

# Effect of the Blooming of Chemical Curatives on the Cyclic Fatigue Life of Natural Rubber Filled with a Silanized Silica Nanofiller

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Received 6 July 2010; accepted 12 September 2010

DOI 10.1002/app.33396

Published online 16 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** When partly soluble chemical curatives are mixed with raw rubber, they migrate to the rubber surface, which can be detrimental to the rubber properties. Two rubber compounds with different amounts of curatives were prepared by mixing natural rubber with a high loading of precipitated amorphous white silica nanofiller. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl)-tetrasulfide coupling agent to chemically adhere silica to the rubber. The chemical bonding between the filler and rubber was optimized via the tetrasulfane groups of bis(3-triethoxysilylpropyl)-tetrasulfide by adding accelerator and activator. The rubber compounds were cured and stored at ambient temperature for up to 65 days. One compound showed extensive blooming as a function of storage time. The cyclic fatigue life of the

rubber vulcanizates was subsequently measured at a constant strain amplitude and test frequency at ambient temperature. The blooming of the chemical curatives reduced the cyclic fatigue life of the rubber vulcanizate by more than 100%. The migrated chemical curatives produced a thin layer approximately 15  $\mu\text{m}$  in size beneath the rubber surface. When the rubber was stressed repeatedly in the fatigue test, cracks initiated in this layer and subsequently grew, causing the fatigue life of the vulcanizate to decrease. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2497–2507, 2011

**Key words:** rubber; additives; diffusion; electron microscopy; fatigue analysis

## INTRODUCTION

Since Charles Goodyear discovered in 1839 that heating raw rubber with sulfur modified the rubber to retain its shape, there has been an increasing trend to use chemical additives to improve processing and mechanical properties of raw rubbers. Industrial rubber articles, for example, passenger car tires, footwear, bridge bearings, and fuel hoses, contain chemical ingredients such as curing agents, accelerators, activators, processing aids, antidegradants, and fillers. These chemicals are added during various stages of mixing with the specific aim of dispersing them uniformly throughout the rubber to achieve the best possible effect on the downstream processing of the compound and mechanical properties of the cured product. When the solubility of the compounding ingredients in the rubber is low, blooming may occur on the surface. Blooming is a process of diffusion of chemical additives dissolved

in the rubber to the surface, followed by crystallization. Crystallization from supersaturated solution takes place more readily on the surface than in the rubber itself. This can be due to lack of equilibrium in concentration, which leads to transport of the ingredients to the surface.<sup>1</sup>

The diffusion of chemical ingredients in rubber has been the subject of numerous studies. For instance, paraffin waxes have been investigated extensively because their diffusion to the surface produces a thin film of the wax, which will act as a physical barrier to ozone attack and protects the rubber.<sup>2</sup> However, diffusion of chemical curatives such as accelerators and activators can be detrimental to the rubber properties. To vulcanize rubber to produce a homogenous product, the chemical curatives must disperse well and remain in the rubber. This can be achieved when the chemicals have a high solubility as well as a high rate of diffusion in the rubber.<sup>1</sup> Studies have shown that accelerators, e.g., sulfenamide types, diffuse to the surface because they are partly soluble in most rubbers.<sup>3</sup> This diffusion can be detrimental to rubber properties such as loss of adhesion<sup>4,5</sup> and also to health, safety, and the environment.

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TABLE I  
Formulations and ODR Test Results for the NR Compounds  
with an Increasing Loading of TBBS

	Compound										
	1	2	3	4	5	6	7	8	9	10	11
Formulation (phr) TBBS	1	2	3	4	5	6	7	7.5	8	9	10
ODR results											
Minimum torque (dN m)	27	29	28	26	26	26	24	21	21	21	18
Maximum torque (dN m)	36	47	60	69	72	81	81	77	76	77	79
$\Delta$ Torque (dN m)	9	18	32	43	46	55	57	56	55	56	61

Formulation: 100 phr NR and 60 phr silanized silica. The compound temperature rose to 48–85°C during mixing.

The aim of this study was to evaluate effect of the migration of a sulfenamide accelerator to the surface on the hardness, tensile strength, elongation at break, stored energy density at break, and cyclic fatigue life of natural rubber (NR) filled with a high loading of a silanized silica nanofiller. These properties were measured after the rubber vulcanizate was stored at ambient temperature for different times up to 65 days. This time was sufficient to allow full blooming to appear.

## EXPERIMENTAL

### Materials and mixing

The raw elastomer used was standard Malaysian NR grade L (SMRL). The reinforcing filler was Coupsil 8113, which was supplied by Evonik Industries AG of Germany. Coupsil 8113 is a precipitated amorphous white silica-type Ultrasil VN3, surface of which had been pretreated with bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), known also as Si69 coupling agent, to chemically bond silica to rubber. It has 11.3% by weight silane, 2.5% by weight sulfur (included in TESPT), a 175 m<sup>2</sup>/g surface area (measured by N<sub>2</sub> adsorption) and a 20–54 nm particle size.

In addition to the raw rubber and filler, the other ingredients were *N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS; a safe-processing delayed action accelerator with a melting point of 109°C) (Santocure TBBS, Flexsys, Dallas, TX), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), and *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (an antidegradant with a melting point of 45°C, Santoflex 13, Brussels, Belgium). The melting temperatures of ZnO and silanized silica are above 1000°C. The cure system consisted of TBBS and ZnO, which were added to fully crosslink the rubber. The antidegradant was added to protect the rubber against environmental ageing by ozone and oxygen.

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter rotating rotors. In these experi-

ments, the Banbury rotors and the mixing chamber were initially set at 48°C, and the rotor speed was set at 45 rpm. The volume of the mixing chamber was 78 cm<sup>3</sup>, and it was 58% full during mixing. PolyLab Monitor 4.17 software was used for controlling the mixing condition and storing data.

For preparing the rubber compounds, a total mixing time of 16 min was used, which was long enough to fully disperse the silica particles in the rubber.<sup>6</sup> The filler and rubber were placed in the mixing chamber and mixed for 13 min, and then TBBS, ZnO, and anti-degradant were added and mixed for an extra 3 min. In total, 29 rubber compounds were made.

Finally, when mixing ended, the rubber was recovered from the mixer and milled to a thickness of about 6 mm for further work. The compounds were kept at ambient temperature (21°C ± 2°C) for at least 24 h before their cure properties were measured.

### Addition of TBBS to the filled rubber

To activate the rubber-reactive tetrasulfane groups of TESPT, TBBS was added. The loading of TBBS in the rubber was increased progressively to 10 phr to measure the amount needed to optimize the chemical bonding between the rubber and TESPT and to increase the cross-link density of the rubber. The idea was to add a minimum amount of TBBS to the rubber and produce the largest effect on  $\Delta$ torque, which is an indication of cross-link density changes in the rubber. The formation of cross-links strengthened interaction between the rubber and filler, which was beneficial to the rubber reinforcement.<sup>7,8</sup> In total, 11 compounds were made (compounds 1–11; Table I).

### Addition of ZnO to the filled rubber with TBBS

The loading of ZnO in the filled rubbers with TBBS was raised to 3.5 phr to determine the amount needed to maximize the efficiency of TBBS and chemical bonding between the filler and rubber. In total, 16 compounds were prepared (compounds 12–20, Table II; and compounds 21–27, Table III).

**TABLE II**  
Formulations and ODR Test Results for the NR Compounds with an Increasing Loading of Zinc Oxide

	Compound								
	12	13	14	15	16	17	18	19	20
Formulation (phr) zinc oxide	0	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0
ODR results									
Minimum torque (dN m)	26	24	23	23	24	22	24	24	24
Maximum torque (dN m)	81	102	107	114	120	120	125	134	136
$\Delta$ Torque (dN m)	55	78	84	91	96	98	101	110	112

Formulation: 100 phr NR, 60 phr silanized silica, and 6 phr TBBS. The compound temperature rose to 48–74°C during mixing.

### Viscosity and cure properties of the rubber compounds

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to a British Standard.<sup>9</sup> The results were expressed in Mooney Units (MU).

The scorch time,  $t_{s2}$ , which is the time for the onset of cure, and the optimum cure time,  $t_{95}$ , which is the time for the completion of cure, were determined from the cure traces generated at 140°C  $\pm$  2°C by an oscillating disc rheometer curemeter (ODR) (Monsanto, Swindon, UK).<sup>10</sup> The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described previously.<sup>11</sup> The rheometer tests ran for up to 2 h. Figure 1 shows typical cure traces produced for the rubbers with TBBS and ZnO.

$\Delta$ Torque is the difference between the maximum and minimum torque values on the cure trace of the rubber and, as mentioned earlier, indicates cross-link density changes<sup>12</sup> and was calculated from these traces.  $\Delta$ Torque was subsequently plotted against the loading of TBBS and ZnO.

**TABLE III**  
Formulations and ODR Test Results for the NR Compounds with an Increasing Loading of Zinc Oxide

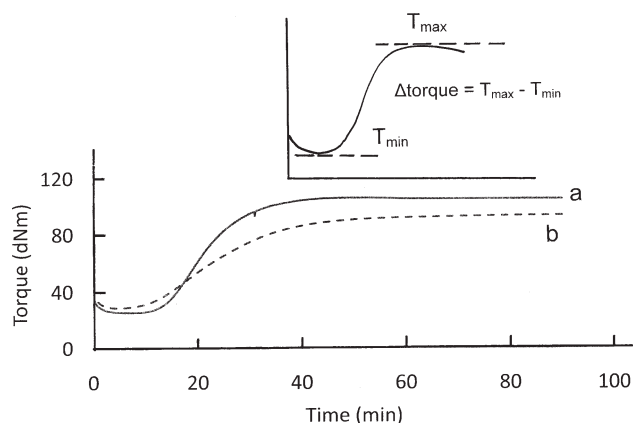
	Compound						
	21	22	23	24	25	26	27
Formulation (phr) zinc oxide	0.5	1.0	1.5	2.0	2.5	3.0	3.5
ODR results							
Minimum torque (dN m)	26	28	30	26	30	29	30
Maximum torque (dN m)	71	81	86	86	91	91	93
$\Delta$ Torque (dN m)	45	53	56	60	61	62	63

Formulation: 100 phr NR, 60 phr silanized silica, and 3 phr TBBS. The compound temperature rose to 48–79°C during mixing.

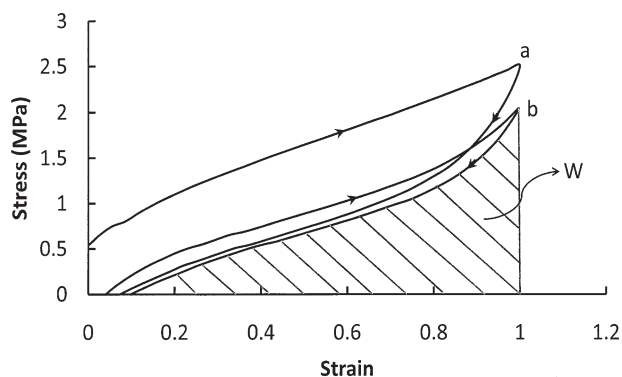
### Examination of the rubber surfaces and internal structure of the test pieces

To study blooming of the rubber curatives on the rubber surfaces and inspect the internal structure of the test pieces before and after cycling, a Cambridge Instrument Stereoscan 360 scanning electron microscope (SEM) was used. The composition of solid particles in the rubber was determined by an energy dispersive X-ray microanalyser (INCA System, Oxford Instruments, UK). To examine the internal structure of the rubber before cycling, small pieces of the vulcanizates were placed in liquid nitrogen for 5 min. They were recovered and fractured into two pieces to create fresh surfaces, approximately 11 mm<sup>2</sup> in area and 3 mm thick, which were coated with gold and placed in the SEM. Similarly, after the test pieces were cycled to failure, the fracture surfaces were examined in the SEM.

To study effect of the blooming of chemical curatives on the rubber surface, samples 4 mm  $\times$  6 mm were cut from the vulcanized sheets of rubber and examined in the SEM. SEM photographs were subsequently used to analyze the results.



**Figure 1** Torque versus time traces by ODR for the filled rubbers. (a) compound 28 and (b) compound 29.



**Figure 2** Stress versus strain data for calculating the stored energy density at 100% strain amplitude. (a) First cycle and (b) 10th cycle. Data for compound 28.

### Analysis of the rubber surfaces by Fourier transform infrared spectrometer

A Fourier transform infrared (FTIR) spectrometer (FTIR-8400S) (Shimadzu Scientific Instruments, USA) was used to provide molecular fingerprint information to positively identify compounding chemical components that underwent surface migration. The migrated layer was gently removed from the rubber surface with a clean blade and mixed and ground with KBr powder. The mixture was poured into a chamber and pressed manually to form a semitransparent disc 1 mm thick and 10 mm in diameter. The disc was then placed in a sample holder and tested. A similar procedure was used to analyze TBBS, ZnO, antidegradant, and silanized silica nanofiller, which were the compounding ingredients. The test produced spectra, which were examined to determine the chemical components that underwent surface migration. The chemical composition of the bloom was subsequently identified.

### Test pieces and test procedure

After these measurements were completed, the compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. For measuring the mechanical properties of the vulcanizates, sheets 23 cm × 23 cm in dimensions by approximately 2.8 mm thick were used from which various samples for further tests were cut.

### Hardness

For determining the hardness of the rubber, cylindrical samples 12.5 mm thick and 28 mm in diameter were cured. The samples were then placed in a Shore A Durometer hardness tester (The Shore Instrument and MFG, New York) and the hardness of the rubber was determined at 20°C after 15-s interval. This was repeated at three different positions on each sample,

and the median of the three readings was subsequently indicated.<sup>13</sup>

### Young's modulus and tensile properties of the rubber vulcanizates

The Young's modulus, tensile strength, elongation at break, and stored energy density at break of the rubber vulcanizates were determined in uniaxial tension in a Lloyd testing machine LR50K (Hampshire, UK) with dumbbell test-pieces 75 mm long with a central neck 25 mm long and 3.6 mm wide. For each rubber, three test pieces were fractured, and the median of the three values was subsequently noted.<sup>14</sup> To calculate the stored energy density at 100% strain amplitude at which the fatigue tests were performed, dumbbell test pieces were repeatedly cycled at a cross-head speed of 60 mm/min at 20°C until the force–extension curve settled to a virtually steady state after seven or so cycles. Values of the stored energy density,  $W$ , were calculated from the area under the retraction curve produced after 10 cycles (Fig. 2). Lloyd Nexygen 4.5.1. software was used for storing and processing the data. The hardness, Young's modulus, and tensile properties were measured after the rubber vulcanizates were stored at ambient temperature (21°C ± 2°C) for 65 days.

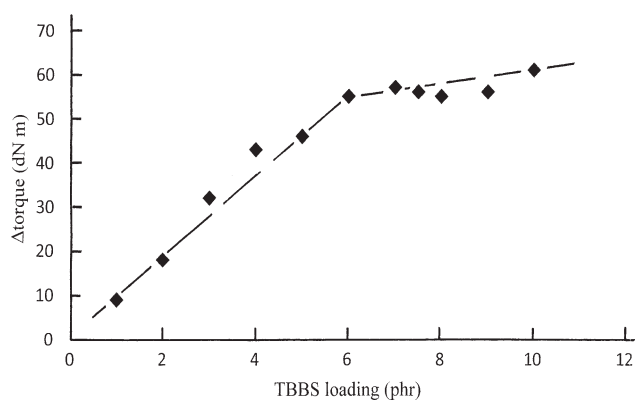
### Cyclic fatigue life

The cyclic fatigue life (the number of cycles to failure),  $N$ , of the vulcanizates was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK), with dumbbell test pieces. The test pieces were die-stamped from the sheets of cured rubber. The tests were performed at a constant maximum deflection of 100% (the central neck was stretched to 50 mm) and a test frequency of 1.4 Hz. The test temperature was 21°C ± 2°C, and the strain on each test piece was relaxed to zero at the end of each cycle.<sup>15</sup> In total, for each rubber vulcanizate, 64 test pieces were cycled to failure after they were kept in storage for different times over a period of up to 65 days.

## RESULTS AND DISCUSSION

### Effect of TBBS and ZnO on the $\Delta$ torque of the silanized silica-filled rubber

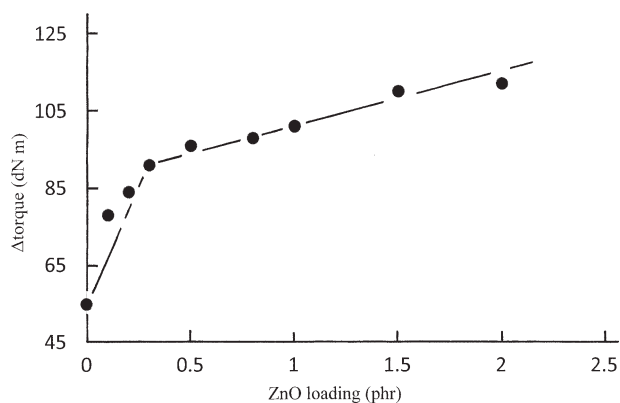
Figure 3 shows  $\Delta$ torque as a function of TBBS loading for the filled rubber.  $\Delta$ Torque increased from 9 to 55 dN m as the loading of TBBS was raised to 6 phr, and it continued rising at a much slower rate to about 61 dN m when the loading of TBBS reached 10 phr. Evidently, the addition of 6 phr TBBS to the filled rubber was sufficient to react the rubber-reactive tetrasulfane groups of TESPT with the



**Figure 3**  $\Delta$ Torque versus TBBS loading for the filled rubber.

rubber to form cross-links and optimize the chemical bonding between the two.

To improve the efficiency of TBBS in the filled rubber, ZnO was added.  $\Delta$ Torque increased sharply to 91 dN m when 0.3 phr ZnO was included, and it continued rising at a much slower rate to 112 dN m when the loading of ZnO reached 2 phr (Fig. 4). The addition of 0.3 phr ZnO was sufficient to maximize the efficiency of TBBS and to optimize further the chemical bonding between TESPT and the rubber. After these measurements were completed, compound 28 (Table IV) was made by mixing the raw rubber with 60 phr silica, 6 phr TBBS, 0.3 phr ZnO, and 1 phr antioxidant. The rubber was then cured to produce thin sheets and stored at ambient temperature for different times up to 65 days. The rubber surfaces were inspected regularly, and, after a few days, a white bloom appeared, which was examined in the SEM. There were needle-shaped objects covering the rubber surface entirely (Fig. 5). In some cases, bloom started from a center point, producing a regular structure on the rubber surface (Fig. 6), and, sometimes, it formed a leaf-shaped pattern (Fig. 7).



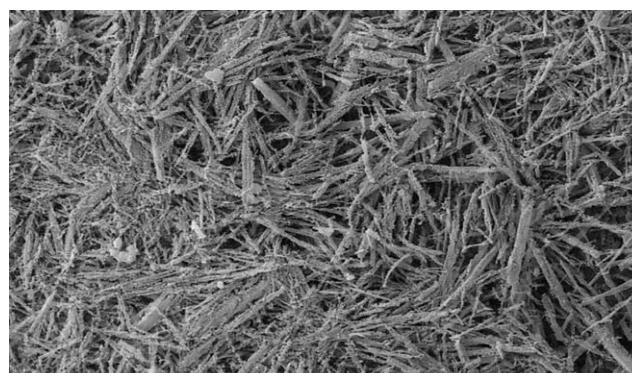
**Figure 4**  $\Delta$ Torque versus ZnO loading for the filled rubber with 6 phr TBBS.

**TABLE IV**  
Recipe, Mooney Viscosity, ODR Results, and Mechanical Properties of the Rubber Compounds

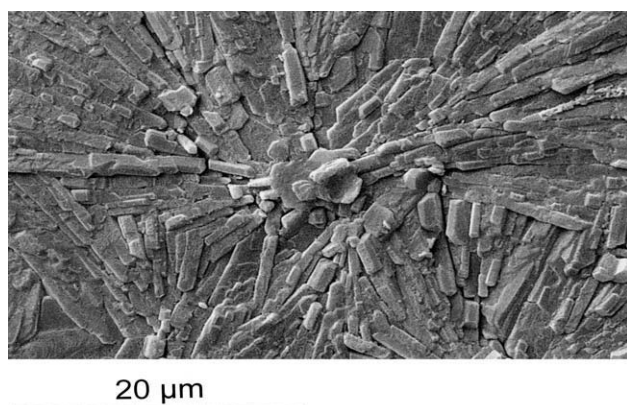
	Compound	
	28	29
Formulation (phr)		
NR (SMRL)	100	100
Silanized silica	60	60
TBBS	6	3
ZnO	0.3	2.5
Santoflex 13	1	1
Mooney viscosity (MU)	95	104
ODR results		
Minimum torque (dN m)	28	29
Maximum torque (dN m)	108	97
$\Delta$ Torque (dN m)	80	68
Scorch time, $t_{s2}$ (min)	9	10
Optimum cure time, $t_{95}$ (min)	27	53
Cure rate index ( $\text{min}^{-1}$ )	5.6	2.3
Mechanical properties		
Hardness (Shore A)	76.5	71
Young's modulus (MPa)	13	6
Tensile strength (MPa)	34.5	35.3
Elongation at break (%)	754	822
Stored energy density at break ( $\text{MJ}/\text{m}^3$ )	114	120
Stored energy density at 100% strain amplitude after 10 cycles ( $\text{MJ}/\text{m}^3$ )	0.76	0.66

The compound temperature rose to 48–79°C during mixing.

FTIR analysis revealed characteristic bands for TBBS at  $1641.48 \text{ cm}^{-1}$ , antioxidant at  $2362.88 \text{ cm}^{-1}$ , and NR at  $1126.47 \text{ cm}^{-1}$  in the spectrum to indicate their presence in the bloom. Notably, there were no bands for ZnO and silanized silica filler in the spectrum of the bloom (Fig. 8). The presence of antioxidant in the bloom was expected because it migrated to the surface to protect the rubber against environmental ageing.<sup>16</sup> Small traces of NR in the bloom was from the rubber surface during the



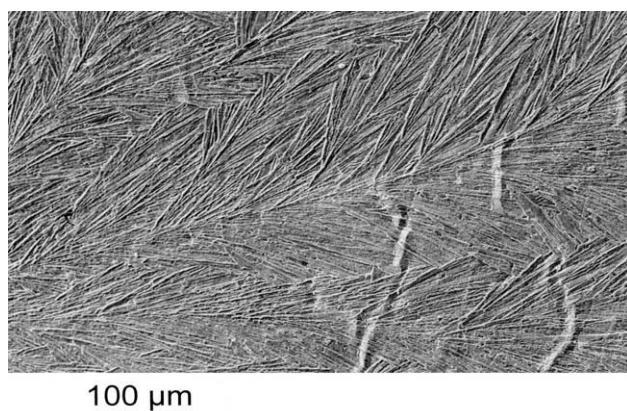
**Figure 5** SEM photograph showing needle-shaped objects on the surface of the unstrained rubber.



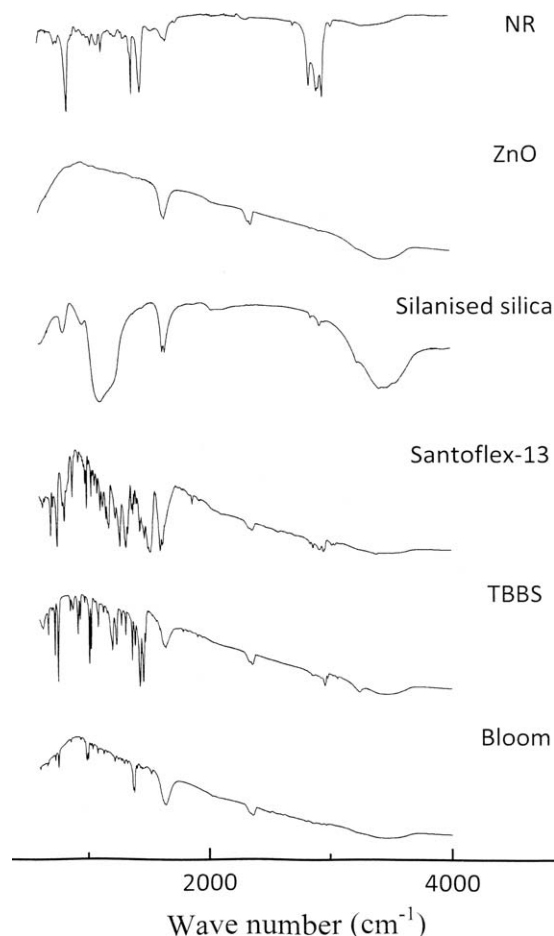
**Figure 6** SEM photograph showing bloom starting from a centre point, producing a regular structure on the surface of the unstrained rubber. Storage time 60 days at ambient temperature.

sampling of the solid layer before the FTIR spectrum was taken. TBBS and antidegradant were identified to be the main compounding ingredients that had undergone surface migration. As mentioned earlier, the melting temperature of TBBS and antidegradant are below the curing temperature of the rubber, and both melted while the rubber was being cured at elevated temperature. When the cured rubber was removed from the mold and cooled down slowly to ambient temperature, TBBS and antidegradant diffused to the rubber surface, forming the bloom. Clearly, there was excessive amount of TBBS in the rubber, which did not react fully during the curing process. For TBBS, a diffusion coefficient of  $0.8 \times 10^{-7} \text{ cm}^2/\text{s}$  at  $100^\circ\text{C}$  in a carbon black-filled NR has been reported.<sup>3</sup>

To assess effect of the blooming on the internal structure of the cured rubber, the rubber was freeze-fractured and then examined in the SEM. There were two distinct regions on the fracture surface. Region beneath the rubber surface approximately



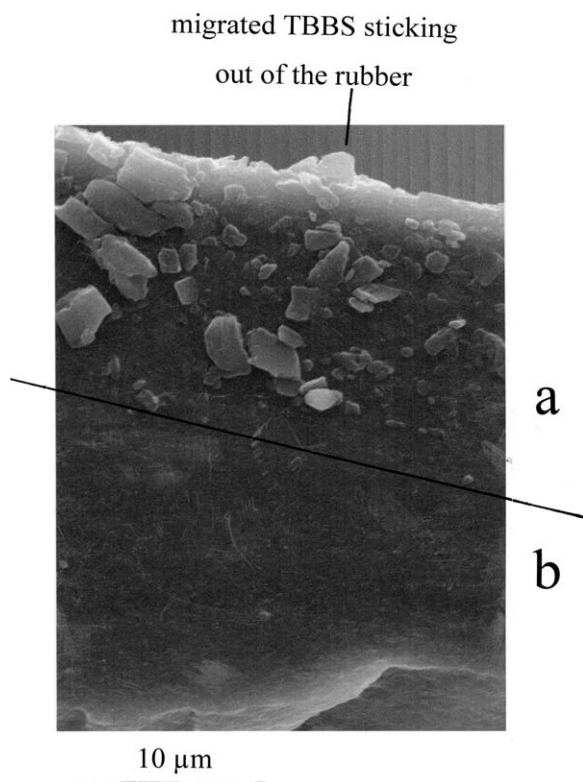
**Figure 7** SEM photograph showing a leaf-shaped pattern on the surface of the unstrained rubber. Storage time 60 days at ambient temperature.



**Figure 8** FTIR spectra for (a) bloom, (b) NR, (c) TBBS, (d) ZnO, (e) silanized silica filler, and (f) antidegradant.

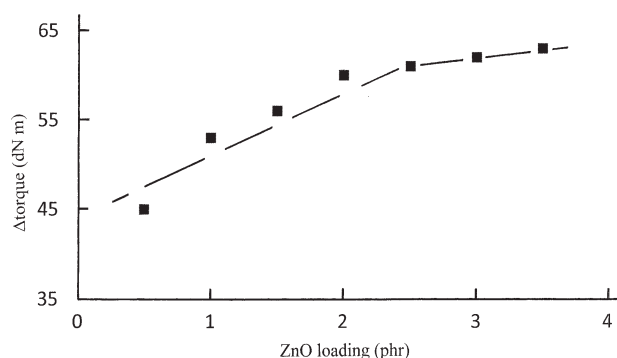
15  $\mu\text{m}$  in size, where there were migrated TBBS particles 0.5–5  $\mu\text{m}$  in size [Fig. 9(a)] (some of these particles were sticking out of the rubber, creating an uneven surface), and region where the surface was smooth entirely [Fig. 9(b)]. The former was due to the crystallization of TBBS from supersaturated solution, which took place more readily on the surface than in the rubber itself.<sup>1</sup>

To eliminate the bloom from the rubber surface, the loading of TBBS in the silica-filled rubber was reduced to 3 phr, and then ZnO was added to increase the efficiency of TBBS (Fig. 10).  $\Delta\text{Torque}$  increased from 46 to 61 dN m when the loading of ZnO was raised to 2.5 phr. Thereafter,  $\Delta\text{torque}$  increased only slightly to 64 dN m until the loading of ZnO reached 3.5 phr. Evidently, a minimum amount of 2.5 phr ZnO was sufficient to increase the efficiency of TBBS and maximize the  $\Delta\text{torque}$  value. After these measurements were done, compound 29 (Table IV) was made by adding 60 phr silica, 3 phr TBBS, 2.5 phr ZnO, and 1 phr antidegradant to the raw NR. The compound was subsequently cured to produce thin sheets and stored at ambient temperature for different times up to 65 days. The sheets

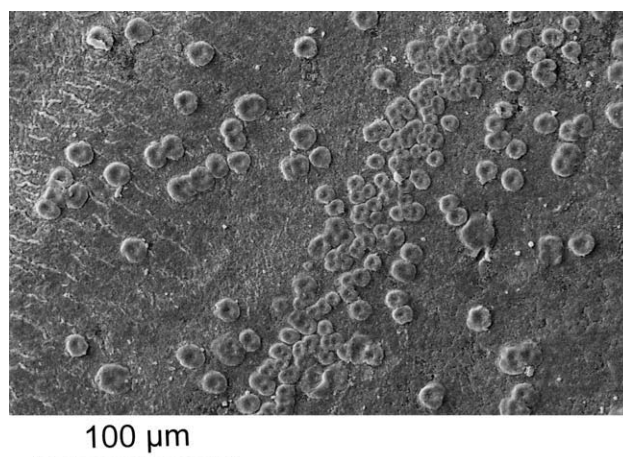


**Figure 9** SEM photograph from freeze-fracture test showing two regions on the fracture surface. Data for compound **28**.

were regularly inspected for bloom, and there was no sign that the compounding ingredients had migrated to the rubber surface. However, when the rubber surfaces were analyzed by X-ray, there were 17 wt % Zn and 7 wt % O, as well as 48 wt % C, 3.4 wt % Si, and 1.6 wt % S. In storage, ZnO continued blooming on the rubber surface, covering almost 80% of the surface area (cf. Figs. 11 and 12). To assess effect of this migration on the internal structure of the rubber, a sample of the cured rubber was freeze-fractured and examined in the SEM. There was no damage to the rubber. In fact, the silica particles dispersed well in the rubber matrix (Fig. 13), which helped to



**Figure 10**  $\Delta$ Torque versus ZnO loading for the filled rubber with 3 phr TBBS.

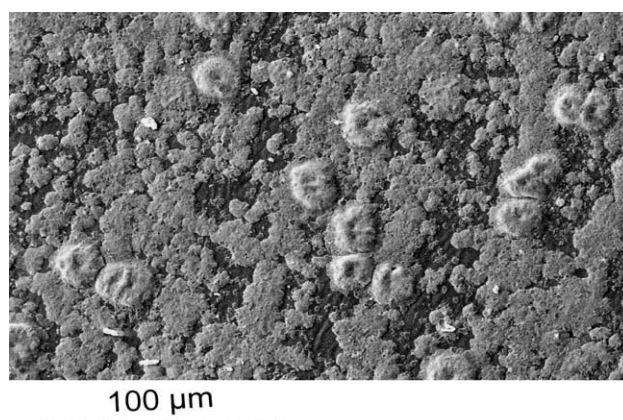


**Figure 11** SEM photograph from the unstrained rubber surface showing ZnO bloom. Storage time 1 day at ambient temperature.

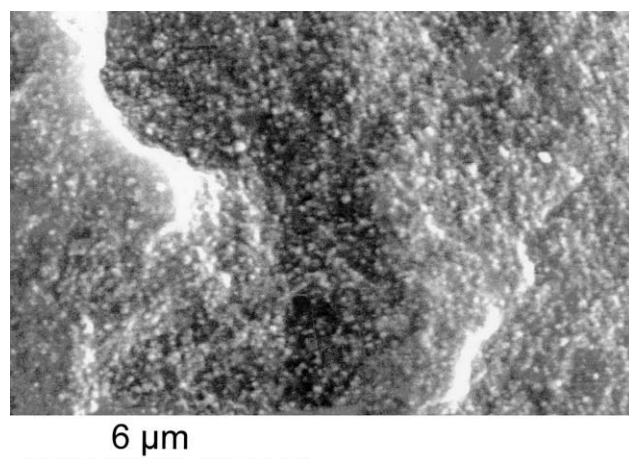
maximize the reinforcing effect of the filler on the mechanical properties of the vulcanizate.<sup>17</sup>

#### Effect of silanized silica nanofiller, TBBS, and ZnO on the viscosity of the rubber

The viscosity of the rubber decreased slightly from 99 (raw rubber) to 95 MU when silica, 6 phr TBBS, 0.3 phr ZnO, and 1 phr antidegradant were added (compound **28**; Table IV). Normally, viscosity increases when solid additives such as fillers, accelerators, and activators are mixed with rubber.<sup>18</sup> Rubber chains break down during mixing when the rubber is mixed for too long. This causes a reduction in the molecular weight and viscosity of the rubber.<sup>19,20</sup> The reduction is due to chain scission<sup>21,22</sup> or the mechanical rupture of the primary carbon-carbon bonds that are present along the backbone of the rubber chains. This is often compensated by the reinforcing effect of the filler. Clearly, in this case, the reinforcing effect of silica did



**Figure 12** SEM photograph from the unstrained rubber surface showing ZnO bloom. Storage time 60 days at ambient temperature.



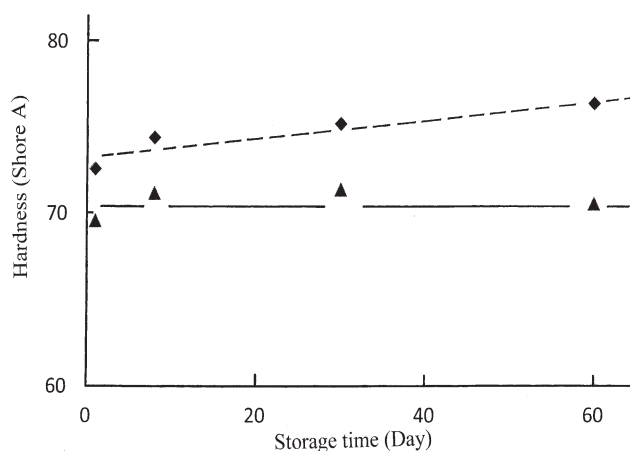
**Figure 13** SEM photograph from freeze-fracture test showing the internal structure of the rubber. Data for compound **29**.

not compensate for the mechanical damage that long mixing time, i.e., 16 min, had inflicted on the rubber chains, and, hence, the viscosity decreased.

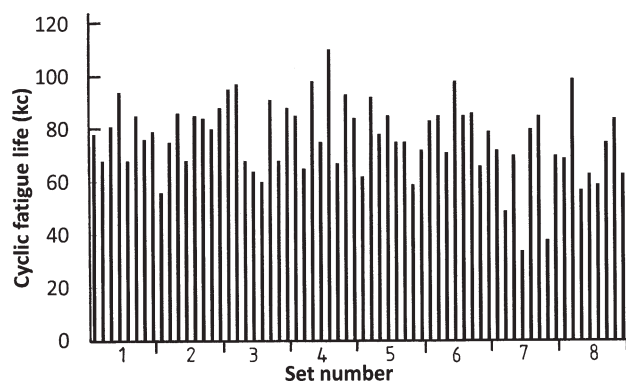
When silica, 3 phr TBBS, 2.5 phr ZnO, and 1 phr antidegradant were incorporated in the rubber, the viscosity increased by approximately 10% (cf. compounds **28** and **29**; Table IV). Metal oxides such as ZnO are reinforcing fillers and impart good properties to rubber compounds.<sup>23</sup> The extra 2.2 phr ZnO in compound **29** produced a stiffer compound with a higher viscosity.

#### Effect of the blooming of TBBS on the hardness, Young's modulus, and tensile properties of the rubber vulcanizate

The blooming had no adverse effect on the mechanical properties of the rubber vulcanizate (cf. compounds **28** and **29**; Table IV). Compound **28** was harder and had a higher Young's modulus. However, the elongation at break and stored energy density at



**Figure 14** Hardness versus storage time for compounds **28** and **29**. (---), compound **28** and (—), compound **29**.



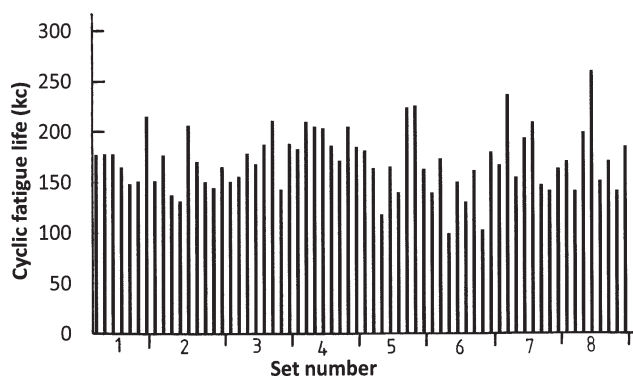
**Figure 15** Cyclic fatigue life versus set number for compound **28**.

break were inferior, and the tensile strength was almost the same for the two compounds. Interestingly, the hardness of compound **28** increased by approximately 2.5% after 8 days, and, thereafter, it continued rising by an extra 2.7% after 65 days in storage (Fig. 14). This indicated that TBBS bloomed continuously in storage albeit at different rates. A similar trend was also observed for compound **29**. However, for this compound, the hardness increased by 2.3% after 8 days and remained unchanged subsequently when the storage time was increased to 65 days. This suggested that ZnO stopped blooming after 8 days in storage. Note that in the durometer a specified indenter is forced into the test material under specified conditions and the depth of penetration measured. The indentation hardness is inversely related to the penetration and is dependent on the modulus of elasticity and the viscoelastic properties of the material.<sup>13</sup> Rubber properties such as fatigue life, stored energy density at break, and tensile strength increase, reaching a maximum, and then deteriorate substantially, whereas, hardness and modulus continue increasing as a function of cross-link density.<sup>24–26</sup> Elongation at break decreases when the cross-link density increases.<sup>25</sup> The  $\Delta$ torque of compound **28** was 15% higher, which indicated a higher cross-link density (Table IV). Our results are in line with the previous findings.

#### Effect of the blooming of TBBS on the cyclic fatigue life of the rubber vulcanizate

As mentioned earlier, 64 dumbbell test pieces were used for each rubber vulcanizate to measure the cyclic fatigue life. The test pieces were divided into eight individual sets, which were then stored at ambient temperature for 1, 5, 8, 15, 25, 35, 60, and 65 days, respectively, before they were tested. The results,  $N$ , versus set number, are presented in Figures 15 and 16. The blooming of TBBS had a detrimental effect on  $N$ . Figure 15 shows the results

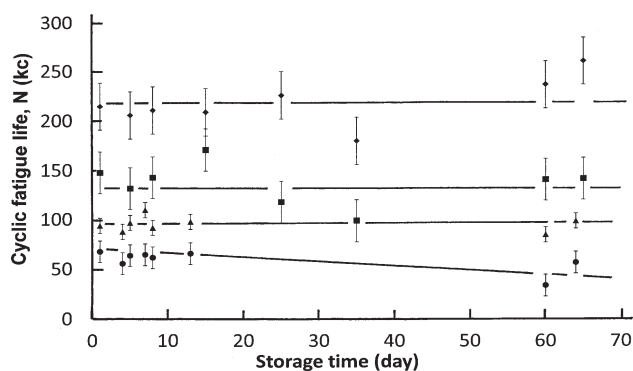




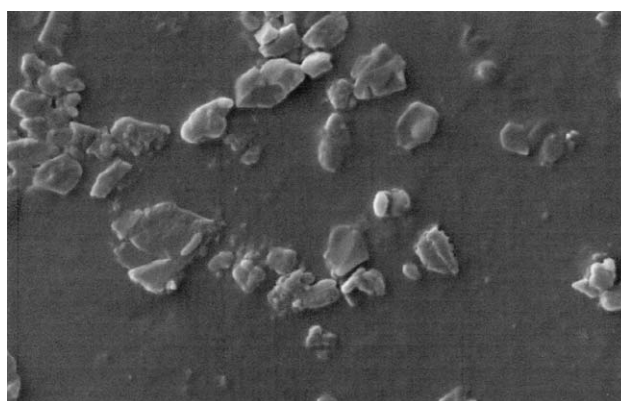
**Figure 16** Cyclic fatigue life versus set number for compound 29.

for compound 28 where  $N$  was 34–110 kc. In the absence of blooming (compound 29),  $N$  increased by more than 100% from 99 to 261 kc over the 65 days storage time (Fig. 16). For both compounds, the data showed a larger scatter after 35 days in storage but there was no trend. It is possible that the rubber was environmentally aged,<sup>27</sup> and its fatigue properties deteriorated as a result. For compound 28, the maximum stored energy density,  $W$ , at 100% strain amplitude was 13% higher (Table IV). For carbon black-filled sulfur-cured NR vulcanizates,  $N$  reduced as  $W$  was raised.<sup>28</sup> The dependence of  $N$  on  $W$  was similar for all the rubbers because the basic fatigue mechanism was the same.<sup>28</sup> It may be that the higher  $W$  contributed to the shorter fatigue life of compound 28. However, a 10-fold decrease in  $N$  required at least a 200% increase in  $W$ .<sup>28</sup> On this basis, the extra 13%  $W$  of compound 28 would have made very little or no difference to the fatigue life of this compound.

Figure 17 summarizes the results for the two compounds at different storage times. Clearly, the cyclic fatigue life benefited significantly from the



**Figure 17** Cyclic fatigue life versus storage time. (●), minimum life and (▲), maximum life for compound 28. (■), minimum life and (◆), maximum life for compound 29. The bars show the standard deviation of the data.

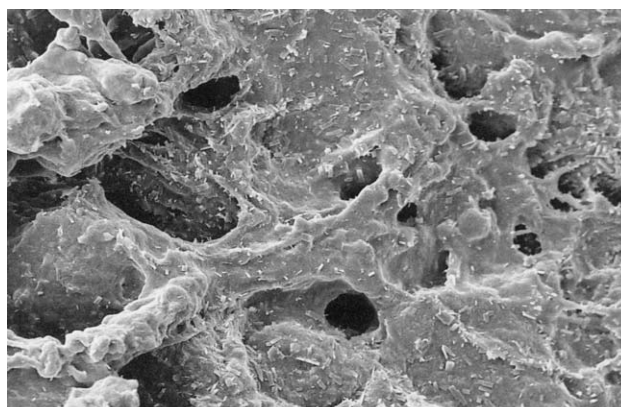


8  $\mu\text{m}$

**Figure 18** SEM photograph from the unstrained rubber surface after the bloom was removed by sellotape showing large solid particles in the rubber.

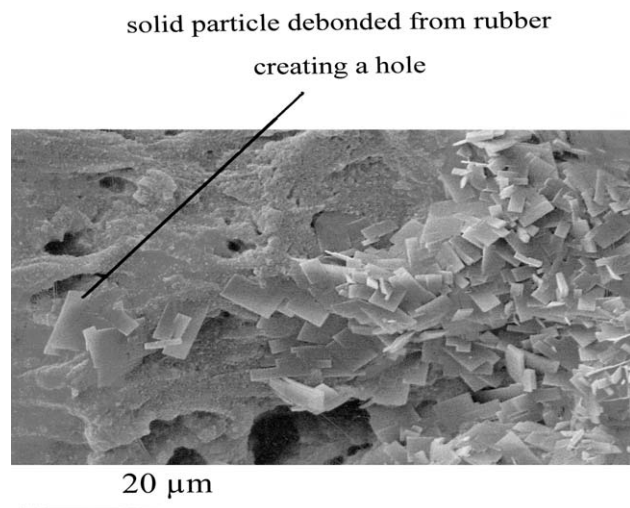
absence of blooming. The decrease in the fatigue life of compound 28 with time was due to the accumulative damage of the blooming.

After the fatigue tests were completed, the fracture surfaces were examined in the SEM. When the bloom was removed from the rubber surface by sellotape, large solid particles were seen in the rubber (Fig. 18). These particles were in the region of high solid concentration near the rubber surface (Fig. 9) and separated from the rubber when the test pieces were stressed and relaxed repeatedly in the fatigue tests. As a result, holes approximately 40  $\mu\text{m}$  in size were created (Figs. 19 and 20), which provided a rapid path for cracks to grow along (Fig. 21). Note also that, in the fatigue tests, cracks started frequently at the edges of the test piece where there was a high concentration of migrated



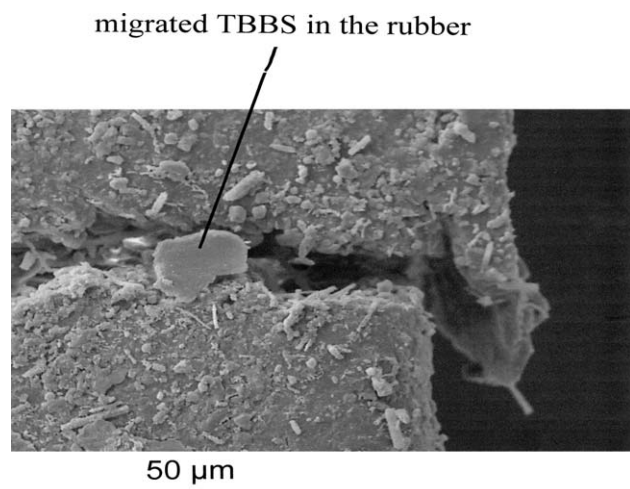
56  $\mu\text{m}$

**Figure 19** SEM photograph showing holes in the rubber after the fracture surface was recovered from the fatigue test. Data for compound 28 after 60 days in storage at ambient temperature.

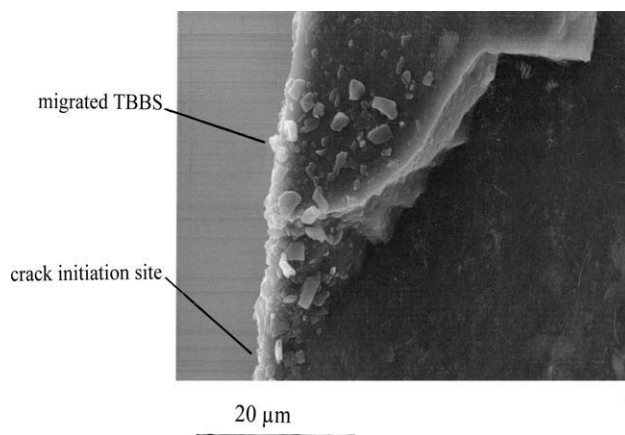


**Figure 20** SEM photograph showing solid particles on the fracture surface after fatigue test. Data for compound 28 after 60 days in storage at ambient temperature.

TBBS (Fig. 22), and propagated until failure occurred (Fig. 23). Therefore, it was concluded that the main reason for the inferior fatigue life of compound 28 was the presence of a thin layer of migrated TBBS beneath the rubber surface where cracks initiated during the fatigue tests. Interestingly, this migration did not damage the interior of the rubber [Fig. 9(b)]. In contrast, the fracture surfaces of compound 29 consisted of small-scale localized tearing, which characterized slow incremental crack growth in the rubber under repeated stressing, and there were no holes in the rubber (cf. Figs. 19 and 24). In the absence of TBBS migration, the cyclic fatigue life of the rubber vulcanizate was noticeably longer.



**Figure 21** SEM photograph showing a crack propagating around a migrated TBBS particle in a dumbbell test piece during cyclic fatigue test. Data for compound 28.

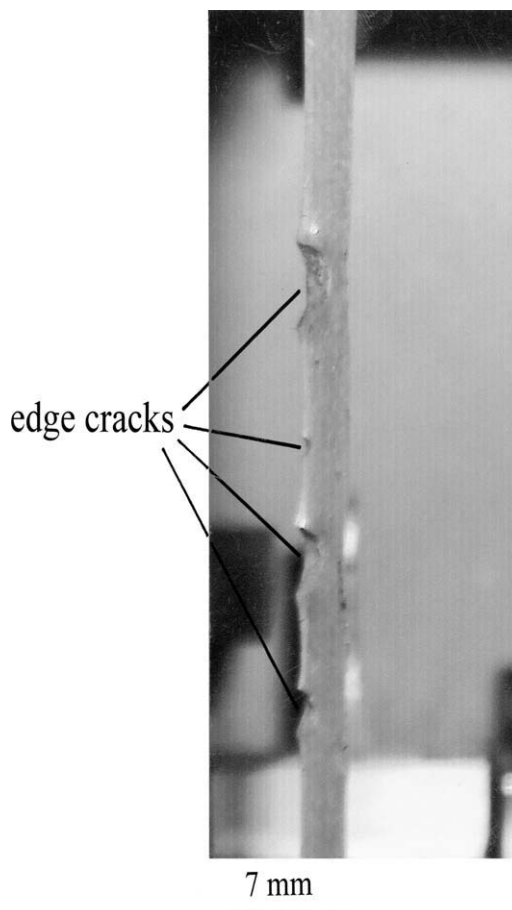


**Figure 22** SEM photograph showing a site of crack initiation in the high solid concentration region of a dumbbell test piece. Data for compound 28.

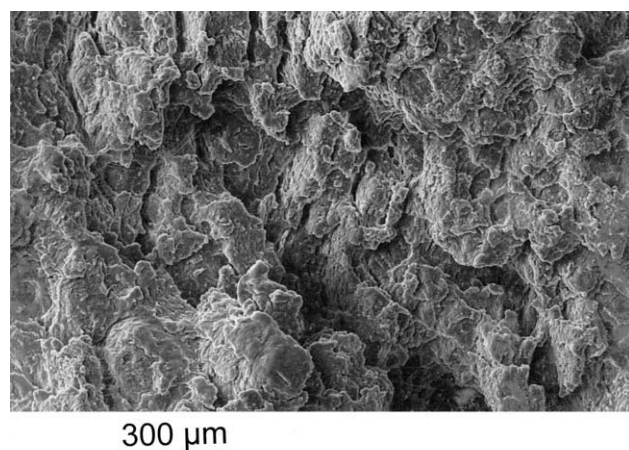
## CONCLUSIONS

From this study, it was concluded that

1. The blooming of TBBS accelerator had no adverse effect on the hardness, Young's modulus, tensile strength, elongation at break, and stored energy density at break of the rubber



**Figure 23** Edge crack on a dumbbell test piece during a fatigue test.



**Figure 24** SEM photograph showing a fracture surface after fatigue test. Data for compound 29.

vulcanizate. In fact, the hardness increased as a function of storage time because of the accumulation of migrated TBBS on the rubber surface. However, the blooming reduced the cyclic fatigue life of the rubber vulcanizate by more than 100%.

2. The migration of TBBS accelerator produced a thin layer approximately 15  $\mu\text{m}$  in size beneath the rubber surface. When the rubber was stressed and relaxed repeatedly in the fatigue test, cracks initiated in this layer and then propagated, causing the fatigue life of the vulcanizate to decrease. The bloom was eliminated by reducing the ratio of TBBS to ZnO from 6/0.3 to 3/2.5 in the formulation.

The authors thank the Loughborough Materials Characterization Centre for carrying out the scanning electron microscopy of the samples. They also thank Evonik Industries of Germany for supplying the silanized silica nanofiller. Figures 1–6, 8–12, and 14–24 were reprinted after permission from Smithers Rapra, UK.

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