LTS, HTS, and the middle part of PTMG-, PEA- and PHA-PUEs. In the PTMG-PUE, the peaks of $\nu\text{C}=\text{O}_{\text{free}}$ and $\nu\text{C}=\text{O}_{\text{bond}}$ of urethane group occurred at 1731 cm^{-1} and 1703 cm^{-1} , respectively. The peak of $\nu\text{N}-\text{H}_{\text{bond}}$ shifted to low wave number from LTS to HTS. The $\nu\text{C}=\text{O}_{\text{bond}}$ intensity was higher than that of $\nu\text{C}=\text{O}_{\text{free}}$ at LTS and the middle part, but the trend of intensity peaks at the HTS was opposite with the

LTS. These results demonstrate that the hydrogen bonding mainly occurred between the NH-group and carbonyl group of urethane linkages at the LTS and the middle part. This bonding exhibited strong cohesive force and tended to agglomerate between hard segments in the structure of PUEs. The microphase mixing was progressed at the HTS of the PUE. In case of polyester based PUEs, the intensity of $\nu\text{C}=\text{O}_{\text{free}}$ showed at 1730 cm^{-1} for the PEA-PUE and at 1728 cm^{-1} for the PHA-PUE. The $\nu\text{C}=\text{O}_{\text{bond}}$ peak of PEA- and PHA-PUEs showed at 1708 cm^{-1} and 1704 cm^{-1} , respectively. It seems that the hydrogen bonding is occurred both between both carbonyl group of urethane and ester groups and NH-groups.

Stress–strain curves of the PUEs with different positions exhibited similar curves for each polymer glycols series in Figure 7. Table II shows Young's modulus, tensile strength, and strain at break of all PUEs. Young's modulus, tensile strength, and strain at break of all PUEs series at the LTS were higher than that of the HTS. This tendency was rapidly increased in polyester-based PUE. Therefore, the polyester-based PUE exhibited almost similar tendency at every position. This result indicates that the crystallization occurred in the polyester series when the strain was increased but not found in the polyether series.

TABLE II
The Young's modulus, Tensile Strength, and Strain at Break of PTMG-, PEA-, and PHA-PUEs at the LTS and the HTS

PUE	Position	Young's modulus (MPa)	Tensile strength (MPa)	Strain at break
PTMG-PUE	LTS	1.11	8.32	2.06
	HTS	1.03	6.89	1.74
PEA-PUE	LTS	1.15	18.46	5.19
	HTS	1.13	17.99	3.68
PHA-PUE	LTS	1.28	32.03	4.04
	HTS	1.00	23.28	3.32

Micro-hardness at every 100 μm depth of specimens of 2 mm thickness of PTMG-, PEA-, and PHA-PUEs is shown in Figure 8. Micro-hardness of the PTMG-PUE significantly increased from 74 at the LTS to 94 at the HTS. Interestingly, the micro-hardness of PEA-PUE slightly increased from the LTS toward the HTS. In addition, PHA-PUEs also exhibited the same trend with PEA-PUE. Difference of micro-hardness between the LTS and the HTS was 7 in PEA-PUE and 9 in PHA-PUE. The temperature gradient dependence of micro-hardness for PHA-PUE had identical tendency as PEA-PUEs. The micro-hardness of polyether-based PUE and polyester-based PUE exhibited dissimilar tendency, that is, the micro-hardness of polyether-based PUE had a big different between the LTS and the HTS. On the other hand, polyester-based PUEs was slightly different between the LTS and the HTS. These results can be suggested that the temperature gradient can be strongly affected on the micro-hardness of PTMG-PUE because the viscosity in polyether-based PUE was very low compared with PEA- and PHA-PUEs.

The spin-spin relaxation times (T_2) and fraction of each segment at each positions of PTMG-, PEA-, and PHA-PUEs are shown in Table III. Every spin was slightly different field due to the same measurement temperature, that is, room temperature. The spin-spin relaxation times of soft segment matrix (T_{2L}) exhibited from 312 to 314 μs in PTMG-PUE, from 150 to 156 μs in PEA-PUE, and from 157 to 170 μs in PHA-PUE. In addition, the spin-spin relaxation times of hard segment domains (T_{2S}) of PTMG-, PEA-, and PHA-PUEs exhibited from 36 to 38 μs ,

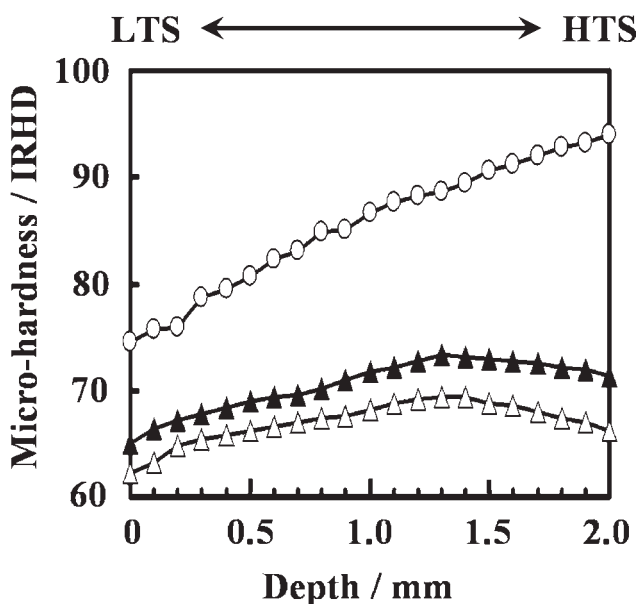


Figure 8 Temperature gradient dependence of micro-hardness for PTMG-, PEA-, and PHA-PUEs from the LTS to the HTS. \circ PTMG-PUE, \triangle PEA-PUE, \blacktriangle PHA-PUE.

TABLE III
The Spin-Spin Relaxation Times (T_2) and Hydrogen Fraction of Each Segment at the LTS, HTS, and the middle part of PTMG-, PEA-, and PHA-PUEs

PUE	Position	Soft segment	Hard segment
		T_{2L} (μs) ^a	T_{2S} (μs) ^b
PTMG-PUE	LTS	314	38
	Middle	313	33
	HTS	312	36
PEA-PUE	LTS	157	36
	Middle	156	35
	HTS	150	34
PHA-PUE	LTS	170	28
	Middle	164	29
	HTS	157	26

^a T_{2L} : Long T_2 .

^b T_{2S} : Short T_2 .

34–36 μs , and 26–29 μs , respectively. T_{2L} and T_{2S} of all three PUEs similarly decreased with increasing mold temperature. The segment of PUEs in contact low temperature mold plate showed easy relaxation by the phase separation. In the case of PUEs in contact high temperature mold plate, the strong intermolecular interaction can be found resulting in microphase mixing. Thus, the mobility of PUEs chain in contact high temperature mold plate was more difficult than that of PUEs in contact low temperature mold plate. These results mean that the relaxation time was dependent on molding temperature. The spin-spin relaxation time (T_2) of PTMG-PUE showed the highest one while T_2 of PHA- and PEA-PUEs were the lower and lowest, respectively. This result indicates that the strong intermolecular interaction due to the carbonyl group of polyester polyol has suppressed the chain mobility of polyester-based PUEs. Moreover, the chain mobility of PEA-PUE was more difficult than that of PHA-PUE because the short methylene chain length in PEA can be induced the strong intermolecular interaction in PUE compared with long methylene chain length in PHA.

CONCLUSIONS

Spherulite size graded PUEs were successfully prepared by using mold with different temperatures of each plate. Microphase separation and the large number of spherulites were observed in the LTS of spherulite size graded PUEs. The number and diameter of spherulites decreased and gradually increased toward the HTS. The number of spherulites of polyester-based PUEs decreased in more amount than that of the polyether-based PUEs. Polyether-based PUEs showed strong microphase separation in comparison with polyester-based PUEs.

Microphase separation of PUE-based polyester with long methylene chain length was stronger than that of PUEs-based short methylene chain length. The spherulite size graded polyether-based PUE had large graded mechanical properties from LTS to HTS, while the polyester-based PUEs had the slight graded mechanical properties.

References

1. Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Gunatillake, P. A.; McCarthy, S. J. *J Appl Polym Sci* 1996, 60, 557.
2. Petrovic, Z. S.; Javni, I.; Divjakovic, V. *J Polym Sci* 1998, 36, 221.
3. *Encyclopedia of Polymer Science and Technology*, Vol. 11, John Wiley & Sons, Inc.: New York, 1969.
4. Furukawa, M. *Recent Res Devel In Macromol Res* 1998, 3, 89.
5. Okinaka, J.; Tran-Cong, Q. *Phys D* 1995, 84, 23.
6. Tran-Cong, Q.; Nakano, H.; Okinaka, J.; Kawakubo, R. *Polymer* 1994, 35, 1242.
7. Liu, X. Q.; Wang, Y. S.; Zhu, J. H. *J Appl Polym Sci* 2004, 94, 994.
8. Okazaki, T.; Furukawa, M.; Yokoyama, T. *Jpn J Polym Sci Technol* 52, 1996, 53, 184.
9. Okazaki, T.; Furukawa, M.; Yokoyama, T. *J Soc Rubber Ind Jpn* 1995, 68, 417.
10. Okazaki, T.; Furukawa, M.; Yokoyama, T. *Polym J* 1997, 29, 617.
11. Furukawa, M.; Hamada, Y.; Kojio, K. *J Polym Sci, Polym Phys* 2003, 41, 2355.