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Characterization of Functionally Graded Polyurethane Elastomers

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Abstract

Functionally graded polyurethane elastomers (FGPUEs) were prepared by poly(oxytretamythylene) glycol (PTMG) and 4,4'-diphenylmethane diisocyanate (MDI) with two molds fixed at different temperature. Effect of temperature gradient on the molecular aggregation state and mechanical properties were studied by differential scanning calorimetry (DSC), polarized optical microscope (POM), Fourier transform infrared spectroscopy (FT-IR) and pulsed nuclear magnetic resonance (NMR). Spherulite size of FGPUEs depended on the temperature gradient. Spherulite content of FGPUEs decreased from the low temperature side to the higher temperature side and spherulite size became greater toward the higher one. The glass transition increased from the lower temperature side to the higher temperature side. This was associated with the strong phase separation of the lower temperature side.

1. Introduction

Polyurethane elastomers (PUEs) have excellent mechanical properties compared with general purpose elastomers. There exist a degree of immiscibility between the hard urethane segment and the soft polyol segment, which means that although macroscopically PUEs are isotropic, microscopically PUEs are not structurally homogeneous. So although there is some degree of mixing of soft and hard segment, phase separation of the two segments occurs,

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producing a structure that can be considered as hard domain dispersed in soft segment matrix. The resultant two-phase micro domain structures exhibited by the PUEs are responsible for their superior physical and mechanical properties, and are believed to contribute to their biocompatibility. The properties are strongly dependent on chemical structures and super-structures of the PUEs. Therefore, high performance PUEs are obtained by regulation of morphology of the PUEs. The functionally graded polyurethane elastomers (FGPUEs) improve the various properties of conventional PUEs.

In this study, the FGPUEs were prepared with two molds fixed at different temperatures and then temperature gradient dependences of aggregation structure and mechanical properties were investigated by differential scanning calorimetry (DSC), polarized optical microscope (POM), Fourier transform infrared spectroscopy (FT-IR) and pulsed nuclear magnetic resonance (NMR).

2. Experimental

2.1. Raw Materials

Poly(oxytetramethylene) glycol (PTMG: M_n = 2000, Nippon Polyurethane Ind., Co., Ltd., Tokyo, Japan), was 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 Ind., Co., Ltd., Tokyo, Japan) was used as received after the determination of isocyanate content. 1,4-Butanediol (BD, Wako Chemical, Co., Ltd., Tokyo, Japan) and 1,1,1-trimethylol propane (TMP, Wako Pure Chemical, Co., Ltd., Tokyo, Japan) as a curing agent were used by purification with vacuum distillation and recystallization, respectively.

2.2. Preparation of functionally graded polyurethane elastomer (FGPUE)

The FGPUE was prepared from poly(oxytretamythylene) glycol (PTMG: M_n = 2000), 4,4'-diphenylmethane diisocyanate (MDI) and a mixture of 1,4-butanediol (BD) and trimethylol propane (TMP) (75/25 wt%) as a chain extender by a prepolymer method. The prepolymer was prepared from PTMG and MDI with a ratio of [NCO]/[OH] = 3.30 at 70 °C for 6 hours under a nitrogen atmosphere. The prepolymer and curing agent were mixed well with the ratio of [NCO]$_{pre}$/[OH] = 1.05 for 5 min and the viscous product was poured into a mold constructed with spacer of 2 mm thickness and two aluminum plates heated at 30 and 150°C. When casting was initiated, temperatures of low and high mold plates were 60 and 120 °C, respectively. The viscous product was cured for 1.5 hours at 130 °C then a sheet of 2 mm thicknesses was demolded, and the sheet was post-cured at 110 °C for 24 hours under an air atmosphere.

2.3. 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 Co., Ltd., ROM-380 model, Japan). These obtained sheets are used for 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 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 equations (1) and (2).

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

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

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, Co., Ltd., Japan). A sensitive color plate with wavelength of 530 nm was used for birefringence analysis.

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

Fourier transfer infrared (FT-IR) spectra of PUEs were recorded by a FI-IR spectrometer (Bio-Rad FTS 3000, Nippon Bio-Rad Laboratories, Inc., 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, Co., Ltd., Japan) in the solid echo mode at 25 ^{o}C was used to determine the 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 (IRHD).

Tensile test was performed by means of the Instron type tensile tester (U-4410 model, Orientec, Co., Ltd., 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.

3. Results and Discussion

Table 1 shows the density, gel fraction and degree of swelling at each part of the FGPUEs. The gel fraction and degree of swelling of the FGPUEs at every part showed similar magnitudes, and former magnitude were greater than 95%. These results indicate that the polymerization of these FGPUEs progressed enough.

Table 1. Properties of functionally graded polyurethane elastomers (FGPUEs) at the lower temperature side (LTS), the higher temperature side (HTS) and the middle part.

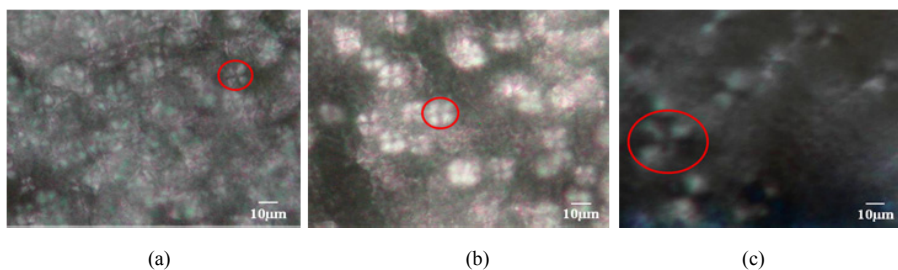| FGPUE	Position	Density (g/cm^3)	Gel Fraction (%)		Degree of Swelling	
			Toluene	DMA	Toluene	DMA
PTMG-FGPUE	LTS	1.06	97.5	95.9	1.79	2.58
	Middle	1.08	96.8	97.7	1.62	2.39
	HTS	1.10	97.3	98.8	1.54	2.41

(a)   (b)   (c)

Fig.1. Polarizing optical microscopic images of each part of FGPUEs. (a) Lower temperature side, (b) Middle part and (c) Higher temperature side.

Figure 1 shows POM images for (a) lower temperature side, (b) middle part and (c) higher temperature side of the FGPUEs. All POM images with sensitive color plates showed negative spherulites, indicating that the molecule orientated perpendicular to the radial direction. The number of spherulites gradually decreased from the lower temperature side to the higher temperature side, and size of spherulite increased toward higher temperature side. This indicates that the nucleus growth in the higher temperature side was much slower, resulting in the formation of larger spherulites.

Figure 2 shows glass transition temperature (T_g) and melting temperature (T_m) at the lower temperature side (LTS), the higher temperature side and a middle part of FGPUEs. T_g of soft segment of FGPUE was increased from -55.3^{o}C to -48.6^{o}C. T_m of hard segment of these FGPUEs was approximately 189°C. These results clearly suggest that the phase separation became weaker toward higher temperature side.
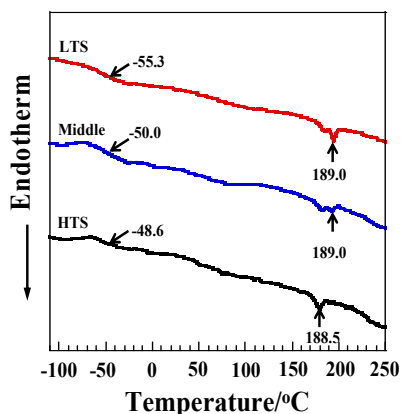

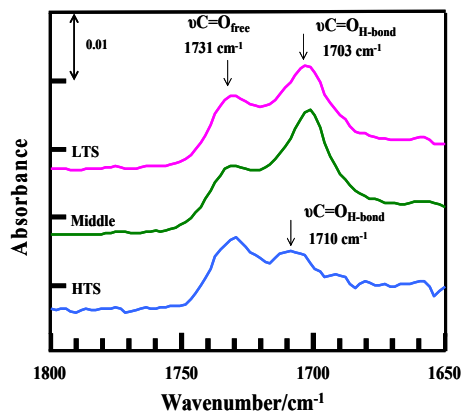Fig. 2. DSC thermograms at each part of PTMG-FGPUEs.

Fig.3. FT-IR spectrums for the lower temperature side (LTS), the higher temperature side (HTS) and the middle part of FGPUEs in the range from 1650 to 1800 cm^{-1}.

Figure 3 shows FT-IR spectrums for the lower temperature side (LTS), the higher temperature side (HTS) and the middle part of FGPUEs in the range from 1650 to 1800 cm^{-1}. In the lower temperature side, the intensity of $\nu C=O_{free}$ at 1731 cm^{-1} was lower than the intensity of $\nu C=O_{H-bond}$ at 1703 cm^{-1} and the intensity of $\nu C=O_{free}$ at 1731 cm^{-1} was higher than the intensity of $\nu C=O_{H-bond}$ at 1710 cm^{-1} in the higher temperature side.

Table 2 The Young's modulus, tensile strength and strain at break of PTMG-FGPUE.

FGPUE	Position	Young's Modulus (MPa)	Tensile Strength (MPa)	Strain at Break
PTMG-FGPUE	LTS	1.11	8.32	2.06
	HTS	0.83	6.89	1.74

Stress-strain curve, young's modulus, tensile strength and strain at break of PTMG-FGPUE at each parts is shown in Figure 4 and Table 2. Stress-strain curves of the specimens which were sliced off from different parts in FGPUE. Young's modulus, tensile strength and strain at break at LTS position of PTMG-FPUE were 1.11 MPa, 8.32 MPa and 2.06 MPa, respectively. Those magnitudes of the HTS position of PTMG-FGPUE were 0.83 MPa, 6.89 MPa and 1.74 MPa, respectively. That is, the lower temperature side of PTMG-FGPUE exhibited showed a higher young's modulus, tensile strength and strain at break than the higher temperature side. In tensile testing, the stress of this FGPUE in LTS position was increased with increase of strain. These results suggest that in the strain

region, the increasing strain induced crystallization progresses and the crystallinity gives reinforced filler effects in LTS position more than HTS position. Therefore, the polyether based polyurethane elastomer exhibited the extremely different tendency between LTS and HTS positions. This result indicates that the crystallization was occurred in the polyether based polyurethane elastomer when increased strain.
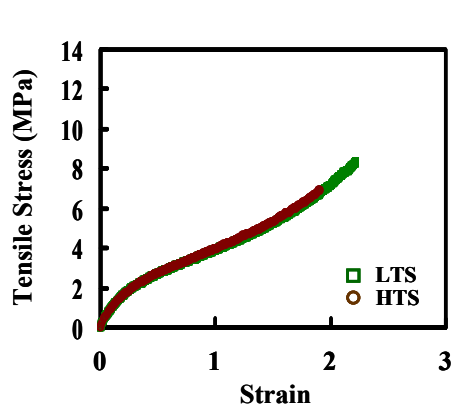

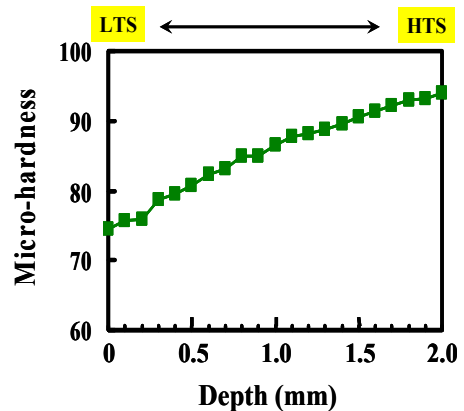Fig. 4. Stress-strain curves at each part of PTMG-FGPUEs.

Fig.5. Micro-hardness at every 100 μm of specimens of 2 mm thickness of PTMG-FGPUEs.

Micro-hardness property at every 100 μm depth of specimens of 2 mm thickness of PTMG-FGPUE is shown in Figure 5. Micro-hardness of PTMG-FGPUE significantly increased from 74 at the lower temperature side to 94 at the higher temperature side. The difference in micro-hardness between the lower temperature side of specimen and the higher temperature side of specimen was approximately 20 in PTMG-FGPUE. Micro-hardness of all specimens still increased with increasing mold temperature. These results suggest that micro-domain at the higher temperature side was larger than that at the lower temperature side and the micro-phase mixing became greater toward the higher temperature. Therefore, the functionally graded polyurethane elastomers can be obtained by use of a mold with temperature gradient.

4. Conclusion

Spherulite size graded polyurethane elastomers were successfully prepared by using mold with different temperature of each plate. Microphase separation and the large number of spherulites were observed in the lower temperature side of spherulite size graded PUEs.The number and diameter of spherulites decreased and gradually increased toward the higher temperature side. Mechanical properties of FGPUEs which depend on the temperature gradient were occurred in the lower temperature side more than in the higher temperature side of polyether based PUEs.

Acknowledgements

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