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Influence of specimen directions on recovery behaviors from circular deformation of polyester cord-inserted rubber composites

Sung-Seen Choi *, Ok-Bae Kim

Department of Chemistry and Sejong Polymer Research Center, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, Republic of Korea

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ABSTRACT

Polyester cord-inserted rubber composites cut with the parallel and perpendicular directions to the fabric cord (RC||FC and RC⊥FC specimens, respectively) were thermally aged and the recovery behaviors from a circular deformation were investigated. The permanent deformation of the RC||FC specimen was more severe than that of the RC⊥FC specimen. Recoveries of the rubber composites without fabric cord were nearly the same irrespective of the cutting directions. Sources to cause the permanent deformation were found to be the increased crystalline region of polyester cord and the increased crosslink density of rubber part.

1. Introduction

In general, rubber articles are reinforced with fabric cords as well as reinforcing fillers. Fabric cord-inserted rubber compounds have been widely used for manufacturing of tires, conveyor belts, hoses, and so on. Polyester and nylon are commonly used as fabric cords for rubber articles. Rubber composites are permanently deformed when they are deformed for a long time, especially at high temperatures [1,2]. One of the principal reasons regarding permanent deformation of a rubber vulcanizate without fabric cord is change in crosslink density [3].

In our previous study [4], a novel test method to estimate the level of permanent deformation of polyester cord-inserted rubber composite was developed. Cord direction in a rubber article is very important because properties and usages of a fabric cord–rubber composite depend on the cord direction. Properties of cord–rubber composites including cord/fabric geometry, adhesion, and theoretical approach had been investigated [5–7]. Direction of fabric cord of a fabric cord-inserted rubber compound is varied according to the purpose. For manufacture of a bias tire, calendered fabric cord is diagonally cut for building a tire. Direction of a cap ply of a tire is parallel with the tread direction. It has been recognized that rubber products can exhibit anisotropy, and properties of a rubber article are dependent on the direction and position of test pieces within the product [8–14]. The modulus, tensile strength, tear resistance, shrinkage, and electrical properties vary with the direction along which the tests are carried out.

In the present work, influence of the specimen direction on the recovery behaviors from deformation was investigated. Poly(ethylene terephthalate) (PET) cord was employed as fabric cord. PET-cord inserted rubber composites (cord–rubber composites) were cut with the parallel and perpendicular directions to the PET cord (RC||FC and RC⊥FC specimens, respectively) to prepare the specimens. Rubber vulcanizates without PET cord (rubber vulcanizates) cut with the parallel and perpendicular directions to the milling direction (RC||M and RC⊥M specimens, respectively) were also prepared. The circular deformation test method was employed, which requires changing a linear sample to a circular form [15–21]. This method is suitable for deformation of the fabric cord–rubber composite since it requires changing a linear sample to a circular form. This method is the simplest and reliable method to measure the degree of deformation of a rubber article since thin specimens with 2 mm thickness in a uniform state are used. When a linear sample of a vulcanized rubber is circularly deformed, the stress and strain vary uniformly across the thickness of the sample [19]. Influence of the aging temperatures on the recovery behaviors was also examined by varying the aging temperatures of 40–90 °C. The rubber compounds were cured at 160 and 170 °C to prepare the specimens with different initial states, and influence of the initial states of the samples on the recovery behaviors was also insvestigated.

2. Experimental

2.1. Sample preparation

Resorcinol formaldehyde latex (RFL)-dipped PET cord (HSP PET tire cord of Hyosung Co. (Korea)) was used as fabric cord. Carbon

* Corresponding author. Tel.: +82 23408 3815.
E-mail address: sschoi@sejong.ac.kr (S.-S. Choi).

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black-filled rubber compound was made of the following: rubber (STR 5L 70.0 phr and Kosyn1502 30.0 phr), filler (N550 50.0 phr), antidegradants (2,2,4-trimethyl-l,2-dihydroquinoline (TMDQ) 2.0 phr and wax 1.0 phr), cure activators (stearic acid 2.0 phr and ZnO 4.0 phr), processing oil (oil 10.0 phr), 2,2′-dibenzothiazole disulfide (MBTS 1.2 phr), diphenylguanidine (DPG 0.3 phr), and sulfur (2.0 phr). Mixing was performed in a Banbury type mixer and the rubber compound was milled using a two-roll mill to make a sheet with 1 or 2 mm thickness. The rubber compound sheet with 2 mm thickness was used for the preparation of rubber vulcanizate. The rubber compound sheet with 1 mm thickness was used for the preparation of cord–rubber composite (RC-FC specimen). The rubber vulcanizates (RC specimens) were prepared by curing the compound at 160 and 170 °C for 15 min using a compression mold. The cord–rubber composite was prepared as follows. First, PET cord was inserted between the rubber sheets of 1 mm thickness. The PET cord direction was arranged to the milling direction. Second, the PET cord-inserted rubber compound was put in a compression mold. Finally, the cord-inserted rubber compounds were cured at 160 °C and 170 °C for 15 min. The volume fraction of PET cord in the rubber composite was about 20%.

2.2. Circular deformation and thermal aging

The RC-FC specimens were cut with the parallel and perpendicular directions to the fabric cord (RC||FC and RC⊥FC specimens, respectively) to prepare the specimens for thermal aging (Fig. 1). The RC specimens were also cut with the parallel and perpendicular directions to the milling direction (RC||M and RC⊥M specimens, respectively). The specimen dimension was 8 mm × 120 mm. The circular deformation experiments were carried out as follows. First, the linear sample was changed into a circular form by fixing both ends of the sample with a pin. Second, the circularly deformed samples were aged at 40, 50, 60, 70, 80, and 90 °C for 7 days in a convection oven. Finally, the pin was removed and the gap distance between both ends of the sample was measured from 1 h to 30 days. The recovery (R) was calculated by the Eq. (1).

$$R(\%) = 100 \times \left(\frac{d}{l}\right) \tag{1}$$

where the d and l are the gap distance after aging and the length of the linear sample, respectively. Previous studies provide a detailed description of the circular deformation test [15–21]. Experiments were performed three times and averaged.

2.3. Measurement of apparent crosslink density and DSC analysis

Apparent crosslink densities of the samples before and after the thermal aging were measured by swelling method. Organic additives in the samples were removed by extracting with THF and n-hexane for 3 and 2 days, respectively. Then, they were dried for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were soaked in toluene for 2 days and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by the Eq. (2).

$$Q = \frac{W_s - W_u}{W_u} \tag{2}$$

where the W_s and W_u are weights of the swollen and unswollen samples. In general, the reciprocal swelling ratio ($1/Q$) was used as the apparent crosslink density. Experiments were also carried out three times and averaged. Melting temperature (T_m) and melting enthalpy (ΔH_m) of the PET cords were measured with differential scanning calorimeter (DSC) of TA instruments DSC 2010. The DSC analysis was performed at temperature range of 30–300 °C and rate of 10 °C/min.

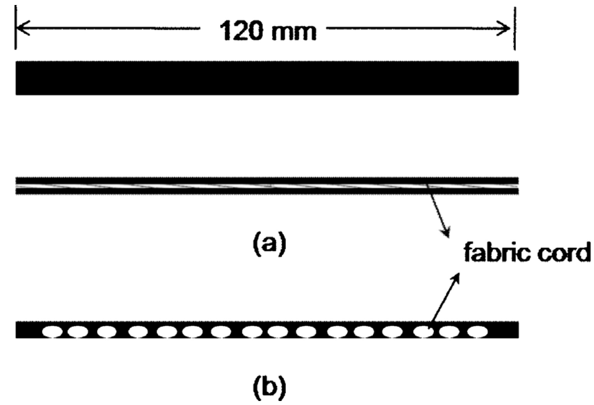

Fig. 1. Cross sections of the parall (a, RC||FC) and perpendicular (b, RC⊥FC) cuts to the sample direction.

3. Results and discussion

The aged samples did not return to the initially linear shape. The cord–rubber composites (RC-FC specimens) were less recovered than the rubber vulcanizates (RC specimens). The RC||FC specimen was less recovered than the RC⊥FC specimen. The recovery

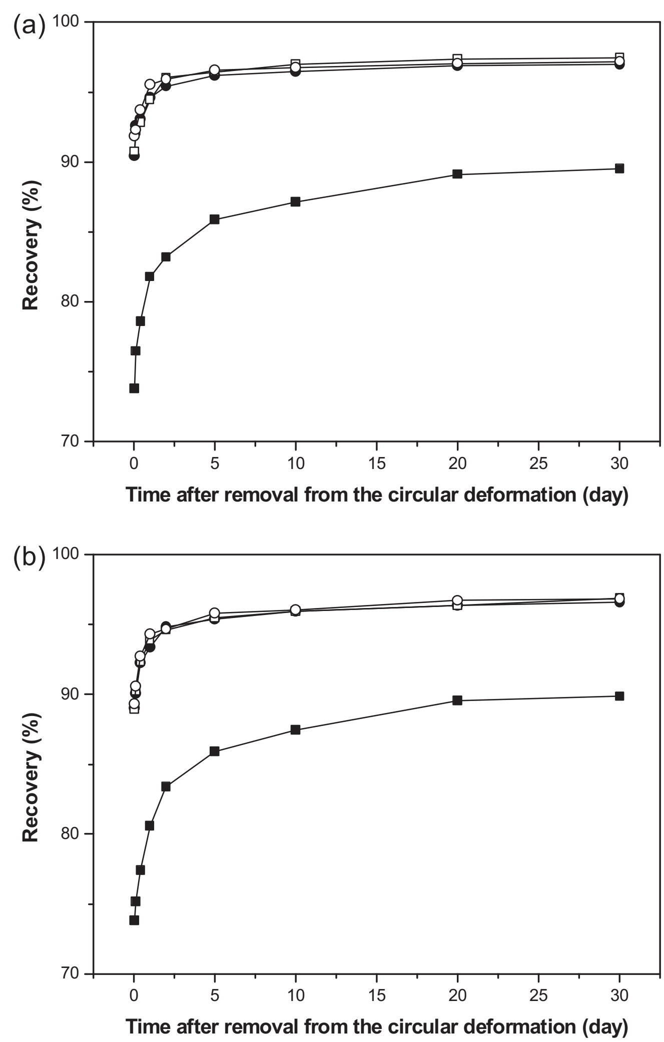

Fig. 2. Recovery variations from the circularly deformed state of the specimens cured at 160 °C (a) and 170 °C (b) after thermal aging at 40 °C with the measurement time. ■ RC||FC specimen; ● RC⊥FC specimen; □ RC||M specimen; ○ RC⊥M specimen.