

Influence of the Rubber Blend Ratio on Blowout Behaviors of Carbon Black-Reinforced Natural Rubber/Styrene-Butadiene Rubber

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ABSTRACT: Blowout behaviors of NR/SBR blend composites reinforced with carbon black were studied using a microwave oven and variation of the blowout time and temperature with the blend ratio was investigated. Morphology of the interior of the sample before exploding was observed and change of the crosslink density was measured. The blowout time became slower and the blowout temperature became higher as the SBR content of the specimen increased. The specimen with higher NR content had more cavities in the interior just before explosion. The crosslink density became lower by coming close to the blowout and crosslink density of the inner part was more

reduced than that of the outer part. New organic materials were found in the burst region after blowout and they might be decomposed products of the polymer chains. The SBR specimen showed better blowout properties than the NR one. Principal sources to cause the blowout were found to be formation of the cavities in a rubber article, reduction of the crosslink density, and dissociation of the rubber chains. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3627–3633, 2009

Key words: blowout; NR/SBR blend; rubber composite; crosslink density change; polymer decomposition

INTRODUCTION

Blend of two types of rubber has been used for the preparation of new materials with desirable properties absent in the each component rubber. Natural rubber (NR) is blended with a synthetic rubber to improve physical and chemical properties. The useful polymer–polymer combination has good intermolecular interactions and exhibits sufficient thermodynamic compatibility. Saad and El-Sabbagh¹ reported that the NR/styrene-butadiene rubber (SBR) and NR/butadiene rubber (BR) blends were compatible while the NR/ethylene–propylene–diene monomer (EPDM), NR/acrylonitrile-butadiene rubber (NBR), and NR/chloroprene rubber (CR) blends were incompatible.

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.^{2–4} It may be attributed to thermal decomposition of the rubber vulcanizate when the heat gener-

ated internally is not conducted away rapidly enough to cause decomposition. Volatile products then develop an internal pressure sufficiently large to tear open a path to the exterior.

Blowout was first thought to be a mechanical fatigue cracking process, aggravated by the high temperature set up by cycling stress.⁵ Failure is attributed to the development of an internal pressure large enough to expand any preexisting internal cavity to the point of rupture. Gent and Hindi³ studied blowout phenomena of rubber vulcanizates using a flexometer and a microwave oven and reported that the blowout temperatures measured using a flexometer were consistent with those using a microwave oven. Blowout time of a carbon black-filled rubber composite was getting faster as the carbon black content was increased and blowout temperature of an overcured rubber vulcanizate was higher than that of an undercured one.²

Blowout behaviors of rubber vulcanizates using a flexometer are consistent with those using a microwave oven,^{2,3} although the times taken to reach blowout (blowout time) using a microwave oven are much faster than those using a flexometer. In this work, we studied the blowout behaviors of NR/SBR blend composites depending on the rubber composition ratios using a microwave oven. Changes of crosslink

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TABLE I
Formulations (phr)

Compound No.	1	2	3	4	5
SMR CV60	100.0	80.0	50.0	20.0	0.0
SBR 1502	0.0	20.0	50.0	80.0	100.0
N330	60.0	60.0	60.0	60.0	60.0
HPPD	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Oil	2.0	2.0	2.0	2.0	2.0
TBBS	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5

SMR CV60, Malaysian standard rubber (natural rubber) with Mooney viscosity of 60; SBR 1502, ML1 + 4 at 100°C = 52; N330, carbon black; HPPD, *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine; TBBS, *N*-*tert*-butyl-2-benzothiazole sulfenamidesulfonamide.

densities before and after blowout were measured and morphology of the interior before exploding was also observed to investigate sources to cause the blowout in detail.

EXPERIMENTAL

Five carbon black-reinforced NR/SBR blend compounds with different rubber content ratios were prepared. The compounds were made of rubbers (NR and SBR), carbon black, processing oil, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). The blend ratios of NR/SBR were 100/0, 80/20, 50/50, 20/80, and 0/100. The formulations were given in Table I. 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 diameter and 25.0 mm height). Blowout experiments were performed using a RE-MC20T microwave oven of Samsung Co. of Korea with a microwave frequency of 2450 MHz. The irradiation power was set with 700 W. Blowout temperatures were measured with a thermocouple thermometer kept in a boiling oil bath of 210°C. The experiments were performed five times.

The crosslink densities of the samples were measured by the swelling method.^{6,7} The procedure to measure the crosslink density was as follows: initially organic additives in the samples were removed by extraction with THF and *n*-hexane for 2 days each and 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 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.

RESULTS AND DISCUSSION

We observed the burst morphology of the exploded sample. Blowout is occurred in the middle of the sample since the heat is concentrated in the interior. The specimen with higher NR content is more

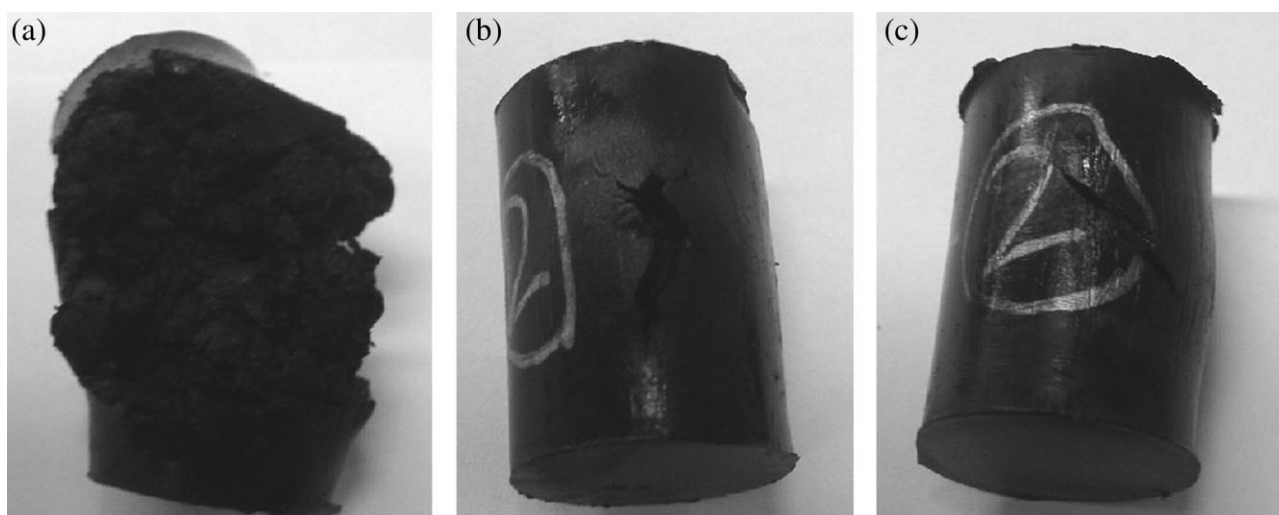


Figure 1 Photographs of the exploded samples with the rubber compositions of NR/SBR = 100/0 (a), 50/50 (b), and 0/100 (c).

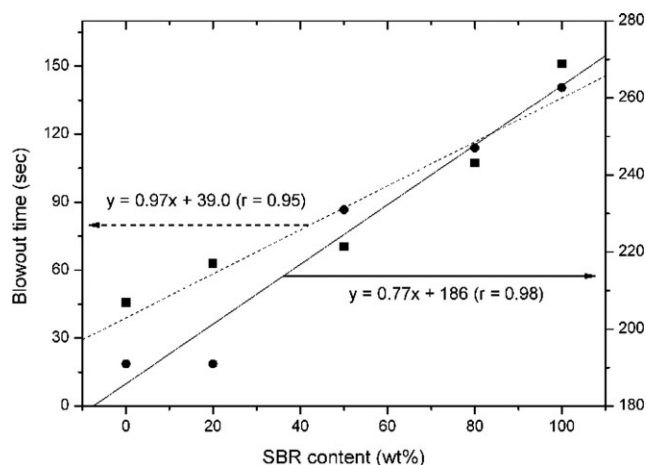


Figure 2 Variations of the blowout time and temperature as a function of the rubber composition ratio.

severely exploded as shown in Figure 1. The burst NR/SBR = 100/0 specimen looks like a popcorn. The exploded NR/SBR = 0/100 specimen shows a large crack on the surface and there is a big cavity in the interior. The blowout time and temperature show a good trend with the rubber composition ratio as shown in Figure 2. The blowout temperature was measured 10 s after explosion for the safe and reduction of measurement error because the just burst sample was so hot and lots of volatile materials were generated. Difference in the blowout temperatures measured just and 10 s after explosion was about 30°C. The blowout time becomes longer and the blowout temperature becomes higher as the SBR content increases. The blowout time increases 9.7 s every 10.0 phr increase of the SBR content and the blowout temperature also increases 7.7°C every 10.0 phr increase of the SBR content. Previous study reported the better blowout properties of SBR compared with NR.²

To investigate the blowout process in detail, a specimen before explosion was cut and divided into five sections as shown in Figure 3, and each morphology was observed and the apparent crosslink density was measured. Figures 4–6 show the interior

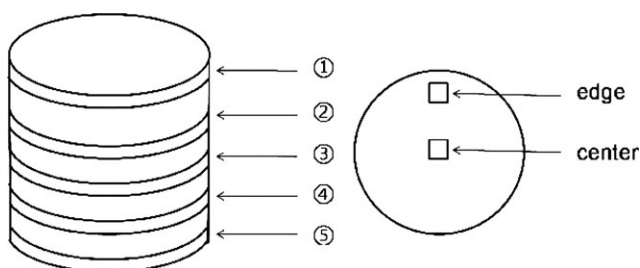


Figure 3 Sample section.

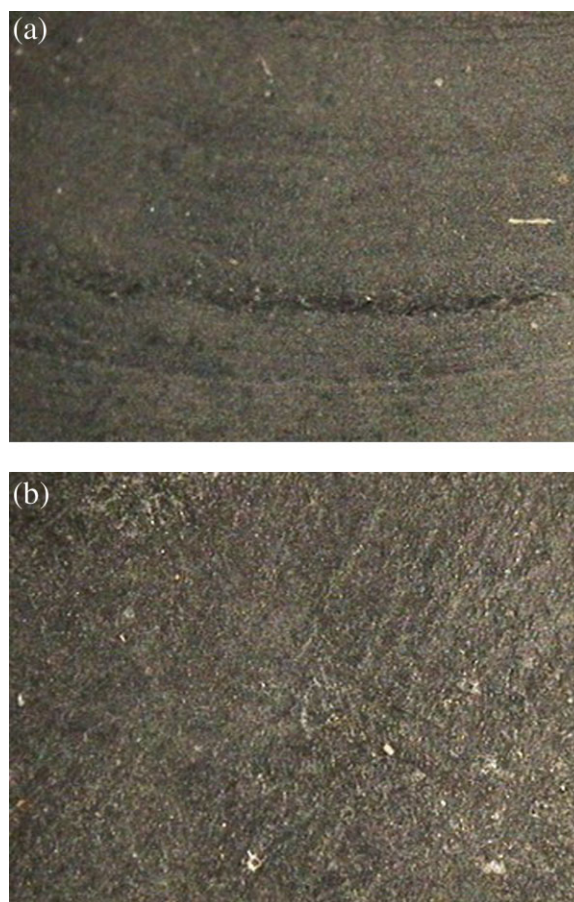


Figure 4 Cross sections of the region no. 1 (or 5) of the NR/SBR = 100/0 vulcanizate 10 s before blowout. The left (a) and right (b) pictures are the center and edge areas, respectively. The magnification was 100.

morphologies of the NR/SBR = 100/0 specimen 10 s before blowout. The center and edge areas were observed. The sections no. 1 and 5 do not show any cavities before explosion as shown in Figure 4 but the sections no. 2 and 4 show some cavities in the edge as well as in the center as shown in Figure 5. The cavity size is about 100 µm and the number of cavities is much more in the center than in the edge. Size and frequency of the cavity increase by coming close to the inner section. Figure 6 shows the morphology of the section no. 3 with lots of cavities. The cavity size is increased by coming close to the explosion. Figure 7 shows the morphology of the interior 5 s before blowout. Big cavities with diameters of above 200 µm are observed and the number of cavities becomes very high so the morphology looks like a polymer foam. The interior morphologies of the NR/SBR = 100/0 vulcanizate indicate that lots of cavities are generated over large area before explosion. Lots of the cavities and their big sizes lead to fast and severe blowout.

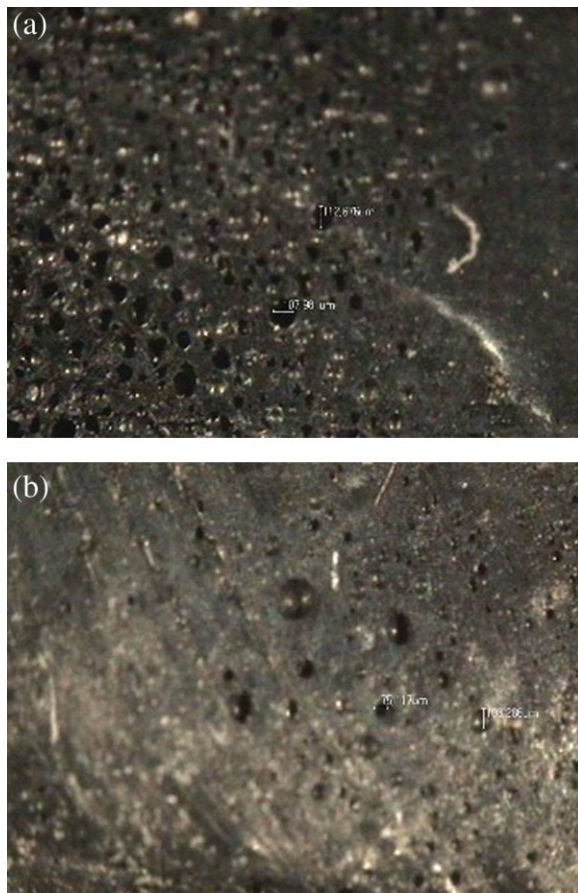


Figure 5 Cross sections of the region no. 2 (or 4) of the NR/SBR = 100/0 vulcanizate 10 s before blowout. The left (a) and right (b) pictures are the center and edge areas, respectively. The magnification was 100.

Generation of the cavities becomes deactivated by increasing the SBR content. Figure 8 shows the interior morphology of the NR/SBR = 50/50 vulcanizate 10 s before blowout and only few big cavities are observed. For the NR/SBR = 0/100 specimen, the number of cavities is remarkably reduced as shown in Figure 9. The interior morphology before explosion is closely related with the exploding pattern. The NR/SBR = 100/0 vulcanizate having lots of cavities over large area before explosion is exploded early at low temperature and the burst area is relatively large whereas the specimen of NR/SBR = 0/100 having few cavities before explosion is exploded lately at high temperature and the burst area is small.

Crosslink density of a rubber vulcanizate directly affects the physical properties.⁸ By increasing the crosslink density of a rubber article, the modulus, hardness, resilience, and abrasion resistance increase, whereas the elongation at break, heat build-up, and stress relaxation decrease. We measured change of the crosslink density after blowout and also investi-

gated variation of the crosslink density change with closing to blowout. Change of the crosslink density was obtained by dividing the difference in the crosslink densities of the initial and burst samples by the crosslink density of the initial sample. The crosslink density changes after blowout were summarized in Table II. The crosslink densities of all the specimens are decreased by blowout and the crosslink density decrement of the burst part is much larger than that of the not burst one. This indicates that the reduced crosslink density may be one of principal sources to cause blowout. The reduced crosslink density leads to reduction of the resistance to the increasing internal pressure by volatile materials. For the not burst parts, level of the crosslink density change is on the whole reduced by increasing the SBR content. For the burst parts, the crosslink density decrement of the NR/SBR = 0/100 specimen is much smaller than those of the other samples. The variation of the crosslink density change is consistent with the blowout time and temperature; the blowout time and temperature are increased by increasing the SBR

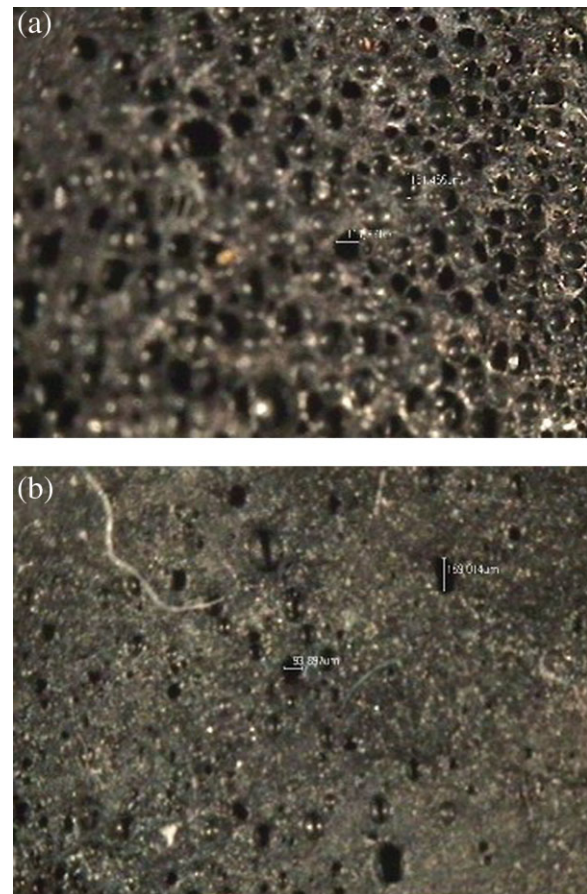


Figure 6 Cross sections of the region No. 3 of the NR/SBR = 100/0 vulcanizate 10 s before blowout. The left (a) and right (b) pictures are the center and edge areas, respectively. The magnification was 100.

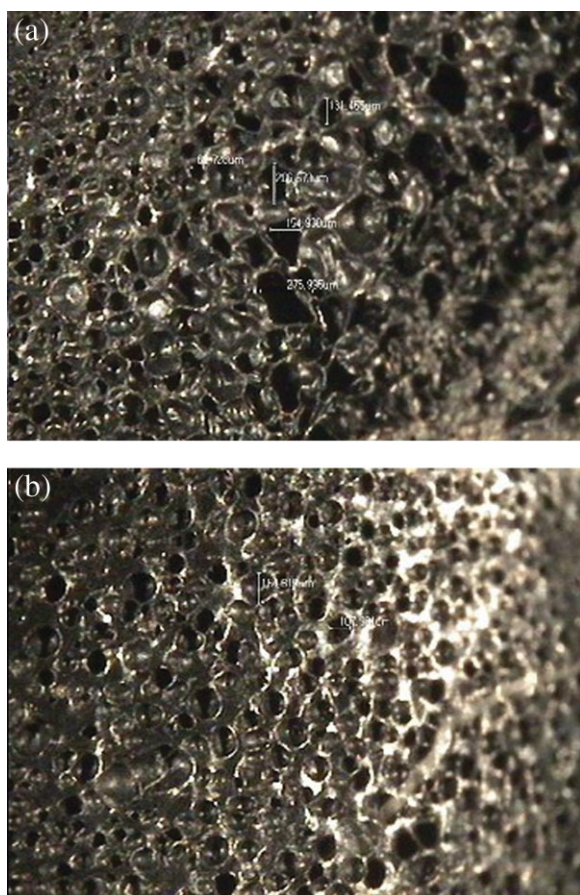


Figure 7 Cross sections of the region no. 3 of the NR/SBR = 100/0 vulcanizate 5 s before blowout. The left (a) and right (b) pictures are the center and edge areas, respectively. The magnification was 100.

content as shown in Figure 2. Therefore, we can say that the reduced crosslink density leads to fast and low temperature blowout by activation of the cavity formation. Big decrease of the crosslink density for the specimens containing NR can be explained with the polysulfidic linkages. A vulcanized NR has lots of polysulfidic linkages⁷ and polysulfides can be easily dissociated by heat since dissociation energies of polysulfides are much lower than those of mono- and disulfides.⁹

We also investigated variation of the crosslink density change with closing to blowout. The inner parts of the sample were selected before exploding and their crosslink density changes were measured. Figures 10–12 show variations of the crosslink densities of the five regions for the NR/SBR = 100/0, 50/50, and 0/100 specimens, respectively. The crosslink densities are reduced by accumulating heat irrespective of the rubber blend ratios and the sections. Level of the reduced crosslink density of the inner section is much higher than that of the outer one. For the NR/SBR = 100/0 vulcanizate, the crosslink

densities 20 s before blowout are slightly reduced and difference in the crosslink density changes according to the sections is negligible, but the crosslink density changes become larger and the difference in the crosslink density changes according to the sections becomes also larger by closing to blowout as shown in Figure 10. The crosslink density decrement of the section no. 3 (the inner section) is larger by about eight times than that of the section no. 5 (the outer section) for the NR/SBR = 100/0 vulcanizate 5 s before blowout. This is concrete evidence about the faster and more severe blowout behaviors of NR. The big decrement of the crosslink density in the interior for a short time can lead to formation of the cavities and reduction of the resistance to the increasing internal pressure. Variation of the crosslink density change of the NR/SBR = 50/50 specimen shows similar trends with that of the NR/SBR = 100/0 one but the crosslink density change 10 s before blowout of the former is much larger than that of the latter as shown in Figures 10 and 11. This phenomenon was also observed in the NR/

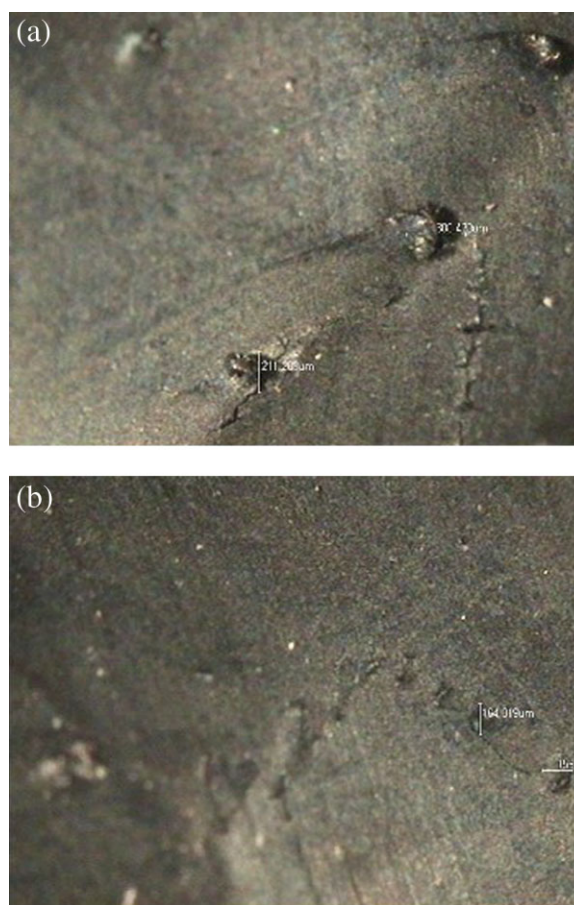


Figure 8 Cross sections of the region no. 3 of the NR/SBR = 50/50 vulcanizate 10 s before blowout. The left (a) and right (b) pictures are the center and edge areas, respectively. The magnification was 100.

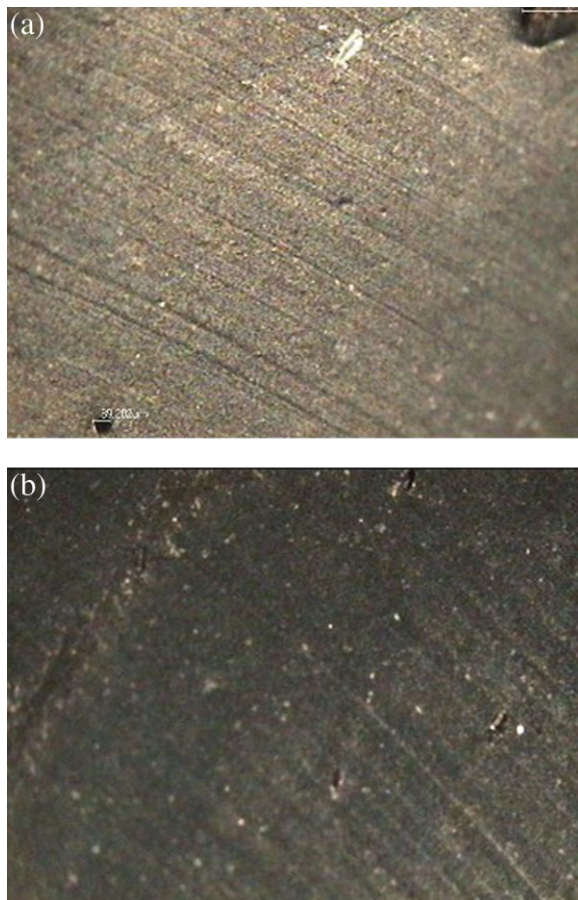


Figure 9 Cross sections of the region no. 3 of the NR/SBR = 0/100 vulcanizate 10 s before blowout. The left (a) and right (b) pictures are the center and edge areas, respectively. The magnification was 100.

SBR = 0/100 specimen as shown in Figure 12. This can be explained with the irradiation time of microwave and heat build-up. At 10 s before blowout, temperature of the sample with higher SBR content is higher than that with lower one and the time to accumulate heat by microwave irradiation for the former is longer than for the latter since the blowout time and temperature are increased by increasing the SBR content as discussed previously. This means that dissociation of sulfur linkages in SBR needs more energy than those in NR.

Some sticky materials and carbonized things were found in the burst region after blowout. The sticky

TABLE II
Change of the Apparent Crosslink Density After Blowout (%)

Compound No.	1	2	3	4	5
Not burst part	-21.4	-20.0	-10.6	-13.2	-12.8
Burst part	-41.1	-43.4	-41.2	-41.3	-19.9

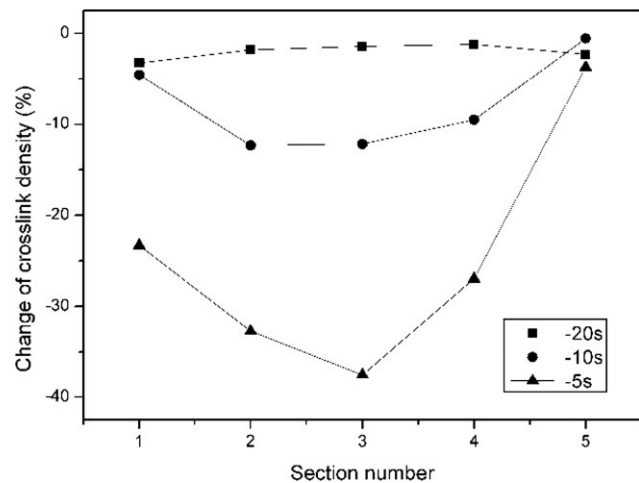


Figure 10 Change of the crosslink density of the NR/SBR = 100/0 vulcanizate before explosion according to the section. Squares, circles, and triangles indicate 20, 10, and 5 s before blowout, respectively.

materials may be organic ingredients in the compound formulation or organic materials produced by decomposition of the polymer chains. Unbound materials in the samples were extracted with THF for 3 days at room temperature and amount of the extracted materials was measured. The extraction experiments were carried out with the initial sample and the burst and not burst regions of the exploded sample and the results were summarized in Table III. Amount of the organic materials extracted from the burst region is much larger than those from the not burst region and the initial sample irrespective of the rubber blend ratios. This indicates that less

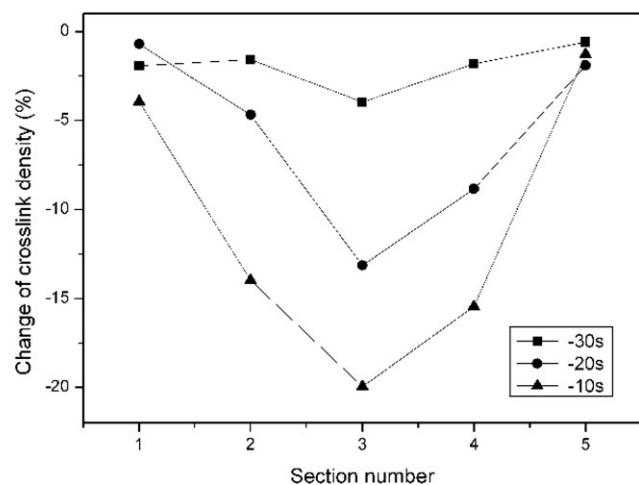


Figure 11 Change of the crosslink density of the NR/SBR = 50/50 vulcanizate before explosion according to the section. Squares, circles, and triangles indicate 30, 20, and 10 s before blowout, respectively.

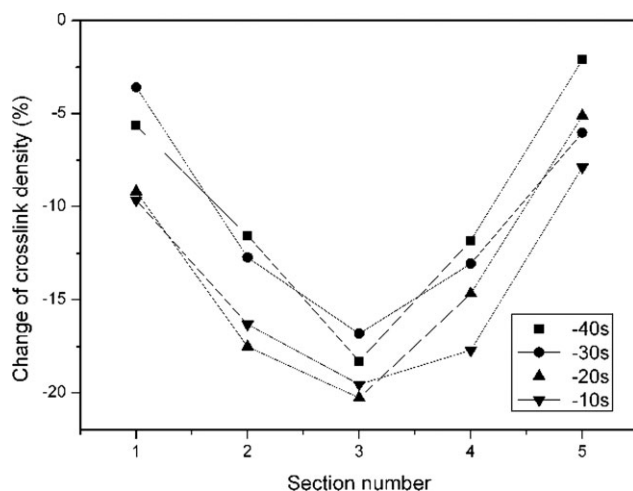


Figure 12 Change of the crosslink density of the NR/SBR = 0/100 vulcanizate before explosion according to the section. Squares, circles, up-triangles, and down-triangles indicate 40, 30, 20, and 10 s before blowout, respectively.

TABLE III
Amounts of the Extracted Materials (wt %)

Compound No.	1	2	3	4	5
Initial specimen	4.9	5.0	5.7	5.8	6.0
Not burst part	5.3	5.7	5.8	6.3	6.6
Burst part	27.7	28.8	16.2	13.4	12.7

volatile materials are newly produced by decomposition of the rubber chains during blowout process. The experimental results can lead to a conclusion that the polymer decomposition is one of principal

sources to cause blowout by activating the cavity formation and increasing the internal pressure.

CONCLUSIONS

By increasing the SBR content of the sample, the blowout time became longer, the blowout temperature became higher, and the burst area was reduced. Cavities were generated in the interior of the rubber article before explosion and the number of cavities was increased by increasing the NR content. The crosslink density was decreased by closing to blowout and degree of the decreased crosslink density was increased with increase of the NR content. There were lots of organic materials produced by decomposition of the rubber chains in the burst part. Principal sources to cause blowout were found to be reduction of the crosslink density, decomposition of the rubber chains, and formation of the cavities. The decreased crosslink density and the rubber chain decomposition lead to activation of the cavity formation, generation of the volatile materials, and reduction of the resistance to the internal pressure.

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