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Thermomechanical Properties and Shape Memory Effect of Chemically Crosslinked EPDM (Nordel® IP)

Young-Wook Chang†, Jung-Eun Han, Shin-Choon Kang, and Ur Ryong Cho*
Department of Chemical Engineering, Hanyang University, Ansan, 426-791 Korea
**Department of Applied Chemical Engineering, University of Technology and Education, Cheonan, 330-708 Korea*
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화학적으로 가교된 EPDM (Nordel® IP)의 열적기계적 특성 및 형상기억거동

장 영 욱† · 한 정 은 · 강 신 춘 · 조 을 룡*
한양대학교 화학공학과, *한국기술교육대학교 응용화학공학과
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ABSTRACT : Thermomechanical and shape memory properties of dicumyl peroxide(DCP) cured semicrystalline EPDM(Nordel® IP) were investigated. From gel content analysis, it can be seen that Nordel can be crosslinked by small amount of DCP and the degree of crosslinking increased with the increase of DCP content. DSC analysis revealed that the melting temperature and degree of crystallinity of the crosslinked rubber decreased with the increase of DCP. Tensile test showed that tensile modulus increased and elongation at break of the rubber decreased with an increase in the degree of crosslinking. The chemically crosslinked semi-crystalline EPDM exhibited excellent shape memory behavior, i.e. the sample was easily deformed to have an arbitrary secondary shape above its melting temperature and was fixed well in its deformed state when it is cooled, and then the fixed shape was recovered to its original shape very fast upon heating above its melting temperature.

요 약 : 결정성을 갖는 에틸렌프로필렌디엔 고무(Nordel®IP)를 과산화물로 가교시키고 열적, 기계적특성과 형상기억거동을 조사하였다. 겔함량 측정결과 가교도는 DCP 함량에 따라 증가되었으며, DSC 분석결과 가교된 고무는 결정상이 존재하고 있음을 알 수 있었다. 인장시험 결과 가교도가 증가함에 따라 고무의 모듈러스는 증가되며 파단신율은 감소되었다. 이와 같이 가교구조 내에 결정상을 함유하는 고무는 우수한 형상기억 특성을 나타내었다. 즉, 이러한 고무는 결정상의 용융온도 이상에서 쉽게 원하는 형태로 변형되고, 변형된 상태에서 냉각시키면 변형된 형태로 잘 고정되었으며, 또한 이렇게 변형된 형상의 시료를 용융온도 이상으로 가열하면 원래의 모양으로 신속히 되돌아오는 것을 관찰할 수 있었다.

Keywords : semicrystalline EPDM(Nordel IP), crosslinking, thermomechanical properties, shape memory behavior

† 대표저자(*e-mail : ywchang@hanyang.ac.kr*)

Ⅰ. Introduction

Shape memory polymer(SMP) is a smart material that can recover its original shape after being deformed into a temporary shape when it is heated or receives any other stimuli.[1] Due to their low cost, low density, and high deformability compared to conventional shape memory alloys, the shape memory polymer have potential applications such as actuators, robotics, microelectromechanical systems, and biomedical devices.

These shape memory polymers basically have two structural features, i.e. the cross-links that determine the permanent shape and the reversible segments having a glass transition or a crystalline melting transition. A temporary shape can be fixed via the quenching of the deformed polymer network to a temperature well below the transition temperature. Reheating the sample above the transition temperature, the temporary shape can be recovered to its permanent shape due to entropy elasticity of polymer chains. Most widely studied shape memory polymer is segmented polyurethanes bearing physically crosslinked segments, but their shape memory effects are deteriorated under cyclic programming due to creeping during repeated deformation.[2,3]

Chemically crosslinked shape memory polymers have been studied to overcome this problem. Some research groups investigated amorphous networks whose glass transition can be tuned above room temperature by proper choice of crosslinking systems, which include soybean based network cured with divinyl benzene,[4] thermosetting polyurethanes,[5] epoxidized natural rubber cured by aromatic amine.[6] The other researchers investigated networks containing crystalline domains, which include peroxide cured ethylene copolymer[7] and photo-cured poly(ε-caprolactone)(PCL).[9-12]

In this study, we demonstrated a thermomechanical and shape memory behavior of crosslinked semicrystalline olefinic elastomer, ethylene-propylene diene terpolymer (EPDM, Nordel® IP). Nordel® IP, produced by DuPont with metallocene catalyst chemistry, has a higher standard performance compared to conventional EPDM.

Ⅱ. Experimental

1. Materials and curing

Nordel IP 3745P (ML_{1+4} @25℃ = 45, ethylene(wt %)/C3 = 69/30.5, ENB(wt %) = 0.5) was kindly supplied by DuPont-Dow Elastomer. Rubber was melted for 1 min in a Banbury type internal mixer (Haake Polylab 3000) at 60 rpm and at 80℃, followed by DCP loading of various amount (0.1, 0.5, 1.0 and 2.0 parts per hundred rubber, phr) and then mixing was continued for another 10 min. Such samples were coded as Nordel-0.1, Nordel-0.5, Nordel-1.0 and Nordel-2.0, respectively. The rubber mixture was then passed several times through a laboratory mill at a nip gap of 2 mm to make a rubber compound as a sheet. The rubber sheet was cured in an electrically heated press (Carver 2518) at 180℃ for 30 min, which is the optimum cure time(t_{90}) determined from an oscillating disk rheometer (Monsanto, R-100). After curing, the specimen was cooled to room temperature in the mold.

2. Gel fraction measurement

For the measurement of gel fraction of the cured sample, the sample was wrapped with a stainless steel net and then was immersed in xylene at 80℃ for 72 hours. Insoluble portion of the sample was measured after complete drying of the swelled sample in a vacuum oven. The gel fraction was calculated from the weight of the sample before and after the swelling as follows:

$$\text{Gel fraction (\%)} = [(w_g / w_i)] \times 100$$

where w_g is the weight of insoluble portion of the sample and w_i is the initial weight of the sample.

3. Measurement of thermomechancial properties

Melting transitions of the samples were measured

by using a differential scanning calorimeter (TA Instrument DSC 2010). 10 mg of the samples dried completely in vacuum oven was used for the analysis. The sample was heated to 100℃ at a rate of 10℃/min under a nitrogen atmosphere and was kept for 5 min at this temperature to remove thermal history. And then the sample was cooled to -40℃ at a rate of -10℃/min to induce crystallization. The sample was heated again to 100℃ at a rate of 10℃ /min to observe melting behavior.

Ultimate tensile strength, elongation-at-break and tensile modulus were determined according to ASTM D412 specifications. These tests were performed using a universal testing machine (United Co., STM-10E) at 30℃ with a cross-head speed of 500mm/min.

4. Measurement of shape memory properties

The shape memory effect was evaluated by the measurement of recovery strain at various temperatures from its temporary shape prepared by temperature programming.[12] The temporary shape was prepared by stretching it by 100% elongation at a constant draw rate and at temperature $T = T_m + 20$℃, and a subsequent quenching at $T < T_m$-20℃. The recovered strain was measured in a heating process at the heating rate of 2℃/min. Under these conditions, the shape retention and shape recovery is defined as follows,

$$\text{Shape retention } (\%) = \varepsilon_u / \varepsilon_m \times 100$$

$$\text{Shape recovery } (\%) = [(\varepsilon_m - \varepsilon_p) / \varepsilon_m] \times 100$$

where the ε_m is a strain at 100% elongation, ε_u is a retention strain at $T < T_m - 20$℃, and ε_p is a recovery strain at a certain temperature.

Ⅲ. Results and Discussion

The effect of DCP content on the crosslinking of the rubber was investigated by gel content analysis. Variation of the gel content of the rubber with DCP content is provided in Table 1. As shown in Table 1, the extent of gel formation increases with the increased DCP content, indicating an increase in crosslink density of the polymer. It can be seen from the results of gel content measurement that the rubber forms a network structure when it is mixed with DCP and cured at high temperature. The gel content for the DCP cured Nordel is higher than 90% when the dosage of curing agent is higher than 1.0 phr. When a polymer is crosslinked by peroxide, chain scission and crosslinking occur simultaneously. The ratio of chain scission and crosslinking for chemically crosslinked polymers can be determined using the Charlesby-Pinner equation as follows:[13,14]

Table 1. Gel Content of DCP Cured Nordel IP

Samples	DCP content (phr)	Gel content (%)
Nordel-0.0	0.0	0.0
Nordel-0.1	0.1	8.2
Nordel-0.5	0.5	80.2
Nordel-1.0	1.0	90.1
Nordel-2.0	2.0	97.4

$$S + S^{1/2} = 1 / (q_o \mu_1 I) + p_o / q_o$$

where μ_1 is the degree of polymerization based on the number average molecular weight, and p_o and q_o are constants indicating the sensitivity of chain scission and crosslinking to irradiation. I is peroxide

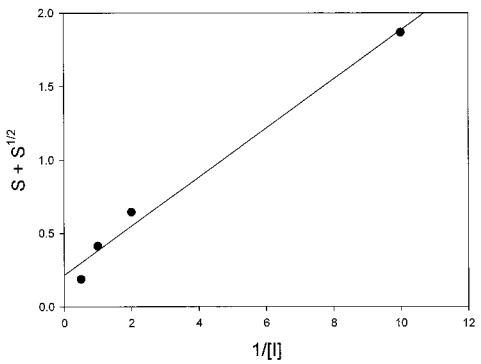


Figure 1. Charlesby-Pinner plot of peroxide(DCP) cured Nordel.

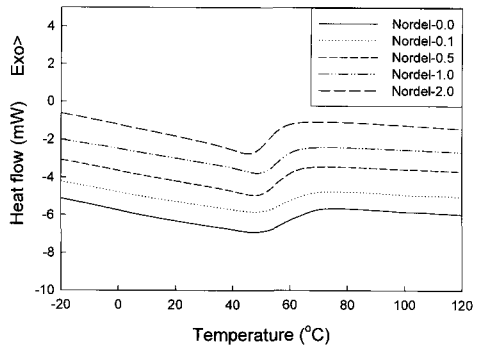


Figure 2a. DSC traces of heating for DCP cured Nordel.

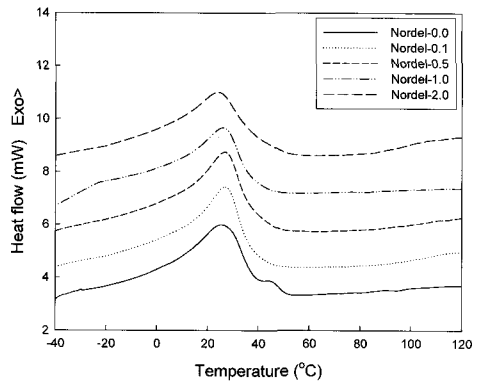


Figure 2b. DSC traces of cooling for DCP cured Nordel.

Table 2. Summary of Thermal Characteristics of DCP Cured Nordel

Samples	T_m (℃)	ΔH_m (J/g)	T_c (℃)
Nordel-0.0	56.94	20.3	26.6
Nordel-0.1	53.9	20.0	26.3
Nordel-0.5	52.7	19.6	26.0
Nordel-1.0	50.7	19.8	25.1
Nordel-2.0	45.7	17.6	24.2

concentration. The experimental data can be analyzed by plotting $S + S^{1/2}$ against $1/I$ as shown in Figure 1. It can be seen that a straight line can be obtained, the intercept at $1/I = 0$ (p_o/q_o) is about 0.2. This value for p_o/q_o indicates that the yield of crosslinking is predominant over chain scission. Thus, polymer chains are undergoing crosslinking rather than chain scission during thermal curing. This result is in accordance with the other ethylene copolymers.[7,15]

DSC thermograms of crosslinked EPDM are shown in Figure 2, and melting temperature (T_m), crystallization temperature(T_c) and the melting enthalpy(H_m) obtained from the figures are summarized in Table 2. It can be seen that the crosslinked rubber crystallized during cooling and variation of the crystallization temperature are marginal with degree of crosslinking. It can also be seen that there is a decrease in melting temperature and melting enthalpy in the crosslinked rubber as the amount of DCP increases. This is due to the decrease in mobility of polymer chains with the increase in the degree of crosslinking. It was noteworthy that the crosslinked rubber is optically transparent even though it contains crystals. This is because sizes of crystals are smaller than the wavelength of visible light, so that the crystals cannot scatter the light.

The stress-strain curves of neat EPDM and DCP cured EPDM are shown in Figure 3. As shown in the Figure 3, stiffness and strength increase with increased DCP content which is accompanied with a decrease in elongation-at-break. It was observed from DSC that the degree of crystallinity is only slightly affected by crosslinking. Since crystallinity is not substantially affected, the increase in the modulus is due to the increase in the degree of crosslinking. As was discussed above, crosslink density increases with the increased amount of DCP content,

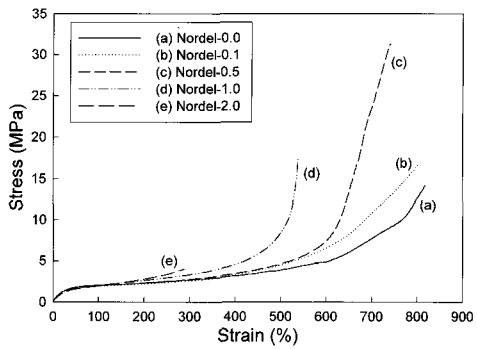


Figure 3. Stress-strain curves of neat Nordel and DCP cured Nordel.

which enhances the stiffness and strength of the material with a decrease in elongation at break. In the DCP crosslinked system, the crosslinking occurs in the melted state (unlike radiation crosslinking which occurs in the solid state) and hinders the packing of the molecules when crystallization occurs from the melt. The hindering of molecule packing causes a decrease in crystallinity. Thus, molecular chain structure affects the crosslinking by DCP. The crosslinking of the chains in the amorphous region produces an integrated network where the crystalline phase reinforces the rubbery amorphous zone of the polymer. This crosslinked network restricts the mobility of the polymer chains and causes the reduction in elongation-at-break.

Figure 4 give the strain recovery curves for the crosslinked EPDM measured at different temperatures. The shape recovery occurred with the increased temperature and 100 % recovery was obtained when the sample was heated above the melting temperature of each sample. This means that the recovery of the fixed elastic strain happened during the melting of the crystals. The strain fixation of all the samples showed a high value of more than 95%. For crosslinked rubber with low gel content the final recovery rate was very low. Only when the gel content of the samples was high enough the final recovery rate can reach 90% or more, indicating an importance of the formation of a network structure for a polymer sample to exhibit the typical shape memory effect. Such high shape retention and

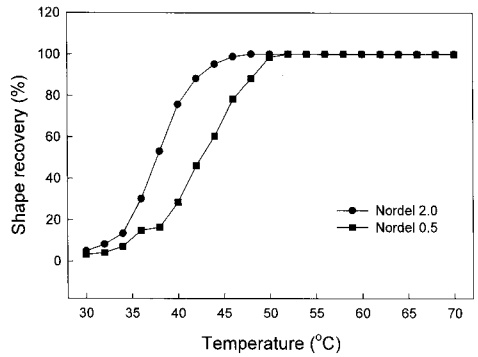
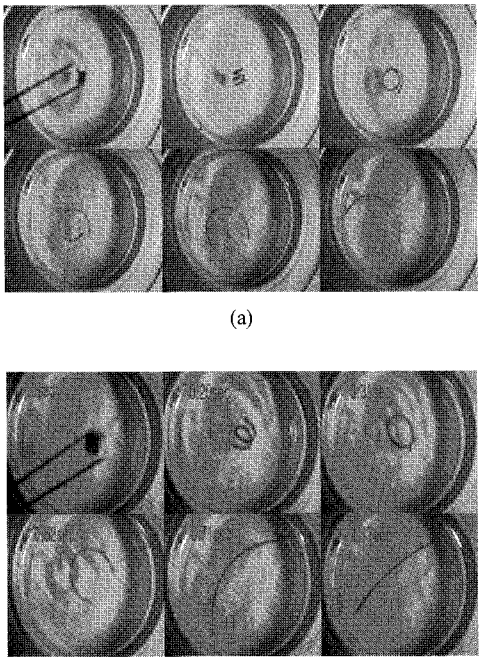


Figure 4. Strain recovery curves of DCP cured Nordel.



(a)

(b)

Figure 5. Series of photographs showing the macroscopic shape-memory behavior of (a) Nordel-0.1 and (b) Nordel-2.0. Permanent shape is a rod, temporary shape is a spiral. The pictures show the transition from temporary to permanent shape at 70℃.

shape recovery was maintained during cyclic testing (it was confirmed upto 5 cycles). This indicates that the DCP cured EPDM network can retain stable shape memory effects under repeated use, which is of importance in practical applications.

Figure 5 demonstrates series of photographs showing the macroscopic shape-memory effect of DCP cured Nordel. Permanent shape is a rod, temporary shape is a spiral. The pictures show the sample can deformed from the transition from temporary to permanent shape at 70℃ in 20 seconds. It is easily deformed to have an arbitrary shape above its melting temperature (about 50℃) and is fixed very well as it deformed when it is cooled at ice water. It shows a very fast recovery rate when it is heated above a melting temperature. The shape memory effects of crosslinked semicrystalline EPDM can be described as follows. When a crosslinked

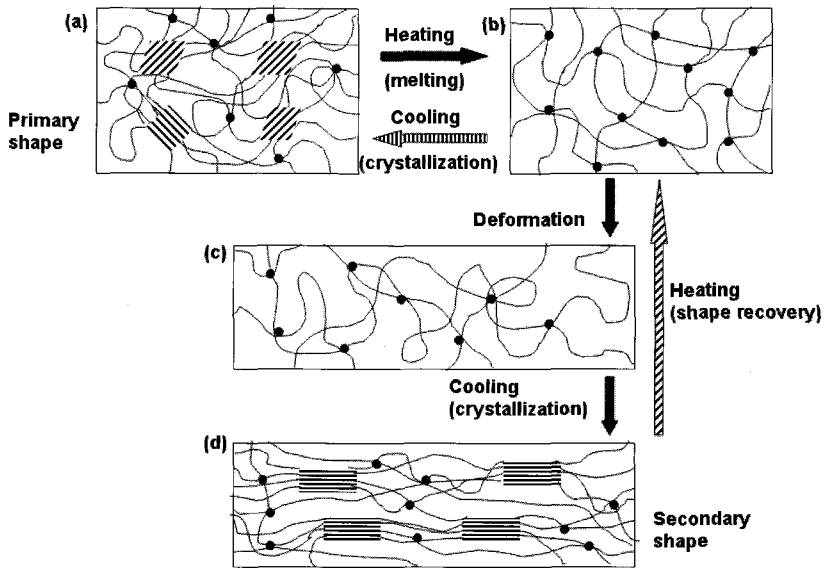


Figure 6. Schematic depiction of shape momory behavior of crosslinked semicrystalline EPDM during a temperature programming.

sample at room temperature is heated, crystalline domains are melted. Then the sample can be easily stretched to a deformed state and is fixed in its deformed state by cooling and crystallization. When the fixed shape is heated above the crystalline melting temperature, the crystals are melted and the sample can be recovered elastically to its original shape. Such mechanism are depicted schematically in Figure 6.

Ⅳ. Conclusions

In this study, thermally triggered shape memory polymer can be fabricated by the curing of metallocene EPDM, Nordel IP, with small amounts of dicumyl peroxide(DCP). The crosslinked rubber exhibited excellent shape fixing and shape recovery during the temperature programming. The response temperature is around 50℃, and it can be tuned by curing the rubber with varying amounts of DCP.

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