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Polyurethane ionomers having shape memory effects

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Polyurethane (PU) ionomers and non-ionomers with various soft segment contents (SSC) and lengths have been synthesized from polycaprolactone diols (PCL), 4,4′-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD) and dimethylolpropionic acid (DMPA), and tested for shape memory behaviour as well as for mechanical and dynamic mechanical properties. It was found that ionomers gave higher hardness, modulus and strength as compared with non-ionomers, 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 behaviour, 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. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Shape memory polymers are temperature-sensitive functional polymers which find broad applications in temperature-sensing elements. These polymers basically consist of two phases, i.e. frozen phase and reversible phase. Accordingly, excellent shape memory effects have often been observed with block or segmented copolymers [1–3]. In some cases, the crystalline soft domains form the reversible phase, with their crystalline melting temperature (T_m) being the shape recovery temperature (T_s), and hard domains become the frozen phases. The frozen phase remains in the glassy state during the second shaping process, which is normally done at a temperature higher than T_s. The reversible phase is subject to softening and hardening upon heating above and cooling below the T_s, respectively.

During primary processing, such as injection moulding, the materials are heated above the softening–hardening transition temperature of the fixed phase (T_h), where the previous memories are completely erased. During the cooling in the mould, 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 moulded specimen is the original shape of the shape memory experiment.

The secondary shapings, such as extension, compression and transfer moulding are typically done at $T > T_s$. The deformed shape is fixed upon subsequent cooling under constant strain. The original shape is recovered during heating to $T > T_s$. The driving force of shape recovery is the elastic strain generated during the deformation. Deformation at high temperature is much easier owing to the lower rubbery modulus of the polymer, and makes the orientations more feasible. However, 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. A high glassy state modulus will provide the materials with high shape fixability, whereas a high rubbery modulus will provide the materials 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. A 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 behaviour of the materials is of basic importance with regard to the shape memory effect evaluations. In addition, the shape memory polymer element is often subjected to cyclic deformation, such as in an 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 sometime, shape memory polymers are low density, highly shape recoverable, easily processed 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. They can be moulded using conventional processing techniques, including extrusion, injection and blow moulding, which allow versatile shapings.

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We have earlier reported shape memory effects of polyurethanes (PU) [5]. In this paper we report the shape memory behaviour of ionomer type polyurethanes prepared from polycaprolactone diols, 4,4′-diphenylmethane diisocyanate, 1,4-butanediol, and dimethylolpropionic acid. The 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, thermal properties and temperature-dependent physical properties. The results from ionomers were favourably compared with those from non-ionomers.

EXPERIMENTAL

Materials and preparations of polyurethanes

Table 1 shows the basic formulations of the present experiments. Polycaprolactone diols (PCL, Daircel) with molecular weight ($\bar{M}n$) 2000, 4000 and 8000 (g/mole) (hereafter called PCL2000 etc.) were dried and degassed at 80°C–100°C under 1–2 mmHg for 5 h before use. Extra pure grade of 4,4′-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD) and dimethylolpropionic acid (DMPA) was used with PCL to prepare segmented polyurethane ionomers and non-ionomers. Ionomers were obtained by neutralizing the COOH groups of DMPA with triethyl amine (TEA). PCL of molecular weight 8000 (g mole^{-1}) was not commercially available, and was prepared from condensation reactions between PCL4000 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 (g.p.c.) was approximately 7950 (g mole^{-1}), and this will be referred to as PCL8000.

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 a reactor to prepare the polyurethanes. Dried PCL and a molar excess of MDI were charged to the dried flask. The urethane-forming reaction was carried out at 60°C for about 1.5 h, 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 1 h. 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].

Film casting and tests

Films were prepared by casting on a glass plate. After standing at 60°C for 3 h, films were further dried at 70°C under 2–4 mmHg for the next 4 days. Microtensile specimens (25 (length) × 4 (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 with compressed air. Loading and unloading together with heating and cooling were controlled by a personal computer which was interfaced with the tensile tester. *Figure 1* defines a thermomechanical cycling test with loading at high temperature (T_l) and unloading at low temperature (T_u). The sample is elongated to a maximum strain (ε_m) at a constant elongation rate ($\dot{\varepsilon}$). While maintaining the strain at ε_m, the sample is cooled to low temperature $T_u(<T_s)$ and unloaded. During the cooling period a substantial recovery of strain ($\varepsilon_m - \varepsilon_u$) occurs. The sample is subsequently heated to T_l in 5 min, and stays 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 that below the unloading curve corresponds to the recovery 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.

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

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

The dynamic mechanical properties of the solution cast films were determined using a Rheovibron (Orientec, DDV-01FP) at 11 Hz, 3°C min^{-1}. Hardnesses (Shore A and D) at 25°C and 65°C were determined to relate the soft segment crystallization with soft segment length, soft

Table 1 Formulation of the polyurethane synthesis

$\bar{M}n$ of polyol	Polyol (mole)	Chain extender (mole)		Diisocyanate (mole)	Soft content (%)	
		BD	DMPA			
2000	1	0.51	0.51	2.02	70	Ionomer
4000	1	2.91	2.91	6.82	55	Ionomer
	1	1.36	1.36	3.72	70	Ionomer
	1	0.65	0.65	2.3	80	Ionomer
	1	0.1	0.1	1.2	90	Ionomer
8000	1	3.06	3.06	7.12	70	Ionomer
2000	1	0.51	0.51	2.02	70	Non-ionomer
4000	1	2.91	2.91	6.82	55	Non-ionomer
	1	1.36	1.36	3.72	70	Non-ionomer
	1	0.65	0.65	2.3	80	Non-ionomer
	1	0.1	0.1	1.2	90	Non-ionomer
8000	1	3.06	3.06	7.12	70	Non-ionomer

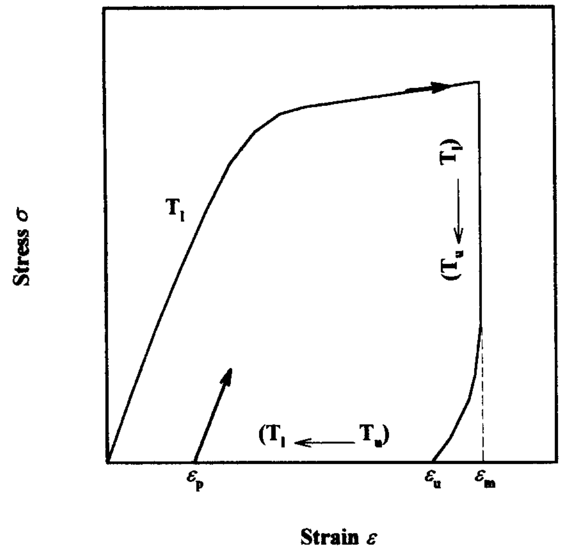

Figure 1 Cyclic tensile test with loading at high temperature

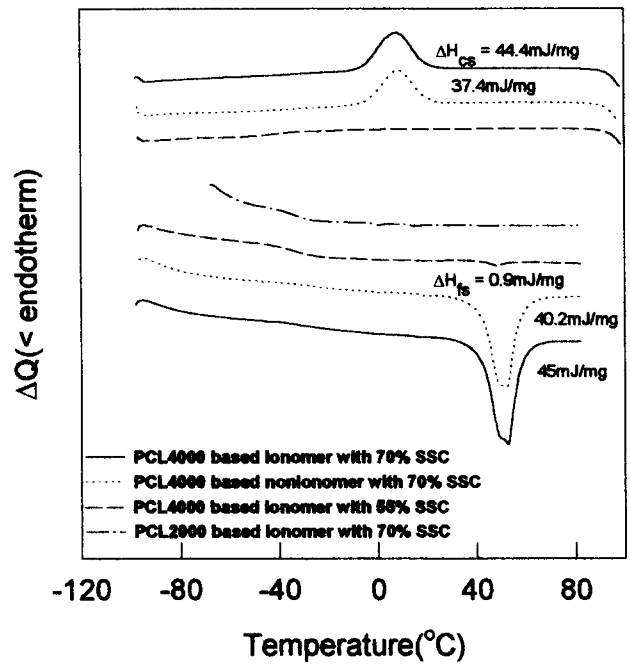

Figure 2 DSC thermograms of PU ionomers and nonionomers

segment content, and soft segment–hard segment phase separations.

Thermal properties were measured using a DSC (Seiko Instrument SCC/5200). Samples were heated and cooled at 10°C min^{-1}, and the exotherm and endotherm were obtained during the second cycle recording the T_m, T_{cs} (crystallization temperature), ΔH_{cs} (heat of crystallization), and ΔH_{fs} (heat of fusion).

RESULTS AND DISCUSSION

Thermal properties

Typical DSC thermograms of PU ionomers and non-ionomers are shown in *Figure 2*. At 70% SSC, soft segments of PCL2000-based ionomer do not crystallize, whereas those of PCL4000-based segments show clear endotherm and exotherm at about 50°C and 10°C, respectively. This implies that soft segment–hard segment phase separation is insufficient with PCL2000 in PU ionomers.

With PCL4000-based PUs with 70% SSC, PU non-ionomers show similar thermal behaviour with ionomers. However, slightly lower or smaller T_m, T_{cs}, ΔH_{cs}, and ΔH_{fs} are obtained with the non-ionomer, implying that microphase separation is increased with the ionomer at high SSC.

Regarding the effect of soft segment content (55 and 70%), 70% SSC gave soft segment crystallization for both ionomer and non-ionomer. However, 55% SSC gave soft segment crystallization for non-ionomers (not shown) but did not induce crystallization for ionomers. It seems that the effect of the ionomer on microphase separation is twofold, i.e. at low SSC, phase separation is decreased and at high SSC phase separation is increased with the ionomer.

Dynamic mechanical properties

Figure 3 shows the storage moduli of PU ionomers and non-ionomers prepared with different molecular weights of

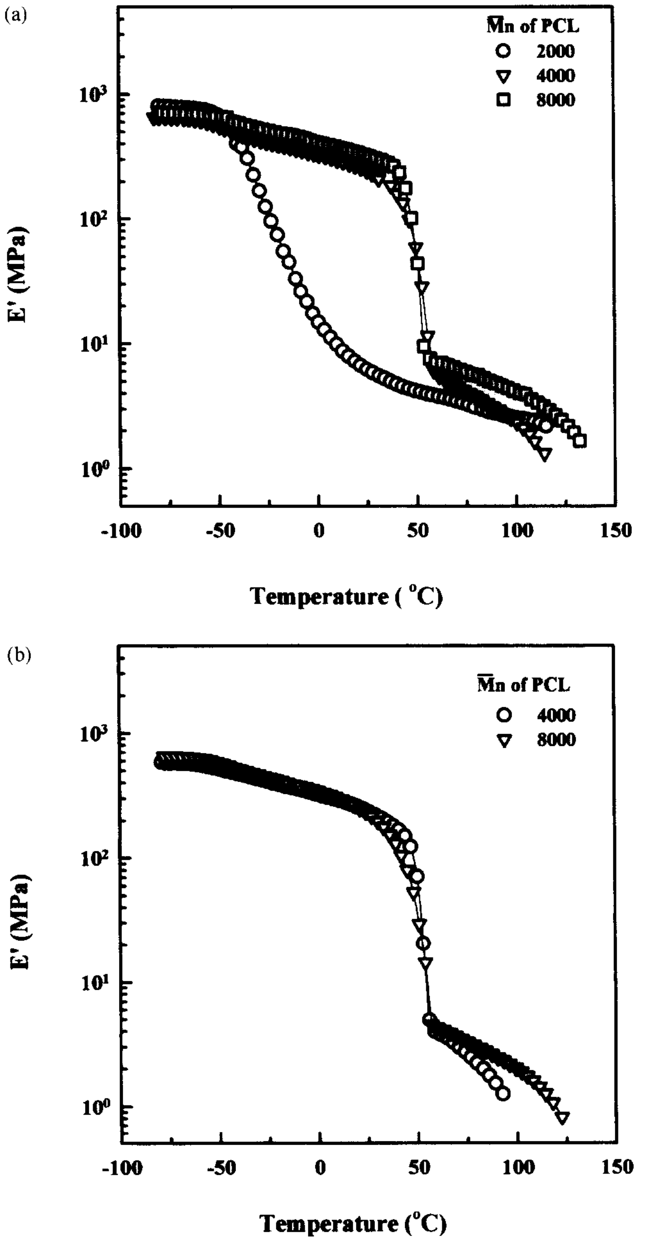

Figure 3 Effect of PCL molecular weight on the storage modulus of PU ionomers (a) and nonionomers (b) with 70% SSC.

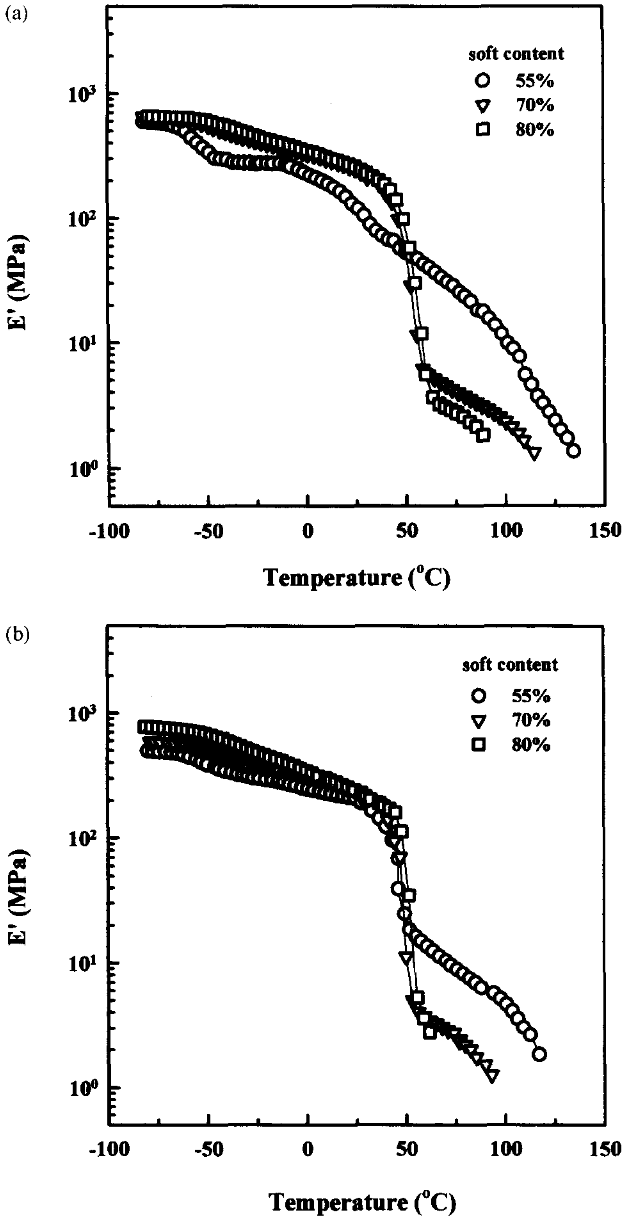

Figure 4 Effect of soft segment content on the storage modulus of PU ionomers (a) and non-ionomers (b) from PCL4000

PCL (70% SSC). It is seen that PCL4000- and PCL8000-based PU ionomers and non-ionomers clearly show a sharp glass–rubber transition at about 50°C, corresponding to the T_m of the soft segment as our DSC results indicated, 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 appeared. This is due to the amorphous nature of the soft segment (*Figure 2*). In addition, the plateau modulus of PCL2000-based PU ionomers is generally lower than the other two ionomers. With the increase in PCL molecular weight, the rubbery state as well as the glassy state modulus increases owing 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 the soft segment length of PCL2000 is insufficient to allow well-organized soft and hard segments. With soft segment–hard segment phase separation, hard segments effectively act as reinforcing fillers for soft segments at temperatures above the T_m of the soft segment. With the same soft segment length and content, ionomers show higher modulus, especially in the rubbery state. Ionomer species augment the modulus via the Coulombic forces. Since the ionic centres are positioned within the hard domains, the hard domain cohesions are increased in ionomers. The increased cohesion and micro-phase separations, lead to an increase in modulus especially in the rubbery state, together with an extended rubbery plateau over the non-ionomers.

Figure 4 show the effect of soft segment content on the elastic modulus of PU ionomers and non-ionomers based on PCL4000. With increasing soft segment content, soft segment glass transition at about −50°C becomes less significant, leading to an increased and extended glass state modulus, followed by a sharp melting transition and rubbery region, both in ionomers and non-ionomers. The increase in glass state modulus is caused by the increased soft segment–hard segment phase separation and soft segment crystallization [9]. The rubbery state region is somehow defined owing to the increased phase separation, since hard segments are totally responsible for the load-bearing capability at $T > T_m$. Regarding the difference between ionomers and non-ionomers, ionomers generally give a bit higher modulus than the non-ionomers, in both the glassy

Table 2 Mechanical properties of PU ionomrs and non-ionomers

$\overline{\mathrm{M}}$n of polyol		Soft content (wt%)	Hardness		Initial modulus (MPa)		Tensile strength (MPa)	
			25°C (Shore D)	65°C (Shore A)	25°C	65°C	25°C	65°C
Ionomer	2000	70	—	—	13.2	0.7	—	—
	4000	55	36.3	67.8	196.2	68.3	35.7	26.7
	4000	70	37.5	40.1	218.6	17.7	39.5	8.5
	4000	80	39.4	31.7	226.0	6.8	40.8	1.1
	4000	90	41.2	24.7	243.3	2.1	47.2	1.0
	8000	70	—	—	265.4	25.2	—	—
Non-ionomer	2000	70	—	—	12.1	0.5	—	—
		55	30.2	58.9	158.3	26.5	21.8	12.3
	4000	70	33.5	36.9	163.3	12.4	22.7	15.5
	4000	80	36.8	26.5	175.2	11.9	31.2	0.8
	4000	90	39.4	—	192.3	—	44.7	—
	8000	70	—	—	212.8	18.5	—	—

and the rubbery state. It is, however, noted that when the SSC is low (55%), the ionomer gives two step transitions at about −50°C and 25°C, while the non-ionomer gives a sharp melting transition at about 50°C, and a small relaxation at about −50°C. This implies that phase separation is more complete with the non-ionomer than with the ionomer at low SSC. This was suggested from the DSC results. With increasing SSC, glass modulus increases and rubbery modulus decreases owing to the decreased soft segment crystallization and decreased hard segment content, respectively.

Mechanical properties

Mechanical properties of PU ionomers and non-ionomers were measured at two temperatures, i.e. at room temperature (25°C) and high temperature (65°C) and these are tabulated in *Table 2*. The room temperature corresponds to the glassy state, whereas the high temperature corresponds to the rubbery state of the PUs, and these two temperatures correspond to the unloading (T_u) and loading (T_l) temperatures in tensile cyclic loading tests of our experiments.

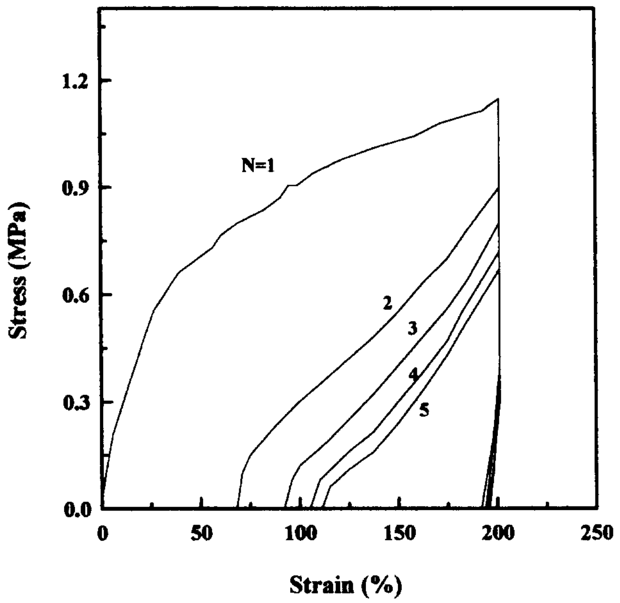

Figure 5 Cyclic loading behaviour of PU ionomer from PCL4000 with 70% SSC

Generally, room temperature properties increase and high temperature properties decrease with increasing soft segment contents. These include hardness, initial modulus and tensile strengths. The increase in room temperature properties is due to the greater soft segment–hard segment phase separation and soft segment crystallization. However, at high temperature the crystalline soft segments are melted and, consequently, the increased soft segment content simply causes the decreased hard segment content, giving rise to decreased mechanical properties. Regarding the two types of PUs, ionomers give enhanced properties over non-ionomers, and the effect is more pronounced with high hard segment content and at room temperature. This seems reasonable, since the ionic centres are located in the hard domains. So, increased hard contents make use of more Coulombic forces which are stronger at low than at high temperatures.

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

Tensile cyclic loading properties were studied with PCL4000-based PU with 70% SSC (*Figures 5 and 6*). It has been found that the slope of loading curve increases with increasing number of cycles (*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 *Figure 7* for the ionomer and

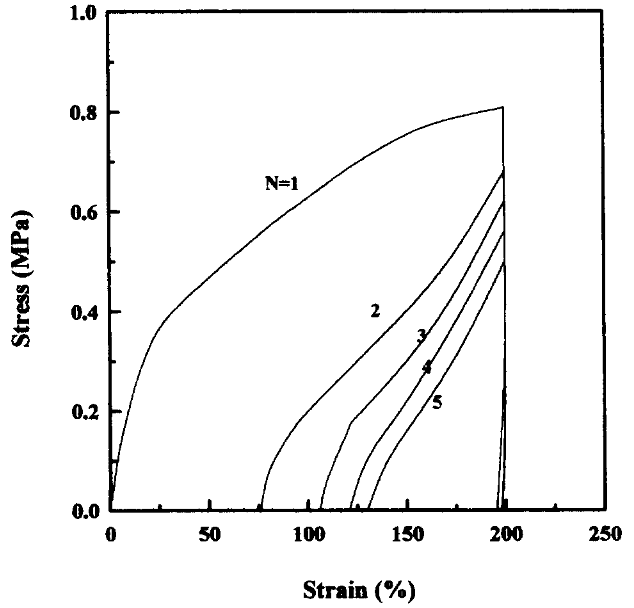

Figure 6 Cyclic loading behaviour of PU non-ionomer from PCL4000 with 70% SSC

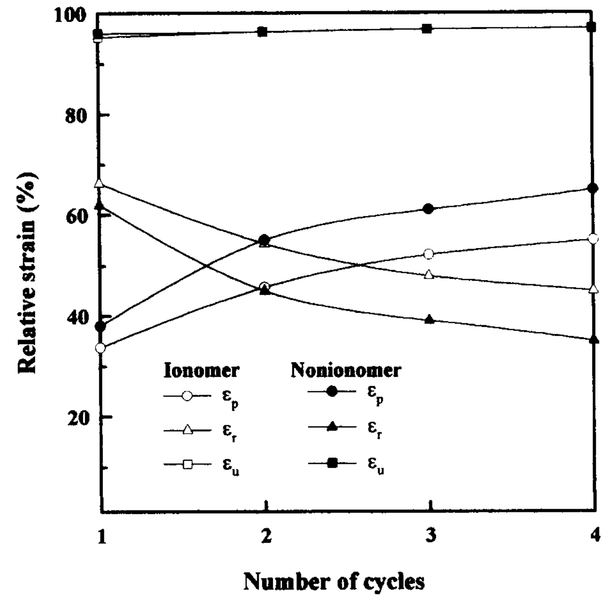

Figure 7 Cyclic dependence of various strains for PU ionomer and non-ionomer from PCL4000 with 70% SSC

the non-ionomer. It can be seen that the ionomer gives higher recovery strain (ε_r) and lower residual strain (ε_p) as compare with the non-ionomer, while the strain upon unloading is almost the same. Since the recovery strain is measured at T_l, i.e. 65°C in our experiments, it should depend on the rubbery state modulus of the PU. In other words, the higher the rubbery state modulus of the ionomer, the higher the recovery strain results. This result is consistent with our dynamic mechanical measurements, mentioned earlier.

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