Analysis of Origin to Cause Blowout of Carbon Black-Reinforced Rubber Composites Using GC/MS

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ABSTRACT: To investigate the sources to cause blowout of a rubber article gaseous materials (blowout gas) generated from the NR and SBR composites by blowout and organic materials extracted from the burst region after explosion of the specimen were analyzed using GC/MS. 1-Methyl-4-(1-methylethenyl)-cyclohexene was detected from the blowout gas of the NR vulcanizate and 4-vinylcyclohexene and styrene were detected from the blowout gas of the SBR vulcanizate. They were the repeat units of the used rubbers and were produced by decomposition of the polymer chains. Organic additives contained in the initial specimen were not detected in the burst region after blowout but lots of hydrocarbon components were detected instead. We believe that a principal source to cause the blowout was decomposition of the polymer chain, and it leads to activation of the cavity formation in the rubber article and reduction of the resistance to the increasing interior pressure. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3068–3072, 2008

Key words: blowout; rubber composite; GC/MS; polymer decomposition

INTRODUCTION

When thick rubber blocks such as tank track pads and tire treads for truck and bus are subjected to repeated deformation, they become so hot in the interior that they explode. This phenomenon is known as blowout and its sources were known to be nucleation and growth of cavity and increase of the inner pressure by vaporization of volatile organic materials.[1–3] Blowout was first thought to be a mechanical fatigue cracking process, aggravated by the high temperature set up by cycling stress.[4] Failure is attributed to the development of an internal pressure large enough to expand any preexisting internal cavity to the point of rupture. Blowout time of a carbon black-filled rubber composite became faster by increasing the carbon black content and blowout temperature of an overcured rubber vulcanizate was higher than that of an undercured one.[1] Gent and Hindi[2] reported that different elastomers had different blowout temperatures and different vulcanizate structures also had different blowout temperatures. Butyl rubber (IIR) vulcanizate blew out at relatively low temperatures whereas natural rubber (NR) and styrene-butadiene rubber (SBR) vulcanizates blew out at relatively high temperatures. Rubber vulcanizates with C—C or monosulfidic crosslinks showed higher blowout temperatures than those with polysulfidic ones.

In this work, we collected gaseous materials generated by blowout from NR and SBR vulcanizates and analyzed them using GC/MS to investigate the sources to cause blowout in detail. Organic materials extracted from the initial rubber articles and the burst region after blowout were also analyzed using GC/MS. Blowout was generated using a microwave oven because blowout behaviors of a rubber vulcanizate using a flexometer are consistent with those using a microwave oven,[1,2] and collection of the blowout gas is much more convenient and efficient using a microwave oven.

EXPERIMENTAL

Two carbon black-reinforced rubber compounds were made of rubber (NR or SBR), carbon black (N330, 60.0 phr), processing oil (2.0 phr), cure activators (stearic acid 2.0 phr and ZnO 4.0 phr), antidegradants (*N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) 2.0 phr and wax 2.0 phr), and curatives (*N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS) 1.5 phr and sulfur 1.5 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 the MB and FM stages, respectively. Thick rubber specimens for the blowout test were made by curing at 160°C for 20 min in a compression mold (17.6 mm

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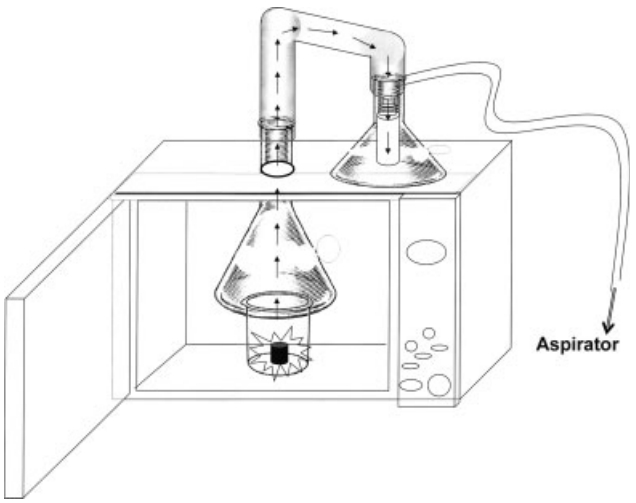

Figure 1 Apparatus for collection of blowout gas using a microwave oven.

diameter and 25.0 mm height). Blowout was generated using a RE-MC20T microwave oven of Samsung of Korea with a microwave frequency of 2450 MHz. The irradiation power was set with 700 W. The blowout gas was collected just after explosion in THF as shown in Figure 1. Organic materials in the initial sample and the burst region of the exploded specimen were extracted with THF at room temperature for 3 days.

Analysis of the blowout gas and the extracted organic materials was performed with GC/MS. GC/MS chromatograms and the mass spectra were acquired with 6890N/5987 GC/MS of Agilent. DP-1MS capillary column (length 30 m) was used. Injector temperature of the GC was 250°C. The GC oven temperature program was as follows: (1) The initial temperature was 70°C and kept for 3 min. (2) The temperature was then increased from 70 to 300°C at a rate of 10°C/min.

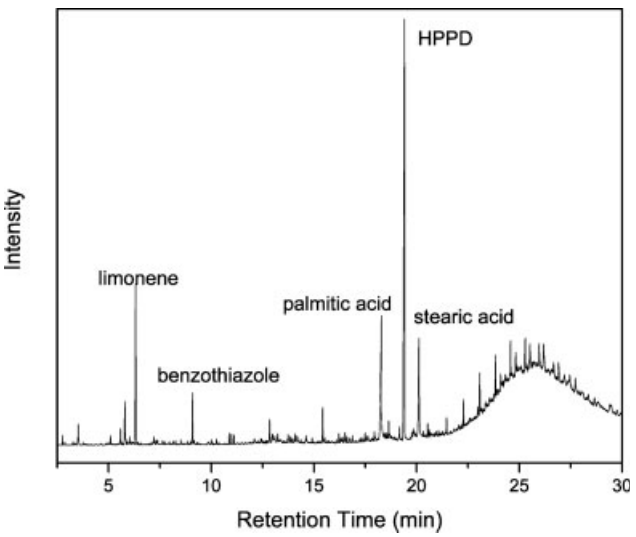

Figure 2 GC/MS chromatogram of blowout gas collected from the NR vulcanizate.

TABLE I
Major Product Ions and Their Relative Intensities of the Principal Species Formed from the NR Vulcanizate

Peak	*m/z* (Relative intensity)
6.32 min	68 (100.0), 79(38.6), 93 (79.8), 107.1 (26.0), 121 (29.2), 136 (28.9)
9.10 min	69 (13.9), 108 (30.8), 135 (100.0)
18.28 min	41 (53.3), 43 (66.3), 55 (60.2), 57 (61.1), 69 (38.7), 71 (39.4), 73 (100.0), 83 (29.1), 85 (28.3), 87 (20.7), 97 (24.6), 115 (19.4), 129 (53.0), 157 (20.6), 171 (19.2), 185 (20.6), 213 (34.6), 256 (50.8)
19.41 min	167 (13.7), 169 (12.3), 183 (36.6), 211 (100.0), 212 (16.08), 226 (76.7), 227 (13.2)
20.12 min	41 (58.0), 43 (77.9), 55 (71.1), 57 (73.4), 69 (47.3), 71 (46.8), 73(100.0), 83 (38.1), 85 (32.7), 87 (22.9), 97(33.8), 115 (18.2), 129 (62.2), 143 (11.3), 171 (13.4), 185 (33.6), 199 (11.7), 241 (34.2), 284 (64.0), 285 (14.8)
22.99 min	41 (26.4), 43 (60.7), 55 (35.2), 57 (100.0), 69 (28.0), 71 (80.1), 83 (23.2), 85 (60.8), 97 (24.0), 99 (21.1), 111 (15.7), 113 (14.00)

RESULTS AND DISCUSSION

The blowout gas was collected for 10 s after blowout of the rubber specimen in THF and analyzed with a GC/MS. Figure 2 shows GC/MS chromatogram of the blowout gas collected from the NR specimen. The peaks at 6.32, 9.10, 18.28, 19.41, and 20.12 min can be assigned to 1-methyl-4-(1-methylethenyl)-cyclohexene (limonene), benzothiazole, palmitic acid, HPPD, and stearic acid, respectively. The some regular peaks at 21–27 min (21.46, 22.28, 22.99, 23.84, 24.58, 25.29, 25.97, and 26.67 min) are assigned to waxes, saturated hydrocarbons of $C_{25}H_{52}$, $C_{26}H_{54}$, $C_{27}H_{56}$, $C_{28}H_{58}$, $C_{29}H_{60}$, $C_{30}H_{62}$, $C_{31}H_{64}$, and $C_{32}H_{66}$, respectively, while the broad band around 26 min is assigned to hydrocarbon oil. Relative intensities of product ions of the important peaks are listed in Table I. The peaks at 18.28, 19.41, 20.12, and 22.99 min (which assigned to palmitic acid, HPPD, stearic acid, and $C_{27}H_{56}$, respectively) are the ingredients contained in the initial specimen. The peak at 9.10 min assigned to benzothiazole is the TBBS residue. TBBS participates in crosslinking reactions and benzothizole is generated by dissociation of TBBS during vulcanization.[5,6] The peak at 6.32 min assigned to limonene (1-methyl-4-(1-methylethenyl)-cyclohexene) is one of the isoprene dimers. Figure 3 shows the mass spectrum of the peak at 6.32 min. The *m/z* 136 is the molecular ion peak and the most abundant peak of *m/z* 68 is the fragment ion assigned to $C_5H_8^+$ (isoprene). Detection of limonene is very interesting

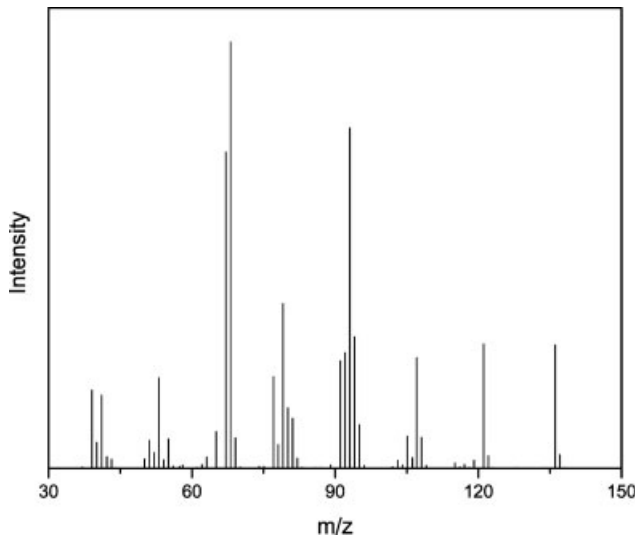

Figure 3 Electron impact ionization mass spectrum of the peak at 6.32 min in the GC/MS chromatogram of blowout gas collected from the NR vulcanizate.

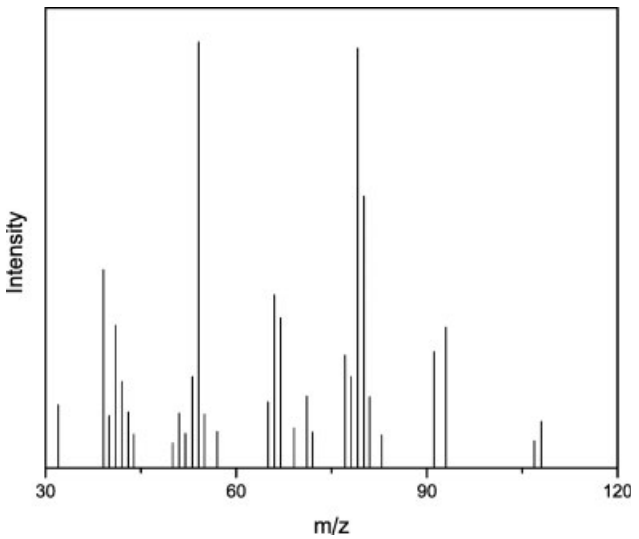

Figure 5 Electron impact ionization mass spectrum of the peak at 3.12 min in the GC/MS chromatogram of blowout gas collected from the SBR vulcanizate.

because limonene should come from NR not any ingredients or carbon black in the rubber specimen. In general, major pyrolysis products of polymeric materials are the monomer and dimers of the sample. For NR, the major pyrolysis products are isoprene and isoprene dimers such as 1-methyl-4-(1-methylethenyl)-cyclohexene, 1,4-dimethyl-4-vinylcyclohexene, 1-methyl-5-(1-methylethenyl)-cyclohexene, and 1,5-dimethyl-5-vinylcyclohexene.[7,8] Of the isoprene dimer species the 1-methyl-4-(1-methylethenyl)-cyclohexene is the most abundant product. Generation of limonene by blowout of the NR composite means that NR is decomposed by blowout. The decomposed rubber chain produces volatile small materials to increase the inner pressure and activates the formation of cavity.

Figure 4 shows GC/MS chromatogram of the blowout gas collected from the SBR specimen. The peaks at 3.12, 3.80, 6.32, 9.10, 18.28, 19.41, and 20.12 min can be assigned to 4-vinylcyclohexene, styrene, benzothiazole, palmitic acid, HPPD, and stearic acid, respectively. Wax peaks at 21–27 min and oil broad band around 26 min are also observed. Figures 5 and 6 are the mass spectra at the peaks at 3.12 and 3.80 min, respectively. The mass spectrum of Figure 5 can be assigned to 4-vinylcyclohexene because the *m/z* 108 is the molecular ion peak and the most abundant peak of *m/z* 54 is the fragment ion assi-

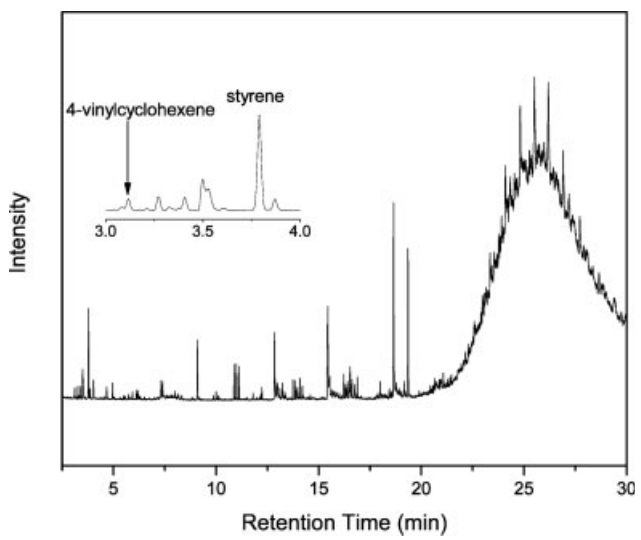

Figure 4 GC/MS chromatogram of blowout gas collected from the SBR vulcanizate.

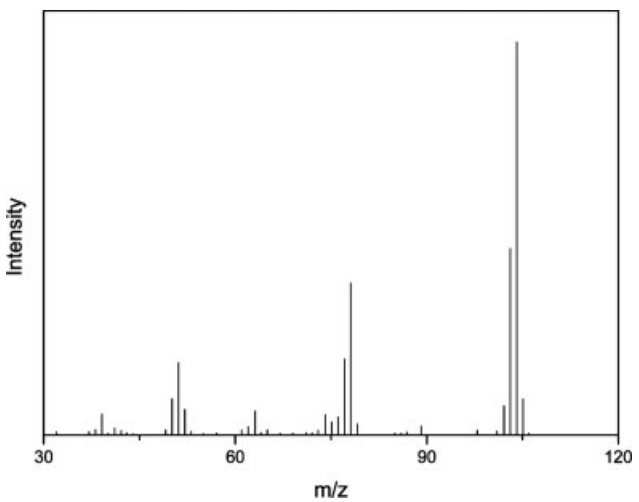

Figure 6 Electron impact ionization mass spectrum of the peak at 3.80 min in the GC/MS chromatogram of blowout gas collected from the SBR vulcanizate.

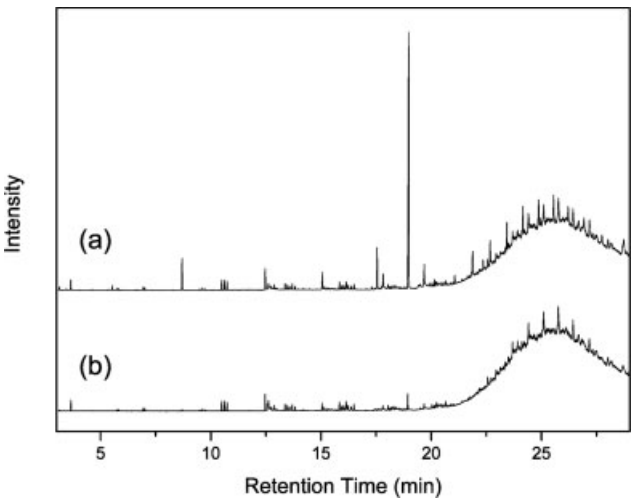

Figure 7 GC/MS chromatograms of the extracted materials from (a) the initial sample and (b) the burst region of the blowed out specimen of the NR vulcanizate.

gined to $C_4H_6^+$ (butadiene). Figure 6 is the typical mass spectrum of styrene, which shows the molecular ion of *m/z* 104 and the benzene ion of *m/z* 78. 4-Vinylcyclohexene is the butadiene dimer come from butadiene sequence of SBR and styrene come from styrene sequence of SBR. Major pyrolysis products of SBR are styrene, butadiene, and butadiene dimer (4-vinylcyclohexene).[9,10] Detection of 4-vinylcyclohexene and styrene means dissociation of SBR by blowout. Thus, we can say that dissociation of a rubber chain is one of principal sources to cause blowout because decomposition of the rubber chains leads to the formation of cavity and the generation of volatile materials to increase the internal pressure.

There were some sticky materials and carbonized things on the burst region after blowout. The burst region was cut with about 1 mm thickness and the unbound materials were extracted with THF at room temperature for 3 days at room temperature to analyze them with a GC/MS. Kinds of the organic materials extracted from the burst region were compared with the organic materials extracted from the initial sample. Figures 7 and 8 are the GC/MS chromatograms of the extracted organic materials from the NR and SBR specimens, respectively. The GC/MS chromatograms of the organic materials extracted from the burst regions do not display HPPD and fatty acids such as palmitic acid and stearic acid, but broad oil peaks over 20–30 min are much larger than those of the organic materials extracted from the initial specimens. The new hydrocarbon materials should be come from the matrix rubber. Polymer chains of the rubber article can be dissociated to form hydrocarbons when the heat generated internally is not conducted away rapidly enough to cause decomposition. The generated hydrocarbons may have various chemical structures with different molecular weights. Peaks of the hydrocarbon products are convoluted in the GC/MS chromatograms since the number of the isomers of the hydrocarbon products is increased as their molecular weights increase. The experimental results lead to a conclusion that most of the initial organic ingredients contained in the rubber specimen are evaporized by blowout and lots of hydrocarbons having about C_{20}-C_{40} are generated by blowout and some of them deposited on the burst region.

From the experimental results, it can lead to a conclusion that one of the principal sources to cause the blowout of a rubber article is generation of volatile organic products by decomposition of the rubber chains as well as the evaporation of the organic additives in the initial sample. Decomposition of the rubber chains also reduces the elastic properties of the rubber composite and decreases the critical value of the resistance to the internal pressure. The increased volatile materials and the reduced resistance to the inner pressure lead to fast blowout.

CONCLUSIONS

Products decomposed from the rubber chains by blowout as well as the organic ingredients contained in the rubber specimen such as benzothiazole, fatty acids, HPPD, and waxes were founded from the blowout gas analysis. 1-Methyl-4-(1-methylethenyl)-cyclohexene (isoprene dimer) was detected from the blowout gas of the NR vulcanizate and 4-vinylcyclohexene (butadiene dimer) and styrene were detected from the blowout gas of the SBR one. Lots of hydrocarbon components were detected in the organic materials extracted from the burst sample. The experimental results lead to a conclusion that one of principal sources to cause the blowout was decom-

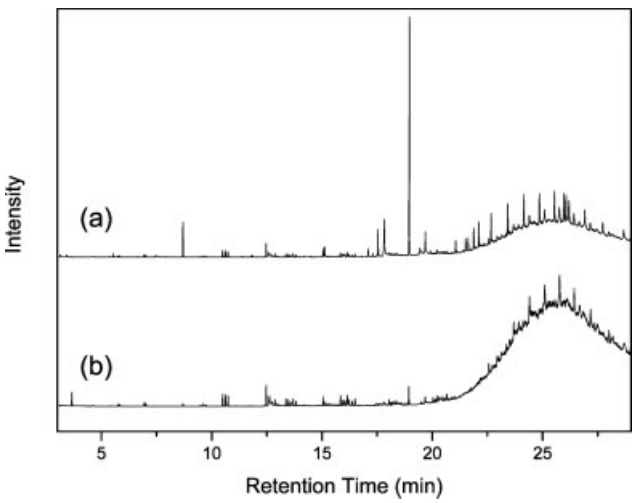

Figure 8 GC/MS chromatograms of the extracted materials from (a) the initial sample and (b) the burst region of the blowed out specimen of the SBR vulcanizate.

position of the rubber chains to activate the cavity formation and reduce the resistance to the increasing interior pressure. Difference in the blow out behaviors of NR and SBR vulcanizates will be elaborated in a separate publication.

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