<연구논문>

형상기억 거동의 동적기계적 해석

김병규 · 이상엽† · 이정삼 · 백상현 · 최영진 · 이장우 · Mao Xu**

부산대학교 고분자공학과, **중국과학원 화학연구소

(1997년 2월 13일 접수)

Dynamic Mechanical Interpretations of Shape Memory Behavior

Byung Kyu Kim, Sang Yup Lee†, Jeong Sam Lee, Sang Hyun Baek,
Young Jin Choi, Jang Oo Lee, and Mao Xu**

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea,
**Polymer Physics Laboratory, Institute of Chemistry, Chinese Academy of Science, Beijing 100080, China
(Received February 13, 1997)

요 약

PCL, MDI, BD 및 DMPA를 이용, 폴리우레탄(PU)을 ionomer 및 nonionomer형태로 제조하였으며, 이때 연질성분의 함량(SSC) 및 길이가 PU의 기계적, 동적기계적 특성은 물론 형상기억특성에 미치는 영향을 연구하였다. Ionomer는 nonionomer에 비하여 경도, 탄성율 및 강도가 모두 우수하였으며 그 효과는 실온에서, 경질성분의 함량(HSC)이 높은 PU일수록 보다 뚜렷하였는데 이는 HSC가 증가할수록 ion중심의 농도가 증가하며 ion중심간의 Coulomb력이 고온보다 실온에서 보다 큰데 기인하는 것으로 해석하였다. 반복인장하중실험에서 ionomer는 nonionomer에 비해 회복변형이 크고 잔류변형이 작았는데 이는 ionomer의 고무탄성율이 보다 큰데 기인한 것으로 해석하였다. 나아가 재료의 형상기억거동은 기본적으로 탄성율의 온도의존성에 크게 의존함을 알 수 있었다.

Abstract — Polyurethane (PU) ionomers and nonionomers with various soft segment contents (SSC) and lengths have been synthesized from polycaprolactone diols (PCL), 4, 4'-diphenylmethane diisocyanate (MDI), 1, 4-butane diol (BD), and dimethylol propionic acid (DMPA), and tested for shape memory behavior as well as for mechanical and dynamic mechanical properties. It was found that ionomers gave higher hardness, modulus and strength as compared with nonionomers, and the effects were more pronounced with increasing hard segment contents (HSC) and at room temperature since the increased HSC makes use of more Coulombic forces which are stronger at room temperature than at high temperature. Regarding the tensile cyclic behavior, ionomers gave higher recovery strain and lower residual strain, and these were interpreted in terms of dynamic mechanical properties, i.e., the higher the rubbery modulus, the higher the recovery strain results. It was found that the shape memory behavior is basically governed by the temperature dependent modulus of the materials.
Keywords: Shape memory polyurethane ionomer, cyclic loading, shape fixability, recoverability.

1. Introduction

Shape memory polymers are fairly recently recognized functional polymers which have a number of potential applications in a broad range of temperature sensing elements. These polymers basically consist of two phases, viz., frozen phase and reversible phase, and excellent shape memory effects have often been observed with block or segmented copolymers [1-3]. In these materials, crystalline soft domains often form the reversible phase, with their crystalline melting temperature (T_m) being the

†Customer Technical Support Team, Samsung Fine Chemicals Co., Ulsan, Korea

shape recovery temperature (T_s), and hard domains become the frozen phases. Frozen phase remains glassy state during the second shaping process which normally is done at temperature higher than T_s. Reversible phase is subject to softening and hardening upon heating above and cooling below the T_s, respectively.

Fig. 1 describes the basic working principles and application procedure of shape memory materials where a linear polymer with its T_m being T_s is assumed. Here T_h is the softening-hardening transition temperature of fixed phase, where T_l and T_u are the typical loading and unloading temperatures, respectively. During the primary processing such as injection molding, the materials are heated
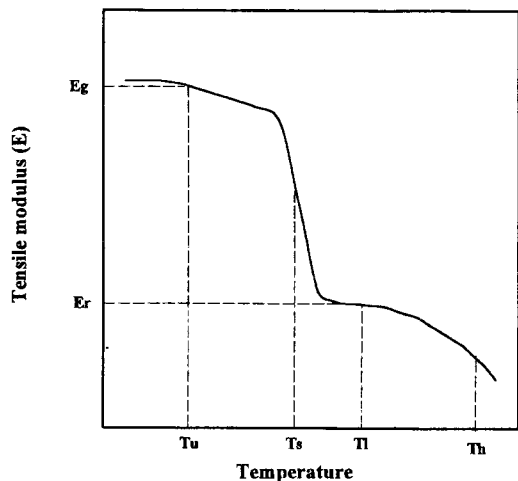
Fig. 1. Typical modulus-temperature curve of shape memory polymer.

above T_h, where the previous memories are completely erased. During the cooling in mold, fixed phases emerge as the temperature (T) decreases below T_h. Upon further cooling below T_m, soft segments crystallize and the materials are frozen to their glassy state. The shape of this molded specimen is the original shape of the shape memory experiment.

The secondary shapings, such as extension, compression, and transfer molding are typically done at $T>T_s$. The deformed shape and hence the chain orientations are fixed upon subsequent cooling under constant strain. The original shape is recovered upon heating to $T>T_s$. The driving force of shape recovery is the elastic strain generated during the deformation. Part of the chain orientations is relaxed before their structures are frozen during the cooling cycle. Even after cooling, a substantial amount of strain is recovered upon removing the strain constraint. High glassy state modulus will provide the materials with high shape fixability whereas the high rubbery modulus with high elastic recovery at high temperature. In addition, a sharp transition from glassy state to rubbery state makes the material sensitive to temperature variation. High elasticity ratio of glassy to rubbery modulus allows easy shaping at $T>T_s$ and great material strength at $T<T_s$.

The stress-strain-temperature behavior of the materials is of basic importance with regard to the shape memory effect evaluations. In addition, shape memory polymer element is often subjected to cyclic deformation such as in actuator, and hence the cyclic characteristics are also of practical importance in evaluating the durability of the shape memory element [4].

As compared with shape memory alloys and bimetal which have been known for sometimes, shape memory pol-

ymers are low density, high shape recoverability, easy processability, and low cost. Especially with polyurethanes, the structure-property relationships are extremely diverse and easily controlled, and hence the shape recovery temperature can be set at any temperature between -30 and 70°C, allowing a broad range of applications possible. They can be molded using conventional processing techniques including extrusion, injection and blow molding, which allow versatile shapings.

We have earlier reported shape memory effects of polyurethanes (PU) [5]. In this paper we report the shape memory behavior of ionomer type polyurethanes prepared from polycarprolactone diols, 4,4'-diphenylmethane diisocyanate, 1,4-butane diol, and dimethylol propionic acid. Effect of polyol molecular weight (2000, 4000, 8000 g/mole) and soft segment content (SSC 55~90%) on cyclic loading characteristics have been determined and interpreted in terms of dynamic mechanical properties and temperature dependent physical properties. The results of ionomers were favorably compared with those from nonionomers.

2. Experimental

2.1. Materials and Preparations of Polyurethanes

Table 1 shows the basic formulations of the present experiments. Polycaprolactone diols (PCL, Daicel) having molecular weight ($\overline{M}n$) 2000, 4000 and 8000 (g/mole) (hereafter called PCL2000 etc.) were dried and degassed at 80°C~100°C under 1~2 mmHg for 5hrs before use. Extra pure grade of 4,4'-diphenylmethane diisocyanate (MDI), 1, 4-butandiol (BD), and dimethylolpropionic acid (DMPA) was used with PCL to prepare segmented polyurethane ionomers and nonionomers. Ionomers were obtained by neutralizing the COOH groups of DMPA with triethyl amine (TEA). PCL of molecular weight 8000 (g/mole) was not commercially available, and was prepared from condensation reactions between PCL 4000 and adipic acid. The reactions were carried out in dimethyl formamide (DMF) at 198°C. The progress of reaction was monitored by measuring the acid value of the reaction mixtures [5]. When the acid value approached 5.2, the reaction was stopped. Molecular weight determined from gel permeation chromatography (GPC) was approximately 7,950 (g/mole), and this will be referred to PCL 8000.

A 500 ml round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube has been used as reactor to prepare the polyurethanes. Dried PCL and a

Table 1. Formulation of the Polyurethane Synthesis

$\overline{M}_n$ of polyol	polyol (mole)	chain extender (mole)		diisocyanate (mole)	soft content (%)	
		BD	DMPA			
4000	1	2.91	2.91	6.82	55	ionomer
	1	1.36	1.36	3.72	70	〃
	1	0.65	0.65	2.3	80	〃
	1	0.1	0.1	1.2	90	〃
2000	1	0.51	0.51	2.02	70	〃
8000	1	3.06	3.06	7.12	70	〃
4000	1	2.91	2.91	6.82	55	nonionomer
	1	1.36	1.36	3.72	70	〃
	1	0.652	0.65	2.3	80	〃
	1	0.1	0.1	1.2	90	〃
2000	1	0.51	0.51	2.02	70	〃
8000	1	3.06	3.06	7.12	70	〃

molar excess of MDI were charged to the dried flask. The urethane forming reaction was carried out at 60°C for about 1.5hrs, followed by chain extension with BD and DMPA for the same period of time. The neutralization reaction was carried out at 50°C for about 1hr. The progress of reactions in preparing the NCO-terminated prepolymers and chain extension step was monitored by measuring the isocyanate value. A standard di-n-butylamine back titration method was employed [6].

2.2. Film Casting and Tests

Films were prepared by casting on a glass plate. After standing at 60°C for 3hrs, films were further dried at 70°C under 2~4 mmHg for the next 4 days. Microtensile specimens (25 (length)×5 (width)×1 mm (thickness)) were prepared according to ASTM D-1822. Tensile and cyclic loading tests were done using a tensile tester (Tinius Olsen Series 1000), attached with a constant temperature heating chamber. Specimens were heated using a bundle of heating lamps, and cooled by spraying the compressed air. Loading and unloading together with heating and cooling were controlled by a personal computer which was interfaced with the tensile tester. Fig. 2 defines a thermomechanical cycling test with loading at high temperature (T_l) and unloading at low temperature (T_u). Sample is elongated to a constant strain (ε_m) at a constant elongation rate $(\dot{\varepsilon})$. While maintaining the strain at ε_m, sample is cooled to low temperature $T_u(<T_s)$ and unloaded, resulting in a substantial recovery of strain $(\varepsilon_m-\varepsilon_u)$. Sample is subsequently heated to T_l in 5 min, and stayed at that temperature for the next 10 min, allowing recovery of strain, ε_r. This completes one thermomechanical cycle leaving a residual strain, ε_p. The

area below the loading curve corresponds to the total strain energy per unit volume, whereas the one below the unloading curve to recoverable strain energy. Consequently the area enveloped by the loading and unloading curves is the dissipated strain energy.

The significance of various strains should be mentioned regarding the shape memory effect. The strain remained after unloading, and the residual strain of each cycle can be used to define the shape fixability and recovery as follows.

$$\text{shape fixability} = \frac{\varepsilon_u}{\varepsilon_m}$$

$$\text{shape recovery} = \frac{\varepsilon_r}{\varepsilon_m}$$

where $\varepsilon_r = \varepsilon_m - \varepsilon_p$.

Dynamic mechanical properties of the solution cast films were determined using a Rheovibron (Orientec, DDV-01FP)
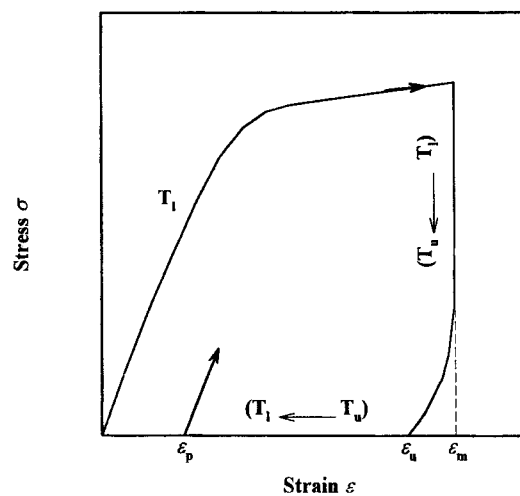
Fig. 2. Cyclic tensile test with loading at high temperature.

at 11 Hz, 3°C/min. Hardnesses (Shore A and D) at 25°C and 65°C were determined to relate the soft segment crystallization with soft segment length, soft segment content, and soft segment-hard segment phase separations.

3. Results and Discussion

3.1. Dynamic Mechanical Properties

Fig. 3 shows the storage moduli of PU ionomers and nonionomers prepared with different molecular weight of PCL (70% SSC). It is seen that PCL4000 and PCL8000 based PU ionomers and nonionomers clearly show a sharp glass-rubber transition at about 50°C corresponding to the T_m of soft segment, and a minor inflection point at about -50°C which corresponds to the glass transition of soft segment. On the other hand, PCL2000 based PU ionomer does not show a sharp transition, instead a broad transition with its point of inflection at around -25°C appeared. In addition, the value of plateau modulus of PCL2000 based PU ionomers is generally lower than the other two ionomers.

With the increase in PCL molecular weight, rubbery state as well as glassy state modulus increases due to the increased soft segment-hard segment phase separation and increased soft segment crystallization [7,8]. These observations indicate that PCL4000 and PCL8000 based PU ionomers are well phase separated to allow soft segment crystallization, whereas PCL2000 is insufficient to allow well organized soft and hard segments [9]. With only soft segment-hard segment phase separation, hard segments effectively act as reinforcing fillers for soft segments at temperature above the T_m of soft segment. Regarding the ionomer effect, ionomers show higher modulus, especially in rubbery state at the same SSC and soft segment length. Ionomer species augment the modulus via the Coulombic forces. Since the ionic centers are positioned within the hard domains, hard domain cohesions are increased in ionomers. The increased cohesion and microphase separations lead to an increase in modulus especially in rubbery state, together with extended plateau region over the nonionomers.

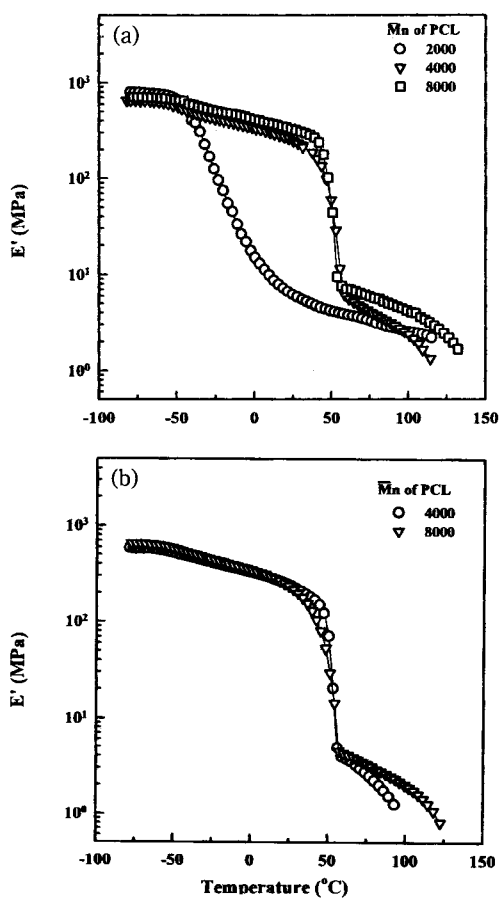Fig. 4 shows the effect of soft segment content on the e-

Fig. 3. Effect of PCL molecular weight on the storage modulus of PU ionomers (a) and nonionomers (b) with 70% SSC.
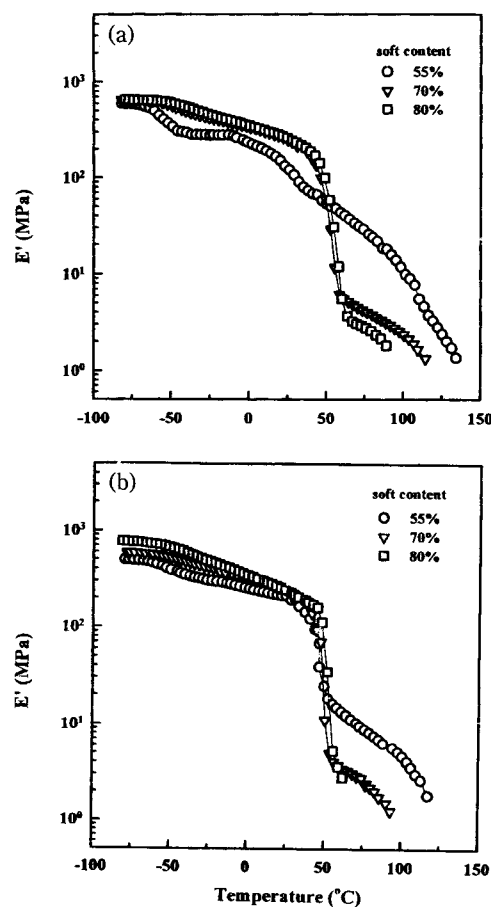

Fig. 4. Effect of soft content on the storage modulus of PU ionomers (a) and nonionomers (b) from PCL4000.
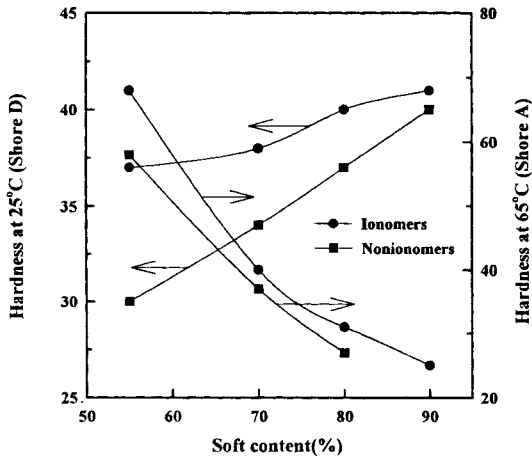
Fig. 5. Hardness of PCL4000 based PU ionomers and nonionomers at 25°C and 65°C.

lastic modulus of PU ionomers and nonionomers based on PCL4000. With increasing SSC, glass state modulus increases and rubbery state modulus decreases, due respectively to the increased soft segment crystallization and decreased HSC. Notably, the soft segment glass transition is clear with 55% SSC and disappeared with 70 and 80% SSC. The straightened modulus curve extends to the high glass state modulus with increasing SSC. It seems that the effect of ionic species depends on the SSC. At high SSC ($\geq 70\%$) ionomer gives higher glassy and rubbery state modulus. This implies that soft segment-hard segment phase separation is greater with ionomer. On the other hand at low SSC (55%) ionomer does not show a melting transition, implying that soft segment-hard segment phase separation is not great enough to allow soft segment crystallization.
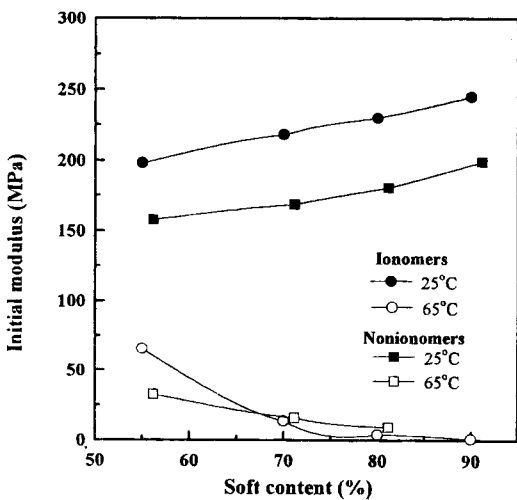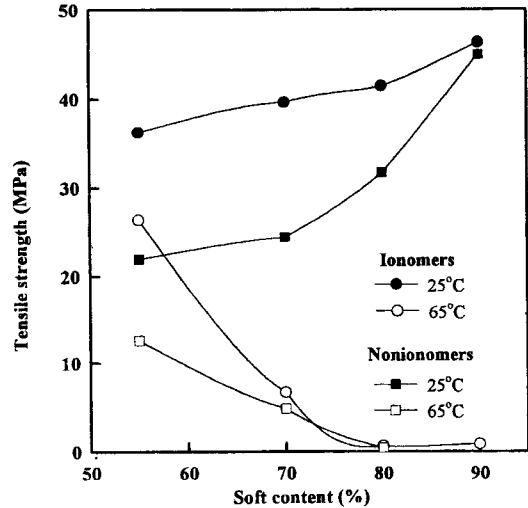

Fig. 7. Tensile strength of PCL4000 based PU ionomers and nonionomers at 25°C and 65°C.

3.2. Mechanical Properties

Mechanical properties of PU ionomers and nonionomers were measured at two temperatures viz., at room temperature (25°C) and high temperature (65°C). The room temperature corresponds to the glassy state whereas the high temperature to the rubbery state of the PUs, and these two temperatures respectively correspond to the unloading (T_u) and loading (T_l) temperatures in tensile cyclic loading tests of our experiments.

Generally room temperature properties increase and high temperature properties decrease with increasing soft segment contents. These include hardness (Fig. 5), initial modulus (Fig. 6), and tensile strengths (Fig. 7). The increased room temperature properties are due to the greater soft segment-hard segment phase separation and soft seg-
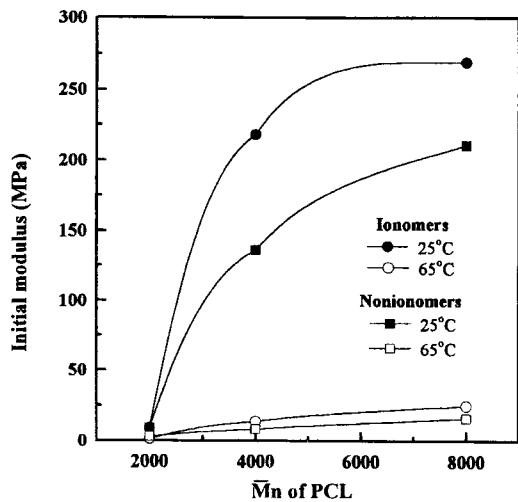

Fig. 6. Initial modulus of PCL4000 based PU ionomers and nonionomers at 25°C and 65°C.

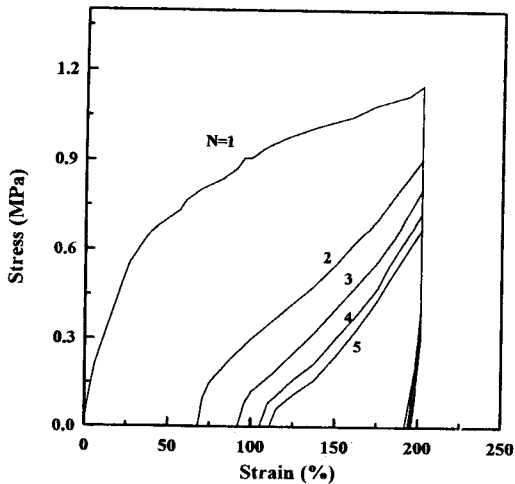**Fig. 8.** Initial modulus of PU ionomers and nonionomers with 70% SSC at 25°C and 65°C.

Fig. 9. Cyclic loading behavior of PU ionomer from PCL4000 with 70% SSC.

ment crystallization. However, at high temperature the crystalline soft segments are melted and consequently the increased SSC simply causes the decreased HSC content, giving rise to the decreased mechanical properties. Regarding the two types of PUs, ionomers give enhanced properties over the nonionomers, and the effect is more pronounced with high HSC and at room temperature. This seems reasonable since the ionic centers are located in the hard domains. So, increased hard contents make use of more Coulombic forces which are stronger at low than at high temperature.

The effect of increasing PCL molecular weight at fixed SSC is to increase the mechanical properties by the increased crystallinity of soft segment (Fig. 8) [10]. Effect of soft segment length is also more pronounced with ionomer than with nonionomer.
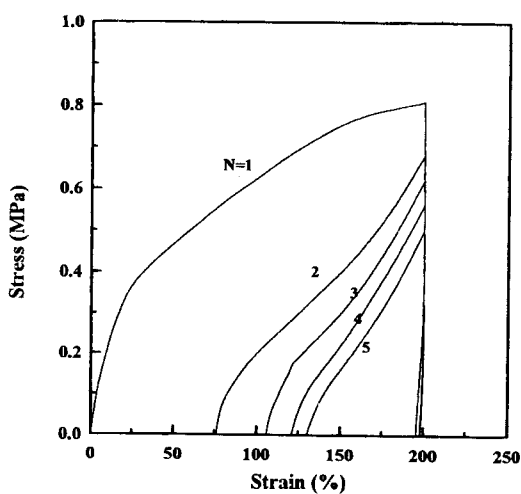

Fig. 10. Cyclic loading behavior of PU nonionomer from PCL4000 with 70% SSC.
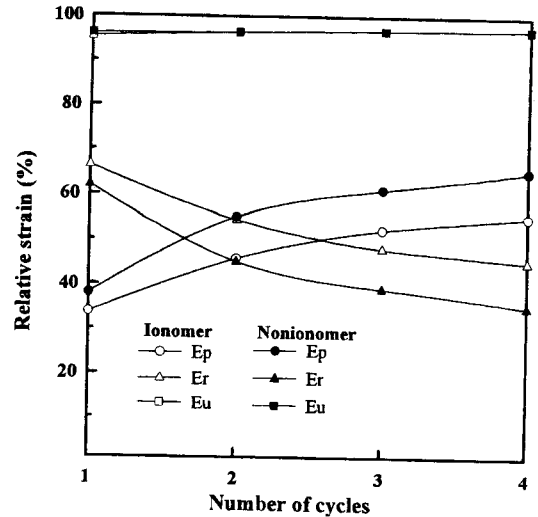
Fig. 11. Cyclic dependence of various strains for PU ionomer and nonionomer from PCL4000 with 70% SSC.

3.3. Cyclic Loadings

Tensile cyclic loading behavior has been studied with PCL4000 based PU having 70% SSC (Figs. 9 and 10). It is seen that the slope of loading curve increases with increasing number of cycle (N), implying that the resistance to deformation increases with cycling. This cyclic hardening is induced by the orientations of PU segments during extension at high temperature and crystallization during cooling. It should be noted however that most of the cyclic hardening and hysteresis are mainly confined to the first couple of cycles. This property can be used to obtain a uniform cyclic deformation, prior to practical applications. Various strains pertinent to cyclic loadings are summarized in Fig. 11 for ionomer and nonionomer. It can be seen that ionomer gives higher recovery strain (ε_r) and lower residual strain (ε_p) as compared to nonionomer, while the strain upon unloading is almost the same. Since the recovery strain is measured at T_b, viz 65°C in our experiments, it should depend on the rubbery state modulus of the PU. Namely, higher rubbery state modulus gave higher recovery strain for ionomers. This result is consistent with our dynamic mechanical measurements, mentioned earlier.

Acknowledgement

References

1. M. Ishii, Plastic Science, June 1989, pp 158-163 (in Japanese).
2. S. Hayashi, Plastic Science, June 1989, pp 169-172 (in Japanese).
3. M. Masao and A. Hirata, Plastic Science, June 1989, pp 173-178(in Japanese).
4. H. Tobushi, S. Hayashi, and S. Kojima, Jap. Soc. Mech. Engrs. Int'l. J. **35**(3), 296, (1992).
5. B.K. Kim, S.Y. Lee, and M. Xu, Polymer, **37**(26), 5781(1996).
6. D.J. David and H.B. Staley, Analytical Chemistry of Polyurethanes, Wiley-Interscience, New York, 1969.
7. J.E. Mark, A. Eisenberg, W.W. Grassley, L. Mandelkern, and J.L. Koenig, Physical Properties of Polymers, Amer. Chem. Soc., Washington, D.C., 1984.
8. J.C. Lee and B.K. Kim, J. Polym. Sci., Polym. Chem. Ed., **32**, 1983(1994).
9. Y. M. Lee, J.C. Lee, and B.K. Kim, Polymer, **35**(5), 1095(1994).
10. B.K. Kim and J.C. Lee, Polymer, **37**(3), 469(1996).