Segment형 폴리우레탄의 열자극변형회복

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Thermally Stimulated Strain Recovery of Segmented Polyurethanes

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초 록   polycaprolactone diol(PCL), 4,4′-diphenylmethane diisocyanate(MDI) 및 1,4-butane diol(BD)로부터 seg-ment형 폴리우레탄을 합성하였으며, 이들의 열변형 회복 특성을 조사한 결과 이들 재료들은 전형적인 형상기억 효과를 발휘함을 알수 있었다. 청상회복온도는 연질성분의 함량 증가와 더불어 증가하였으며, 연질성분의 함량조절로 40∼80℃의 넓은 범위에서 임의로 조절할 수 있었다.

Abstract   Thermally stimulated strain recovery of polyurethane based on 4,4′-diphenylmethane diisocyanate(MDI), 1,4-butane diol(BD) and polycaprolactone diol(PCL) as a soft segment was investigated. It was found that these seg-mented polyurethanes exhibit typical shape memory property of very large strain recovery. The critical shape recovery temperature increased with increasing soft segment content of the segmented polyurethanes, and it ranged from 40 to 80℃ depending on the composition of the segmented polyurethane.

key words : polyurethanes, shape memory, cyclic loading

1. Introduction

Deformation of polymer materials usually consists of two parts ; irreversible plastic strain and reversible elastic one. The recovery of the elastic strain may occur immediately after withdrawing the external stress at higher temperatures in a heating process. This is one important performance of functional polymer materials. However, the amount of thermally recoverable elastic strain of conventional plastics is usually too low to be used practically for the thermally stimulated shape recovery function. Several methods are now available to resolve this problem[1,2]. One is to prepare a composite with parallel alignment of a rubber and plastic material. Another method is to make a crystalline polymer slightly crosslinked. Example of the latter is polyethylene crosslinked by a reaction with ionizing radiation. The use of block or segmented copolymers is believed to be a versatile way to provide a high recoverable strain, once the polymers are properly designed. Segmented polyurethanes are multiblock copolymers. Their molecular structures are characterized by the alternating sequence of chemically different two segments. The two segments are different from each other in molecular motion. Generally, the glass transition temperature of the hard segments is above the room temperature, while the soft segments are in a rubbery state at room temperature[3-5]. Since hard and soft segments are thermodynamically immiscible in most cases, micro-phase separation of the segments occurs in these specimens. The hard segment domains can serve as physical crosslinks for the rubbery soft segments, imparting high elasticity to the material. Since the polymers are physically crosslinked in nature, they can be processed like thermoplastics.

It is believed that if soft segments with glass transition or melting temperature higher than room temperature are introduced into a segmented copolymer, then it may also show the thermally stimulated shape recovery effect. The advantage of using segmented copolymers as shape memory materials is the possibility of controlling the critical recovery temperature to meet the needs of various applications[6]. Moreover, the polymers can be processed conveniently because of the thermoplasticity.

We consider the effect of soft segment content(50-90%) on the thermal shape recovery of segmented pol-

Table 1. Formulation of the Polyurethane Synthesis

Run #	M_n of PCL	moles of polyol	moles of MDI	moles of BD	soft segment (%)
1	4000	1	11	10	50
2	〃	〃	7	6	60
3	〃	〃	5	4	70
4	〃	〃	4	3	75
5	〃	〃	3	2	70
6	〃	〃	2	1	85
7	〃	〃	1.3	0.3	90

yurethanes, prepared from polycaprolactone diol (PCL) of molecular weight 4000 (g/mole) and 4,4'-diphenylmethane diisocyanate (MDI).

2. Experimental

Basic formulation for PU synthesis is given in Table 1. PCL (Daicel) was dried and degassed at 80℃ under 1~2mmHg for five hrs before use. Extra pure grades of MDI and 1,4-butanediol (BD) (Fluka) were used. A 500ml round bottom, four-necked separable flask equiped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube was used to prepare the segmented PUs. Isocyanate terminated PU prepolymers were synthesized at 60℃ for about 1.5hr, by the reaction of dried PCL and molar excess of MDI. The PU prepolymers were reacted with BD at the same condition. The progress of reaction was monitored by measuring the isocyanate value. A standard n-dibutylamine back titration method was employed[7]. Films were prepared by casting the solution on a glass plate. After keeping the cast solution at 60℃ for three hours, the films were further dried at 70℃ under 2~4mmHg for three days.

Microtensile specimens (25 (length) ×5 (width) × 1mm (thickness)) were prepared according to ASTM D -1822. The thermally stimulated shape recovery specimens were prepared by stretching the specimen to a draw ratio of three, corresponding to 200% strain at 65℃, followed by cooling down to .16℃ under constant length. The time period of setting at 16℃ was 2min. Then the specimens were heated at a heating rate of 2.7℃/min. The thermal recovery effect was directly observed under microscope and recorded by a special extensometer.

T_m of PCL was measured using a differential scanning calorimeter (DuPont 2100) at the heating and cooling rate of 20℃/min. X-ray photographs were taken at room temperature on a D/max-RB x-ray unit with Cu Kα radiation.

Tensile cyclic loading tests were done using a tensile tester (Tinus Olsen 1000), equipped with a constant temperature heating chamber. Specimens were heated using a bundle of heating lamps, and cooled by spraying compressed air. Loading and unloading, together with heating and cooling were automatically controlled by a personal computer which was interfaced with the tensile tester. Specimen was elongated to a draw ratio of three at 65℃ which is higher than the T_m of soft segment. While maintaining the strain constant, sample was cooled to room temperature and unloaded. Subsequently sample was heated to 65℃ and stayed at the temperature for five minutes to complete one cycle.

3. Results and Discussion

Fig. 1 shows the thermal strain recovery curves of PCL4000 (number designates molecular weight) based PUs having various ranges of soft-hard segment compositions. T_m and T_c (crystallization temperature) of PCL4000 were 49.5℃ and 30.3℃, respectively. The thermal recovery is expressed in terms of recovery ratio, viz $R = S_r/S_o$ where S_r and S_o are the recovered strain and initial strain, respectively. It is seen that the strain recovery at room temperature decreases with increasing soft segment contents. This is due to the increased soft-hard segment phase separation and hence the increased soft segment crystallization. With soft segment crystallization, modulus at low temperature and the shape fixability upon cooling increase. The shape fixability is proportional to the strain retained upon unloading at room temperature. It is seen that the strain recovery remained constant at low temperatures, and increased abruptly with increase of temperature,
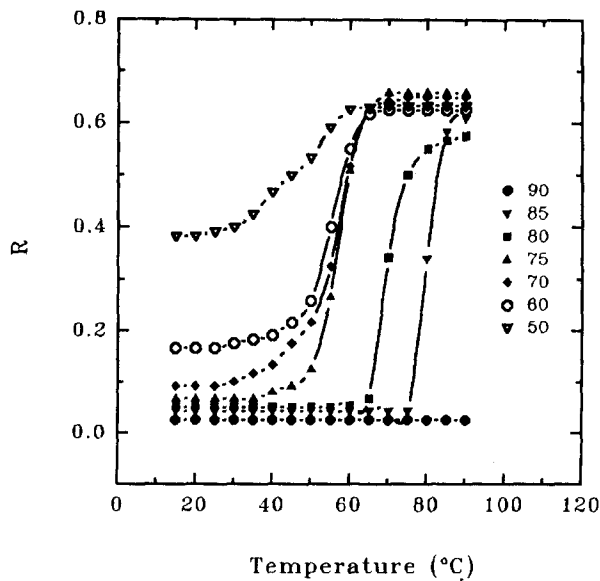
Temperature (°C)

Fig. 1. Recovery ratio vs. temperature for PUs of various compositions (Number designates soft segment content(%)).

Fig. 2. WAXD patterns of specimens, a) original and b) elongated.

and eventually reached to a high constant value depending on the type of specimen. The increase of strain recovery from a low constant value to a high constant value spans over 30 ℃ with 50% soft segment PU. However, the transition curves become sharper and move toward the high temperature with increasing soft segment content. The transition temperature range is approximately 5 ℃ with 85% soft segment. It seems that the transition temperature is not matched with the T_m of soft segments. However, transition temperature increased with increasing T_m of soft segment. Sharp transition is expected with high soft segment content owing to the great phase separation and hence relatively pure soft segment domains. With extremely high soft segment content (90%), strain is not recovered with thermal stimulation within the temperature range tested.

The shape memory effect of these segmented PUs may be attributed to the structural characteristics of the two segment domains at room temperature. The hard segment domains may act as physical crosslinks, and the soft segment domains should freeze the elastic deformation. In the original specimens microphase separation may occur, and both the soft and hard segments crystallize and be randomly distributed with no macroscopic anisotropy. They become highly entropy elastic at temperature above the T_m of the soft segment. The specimen may recover their dimensions by the elimination of stress after stretching to high deformation values. However, when the stretched specimens are cooled to low temperature at that deformation, the elastic de-
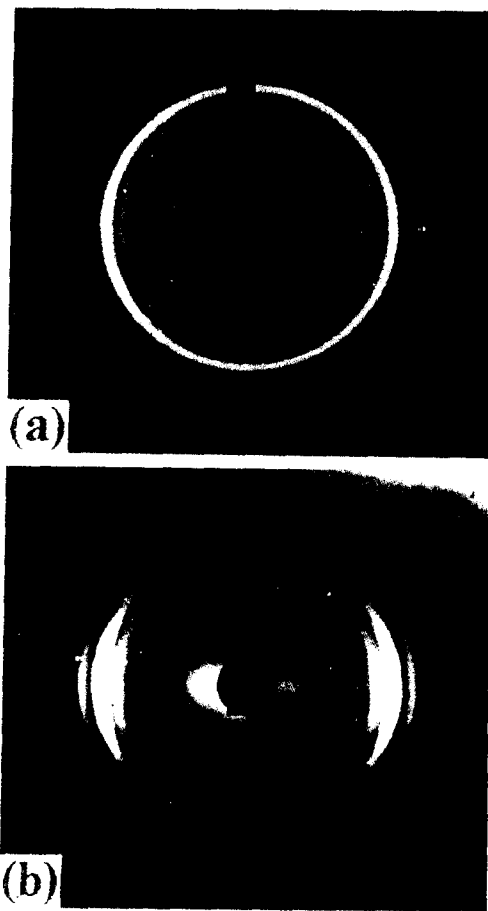
formation can be frozen and retained after withdrawing the external stress due to the crystallization of soft segments. When the specimens are re-heated the soft segment crystals will melt, and the stored elastic energy will push the specimens to take their original shape before stretching.

Fig. 2a shows the typical WAXD pattern of an original PU specimen containing 75% soft segment, which mainly exhibits the diffraction pattern of the PCL crystals. Uniformly distributed intensity in all azimuthal angles indicates that there is no preferred orientation of the crystals. As expected, the PCL crystals oriented in the shape recoverable specimen with the molecular axes parallel to the stretching direction (Fig. 2b). After thermal recovery the specimen goes back to its original state, and the WAXD pattern is identical to that shown in Fig. 2a.

Shape memory polymer element is often used as a part of machines which is subject to cyclic deformation such as actuator. Hence the cyclic deformation characteristics are practically important in evaluating the durability of shape memory elements. Fig. 3 show the typical cyclic stress-strain behavior of PU including 60%
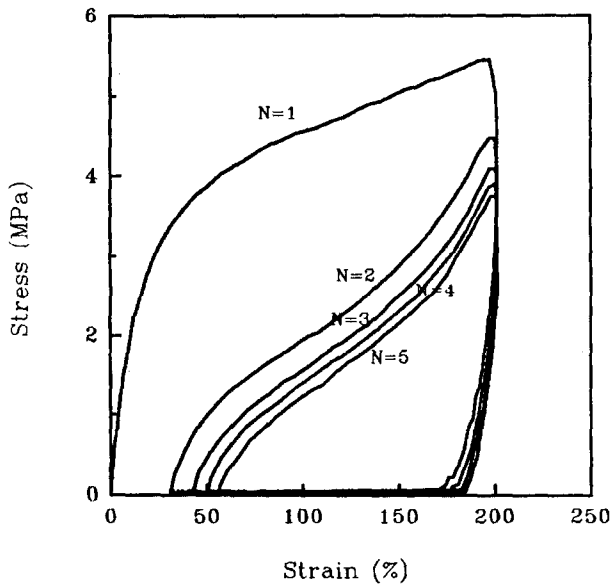
Fig. 3. Cyclic stress-strain behavior of PU including 60% soft segment.

soft segment. For this experiment, specimen was extended three times at 65℃, followed by cooling to 16℃ which is below the T_c of soft segment, and unloaded. It is seen that the hysteresis of stress-strain curve is mostly confined to the first several cycles and no significant variation is observed with further cyclings. The

insensitivity of cyclic properties with repeated cycles can be used to obtain a uniform cyclic deformation, prior to their practical applications. Regarding the effect of soft segment content, higher soft segment generally gave poorer shape fixability and greater strain recovery. More systematic investigations are undergoing.

4. Acknowledgements

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