Influence of Thermal Aging on Pyrolysis Pattern of Carbon Black-Filled NR Composite

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Introduction

Pyrolysis has been used widely to characterize polymeric materials such as plastics and elastomers.[1-5] Pyrolysis-gas chromatography (Py-GC), pyrolysis-mass spectrometry (Py-MS), and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) have been used for decades to elucidate the structures of rubbers.[6-12] Py-GC/MS has been used extensively for qualitative and quantitative analyses of polymer blends as well as single polymers.[13-15] Ghebremeskel and coworkers[14] analyzed the styrene content of SBR copolymer using Py-GC/MS. Lee and coworkers[15] studied on analysis of NR/SBR/BR ternary blend system using various analytical methods such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Py-GC/MS and reported that the quantitative analysis of compositions using Py-GC/MS was the most precise because each characteristic peak on the Py-GC/MS pyrograms was unique.

Rubber articles are aged by heat, UV, radicals including ozone, oxygen, and moisture and which leads to crack formation on the surface, change of the crosslink density, and migration of the organic materials.[16-18] Permanent deformation of a rubber vulcanizate results from the crosslink density change by thermal aging under the deformed state.[19] Change of the crosslink density occurs by formation of new crosslinks and dissociation of the existing crosslinks.[20-22] In this study, we investigated the influence of the aged level of an NR composite on the pyrolysis pattern using Py-GC/MS. The sample was aged at 60 °C in a convection oven for 10 to 185 days and the aged specimens were pyrolyzed and the volatile products were analyzed with GC/MS. We focused on the variation of dimers/monomer ratio of isoprene with the aging time.

Experimental

The carbon black-reinforced NR compound was composed

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of rubber (SMR CV60, 100.0 phr), carbon black (N220, 50.0 phr), zinc oxide (2.0 phr), stearic acid (2.0 phr), *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD, 2.0 phr), wax (2.0 phr), *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS, 1.4 phr), and sulfur (1.4 phr). Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80 °C for MB and FM stages, respectively. The MB compound was prepared as follows. (1) The rubber was loaded into the mixer and preheated for 0.5 min. (2) The carbon black and the ingredients were compounded into the rubber for 3.0 min and the resulting compound was discharged. The FM compound was prepared by mixing the MB compound with the curatives for 1.5 min. The vulcanizate was prepared by curing at 160 °C for 20 min in a compression mold (2 × 140 × 140 mm³).

Thermal aging was performed at 60 °C for 10, 15, 25, 30, 35, 45, 55, 65, 75, 85, 105, 125, 145, 165, and 185 days in a convection oven. Sample dimension for the thermal aging experiment was 30 × 60 mm² with 2 mm thickness. Analysis of the pyrolysis products was performed with pyrolysis-GC/MS. Pyrolysis-GC/MS chromatograms of the samples were acquired with Pyroprobe 2000 of CDS Analytical Inc. and 6890GC gas chromatograph and 5973MS mass spectrometer of Agilent Co. The sample (about 0.2 mg) was pyrolyzed at 700 °C for 3 sec under He atmosphere. HP-5 capillary column (length 30 m) was used. The temperature of the injector was 250 °C and that of the interface was 200 °C. The GC oven temperature program was as follows. (1) The initial temperature was 30 °C and was maintained at that for 3 min. (2) The temperature was then increased from 30 to 160 °C at a rate of 8 °C/min.

Crosslink densities of the samples 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, and they were dried for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were soaked in *n*-decane for 2 days and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by the equation of $Q = (W_s - W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples. The reciprocal swelling ratio ($1/Q$) was used as the apparent crosslink density. Experiments were carried out three times and they were averaged.

Results and Discussion

Figures 1(a) and (b) show the pyrolysis-GC/MS chromatograms of the carbon black-filled NR vulcanizates before and after the thermal aging at 60 °C for 105 days, respectively. The pyrolysis products were identified with
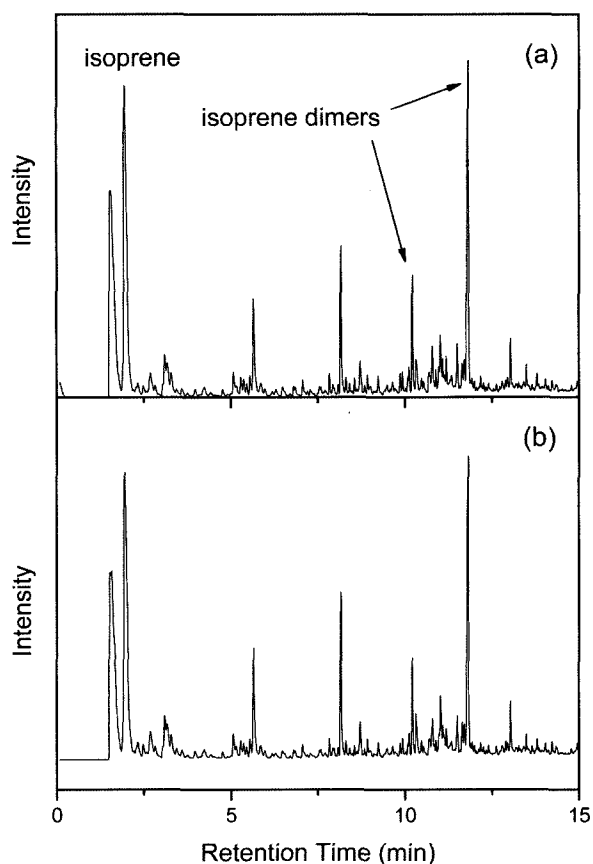
Figure 1. Pyrolysis-GC/MS chromatograms of the carbon black-filled NR vulcanizates before aging (a) and aged at 60 °C for 105 days (b).

their mass spectra. The major volatile products are the peaks at 1.95, 5.65, 8.16, 10.22, and 11.85 min assigned to isoprene, toluene, xylene, 1,4-dimethyl-4-vinylcyclohexene, and 1-methyl-4-(1-methylethenyl)-cyclohexene, respectively. The peak at 1.57 min is the carbon dioxide. Among pyrolysis products formed from a polymeric material, the finger prints to identify the analyte are its repeat unit such as monomer and dimers. The isoprene is the monomer of NR and the 1,4-dimethyl-4-vinylcyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene are the isoprene dimers. The 1,4-dimethyl-4-vinylcyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene are formed from the head-to-head and head-to-tail sequences of NR as shown in Scheme I.[23,24] The sequence of a homopolymer is determined by polymerization types of head-to-tail and head-to-head (or tail-to-tail) when the repeat unit is asymmetric. There are head-to-head and tail-to-tail linkages as well as head-to-tail linkage between 1,4-isoprene units in polyisoprene (or NR).[25]

Relative abundances of the pyrolysis products are varied with the aged state. Comparing with the peak intensity of isoprene, relative intensities of the isoprene dimers are decreased in the aged sample as shown in Figure 1. Since
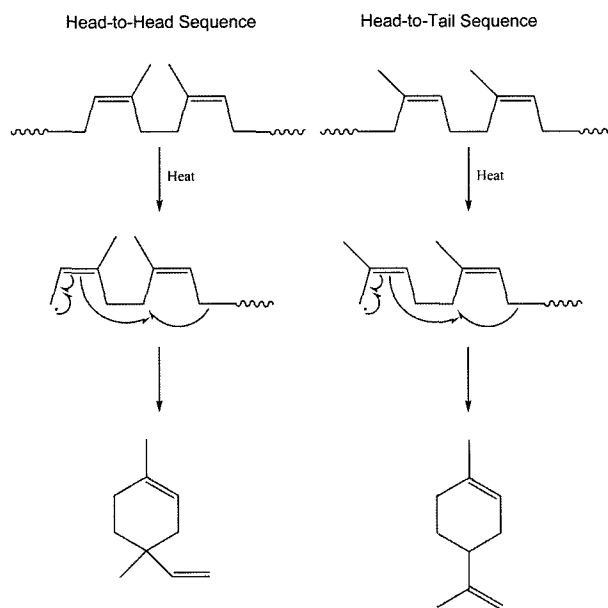
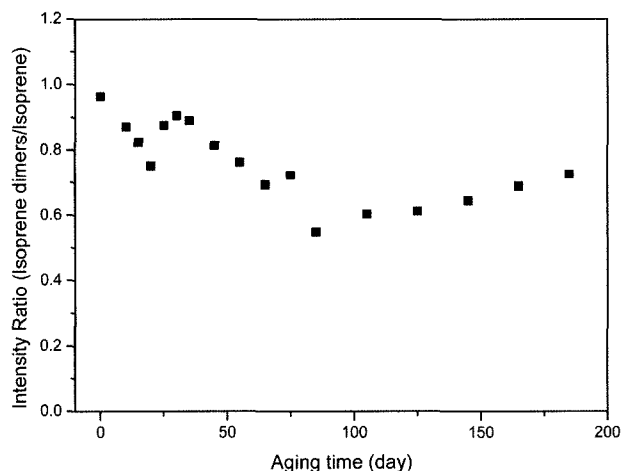**Scheme I.** Mechanism for the formation of isoprene dimers.

Figure 2. Variations of the relative intensity ratio of the isoprene dimers/isoprene with the aging time.

the absolute abundances of pyrolysis products are varied with the experimental conditions such as the sample weight and the pyrolysis conditions, the experimental results were analyzed with the relative abundances not the absolute ones. Relative intensity ratios of the major pyrolysis products were calculated by letting the abundance of isoprene be 100%. Figure 2 shows the variation of the peak intensity ratio of the dimers as a function of the aging time. The peak intensity ratio is varied with the aging time and tends to decrease until about 100 days and then slightly increases. The decreasing trend can be explained with the crosslink density change by the thermal aging. The crosslink density increases with increase of the aging time. Apparent
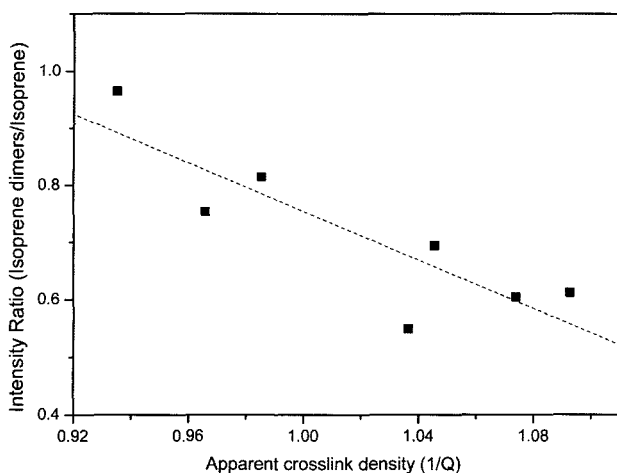
Figure 3. Variations of the relative intensity ratio of the isoprene dimers/isoprene with the apparent crosslink density.

crosslink densities $(1/Q)$ of the specimens aged for 0, 25, 45, 65, 85, 105, and 125 days are 0.935, 0.966, 0.986, 1.045, 1.037, 1.074, and 1.093, respectively.

Figure 3 shows the variation of the peak intensity ratio of the dimers as a function of the apparent crosslink density and the peak intensity ratio tends to decrease with the increase of the $1/Q$. The decreased peak intensity ratio with the $1/Q$ is due to the free chain length between crosslink points.[23] The free chain length between crosslinks becomes shorter as the crosslink density becomes higher. Since production of the isoprene dimer species is inhibited by the crosslink points, the peak intensity ratio of the dimers is reduced by increasing the crosslink density.

The slight increase of the peak intensity ratio of the dimers after 100 days of the aging time can be explained with the distribution of the free chain length between crosslink points. Formation of new crosslinks and dissociation of the existing crosslinks occur simultaneously during the thermal aging. If the formation and dissociation reactions are localized, the distribution of the free chain length between crosslink points will be wider and the long free chain region as well as the short one will become larger. Localization of the formation of new crosslinks and dissociation of the existing crosslinks at long thermal aging time was indirectly shown in variation of the tensile properties of rubber vulcanizates by accelerated heat aging.[26] The elongation at break was decreased and then slightly changed or stayed constant as the aging time elapsed whereas the modulus was increased and then slightly changed or stayed constant. Crosslink density of an NR vulcanizate is continuously increased by increasing the accelerated thermal aging time.[20] The increased crosslink density may lead to the enhanced modulus and reduced elongation at break.[27] If the modulus does not increase or the elongation at break does not decrease although the crosslink density increases, this can be explained

with the free chain length between crosslink points and its distribution. Therefore, it is possible that the formation of new crosslinks and dissociation of the existing crosslinks occur locally at the long aging time and the expanded long free chain region leads to formation of the dimers by pyrolysis.

Conclusions

NR composites were aged at 60 °C for 10 to 185 days and the aged samples were pyrolyzed using pyrolysis-GC/MS. Isoprene, toluene, xylene, 1,4-dimethyl-4-vinylcyclohexene, and 1-methyl-4-(1-methylethenyl)-cyclohexene were detected as the major pyrolysis products. The 1,4-dimethyl-4-vinyl-cyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene are the isoprene dimer species. Peak intensity ratio of the isoprene dimers/isoprene decreased until 100 days of the aging time and then slightly increased. The decreased trend of the isoprene dimers/isoprene ratio before 100 days of the aging time was due to the increased crosslink density by thermal aging. The slightly increased ratio after 100 days of the aging time might be due to the distribution of the free chain length between crosslink points.

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