

## Characterization of Solution Styrene Butadiene Rubber (SBR) Through the Evaluation of Static and Dynamic Mechanical Properties and Fatigue in Silica-Filled Compound†

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This study examined the effects of different types of styrene butadiene rubber (SBR) and blended compounds with various butadiene rubber (BR) ratios. Two areas were considered when selecting the SBRs: microstructure and functionalization. Six types of SBRs were chosen as model polymers and mixed with silica at various SBR/BR ratios. The microstructures, such as the styrene and vinyl contents of SBR, were found to affect the shift in  $\tan \delta$  with increasing butadiene rubber, which might be due to the degree of compatibility of the SBR with butadiene rubber. In addition, the functionalization of SBR led to a better dispersion of silica due to the Payne effect, resulting in a low  $\tan \delta$  at 70 °C. On the other hand, the functionalization of SBR also affected the fatigue properties of the compound. Therefore, these should be considered carefully in the design of low-hysteresis compounds with functionalized SBRs.

**Key Words:** Functionalized solution styrene butadiene rubber, Low hysteresis compound, Fatigue property.

### INTRODUCTION

In recent years, the improvements in the fuel efficiency of vehicles have become an important issue because of the depletion of fossil fuels and the environmental side effects of their continuous usage. From this point of view, the tyre industry has invested in the research and development of low-rolling-resistance tyres, leading to better vehicle mileage. Based on this social and industrial trend, silica has been applied a filler to tread compounds because of its low hysteresis loss, resulting in low rolling resistance<sup>1</sup>. On the other hand, silica is hydrophilic, whereas the raw polymer is hydrophobic. Therefore, enhancing the degree of silica dispersion in the polymer is a key issue in its application. The use of silica coupling agents, such as *bis*(triethoxysilylpropyl)tetrasulfane (TESPT), is a basic solution for maximizing the dispersion of silica and the mixing step is also a critical factor affecting the mechanical properties of silica compounds<sup>2,3</sup>. On the other hand, the microstructure of SBR can be adjusted to secure better affinity for silica. To this end, solution SBR (S-SBR) modified at the end or on the backbone of the polymer chain by functional groups was developed and commercialized.

Modified solution-SBR, however, may not be the same as conventional unmodified solution-SBR or emulsion SBR in terms of its rheology, mechanical properties, fatigue, etc.

Therefore, in this study, typical functionalized and non-functionalized SBR materials were evaluated and characterized for use in silica-filled compounds.

### EXPERIMENTAL

Several experiments were conducted with 18 types of rubber compounds filled with silica to compare the mechanical and fatigue properties with six types of SBRs. The following six types of SBRs were chosen as raw polymers: three types of functionalized solution SBRs, two types of unfunctionalized solution SBRs and one type of emulsion SBR. In addition, three SBR/BR ratios were evaluated: SBR:BR = 100:0, 85:15 and 70:30. Table-1 lists the basic properties of the polymers, including the microstructure, glass transition temperature of the raw polymer ( $T_g$ ) and viscosity. In the case of S-SBR1, S-SBR2 and E-SBR, 37.5 phr of oil was extended to the polymer, whereas FS-SBR1, FS-SBR2 and FS-SBR3 did not contain any oil. Therefore, free oil was added to several versions of the compound to ensure similar conditions in terms of the static physical properties.

Silica (Rhodia, Z115) and carbon black (ORION Engineered Carbons, HP130) were used as fillers and *bis*(triethoxysilylpropyl)tetrasulfide (TESPT), Evonik Industries AG, Si69) was applied to the mixed compound as a silica coupling agent. Several more chemicals were used for the

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TABLE-1  
MICROSTRUCTURE,  $T_g$  AND VISCOSITY OF THE POLYMERS

Item	Styrene (%)	Vinyl (%)	$T_g$ (°C)	Viscosity	Functionalization
S-SBR1 <sup>a</sup>	25.0	67	-29	62	X
S-SBR2 <sup>b</sup>	38.0	39	-29	80	X
E-SBR <sup>c</sup>	40.5	18	-36	54	X
FS-SBR1 <sup>d</sup>	25.0	55	-30	60	o
FS-SBR2 <sup>e</sup>	27.0	57	-28	65	o
FS-SBR3 <sup>f</sup>	21.0	63	-25	62	o

<sup>a-b</sup>Non-modified solution SBR; <sup>c</sup>Emulsion SBR; <sup>d-f</sup>End-modified functionalized solution SBR

TABLE-2  
FORMULATION WITH VARIOUS SBRs/BR RATIOS

Item	S-SBR1 SET			S-SBR2 SET			E-SBR SET		
S-SBR1 <sup>a</sup>	137.5	116.9	96.3						
S-SBR2 <sup>b</sup>				137.5	116.9	96.3			
E-SBR <sup>c</sup>							137.5	116.9	96.3
BR	0	15	30	0	15	30	0	15	30
Vivatech500	0	5.6	11.3	0	5.6	11.3	0	5.6	11.3
Item	FS-SBR1 SET			FS-SBR2 SET			FS-SBR3 SET		
FS-SBR1 <sup>d</sup>	100	85	70						
FS-SBR2 <sup>e</sup>				100	85	70			
FS-SBR3 <sup>f</sup>							100	85	70
BR	0	15	30	0	15	30	0	15	30
Vivatech500	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5

Z115 70 phr, HP130 5 phr, Si69 5.6 phr, ZnO 3 phr, Stearic acid 2 phr, Sulfur 1.5 phr, CBS 1.5 phr, DPG 1.0 phr.

<sup>a-c</sup>37.5 phr oil-extended solution or emulsion SBR; <sup>d-f</sup>Non-oil-extended functionalized solution SBR.

curing system. Table-2 lists the components of the rubber compounds.

**General procedure:** All ingredients were mixed using an internal mixer and the mixed sample was discharged at 145 °C. The master batch was then mixed with the curing chemicals and discharged at 105 °C. The mixed compounds were cured in a hot press for 0.5 h to produce the samples for the tensile tests, dynamic mechanical analysis and Payne effect tests. Samples were also cured for 40 min for the fatigue-test (DMFC: Demattia flex crack). The compatibility between the SBR and BR was examined by evaluating mixed rubber compound samples at various SBR/BR ratios.

**Detection method:** The uncured rubber samples were analyzed using a rheometer (MDR 2000, Alpha technology). A tensile testing system (Instron 3365, Instron) was used to measure the mechanical properties of the cured rubber compounds. Dynamic mechanical analysis test equipment (Eplexor, GABO) was used to measure the dynamic mechanical properties, as well as to provide the Payne effect results related to the silica dispersion<sup>4</sup>. A Demattia flex crack tester (FT-1501, Ueshima) was used to evaluate the fatigue properties. For this test, an initial 1 mm crack was made by punching the sample with a sharp pin and the test samples were then bent 10,000 times at 50 °C. After bending the samples, the crack growth length was measured.

## RESULTS AND DISCUSSION

**Cure rate:** Fig. 1 shows the cure rate of each sample. For all the samples, the cure rate ( $T_{40}$ ) decreased with increasing BR content. Therefore, the larger number of butadiene units in the mixed compound contributes to the reaction with accelerators, such as CBS (*n*-cyclohexyl benzothiazyl-2-sulfenamide) and DPG (diphenylguanidine). The slope of this graph

indicates the  $T_{40}$  sensitivity of each polymer as a function of the BR content. The slopes for FS-SBR1, FS-SBR2 and FS-SBR3 were the steepest followed by S-SBR1, S-SBR2 and emulsion SBR. These differences might be caused by the microstructures of the polymers. A high vinyl content in the polymers means it will react more easily with the accelerators, leading to a faster cure rate for S-SBR than for E-SBR with increasing BR content. Furthermore, the end-modified functional group can affect the cure sensitivity with increasing BR content, *i.e.* the functional groups of SBR can increase the cure rate in the presence of BR.

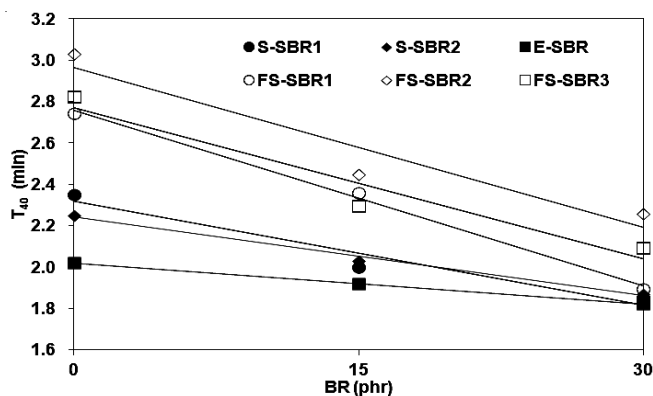


Fig. 1. Cure rate  $T_{40}$  determined by MDR (moving die rheometer) with various SBR/BR ratios (SBR:BR = 100:0, 85:15, 70:30)

**Modulus:** Fig. 2 shows the 300 % modulus of rubber compounds with various SBR/BR ratios. The data suggests that the 300 % modulus of each sample tends to a decrease with increasing BR content. This was attributed mainly to the addition of low-molecular-weight BR leading to a decrease in

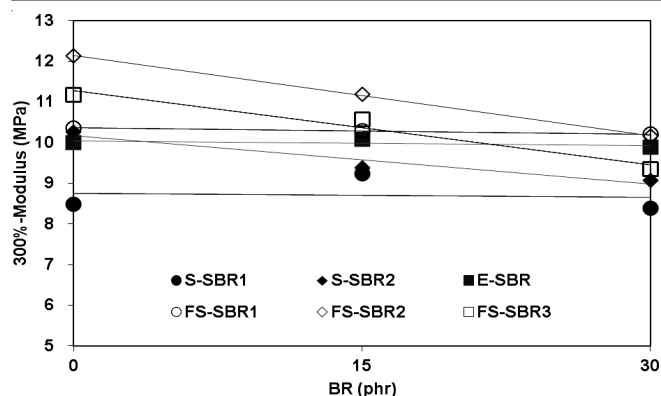


Fig. 2. 300 % modulus with various SBR/BR ratios (SBR:BR = 100:0, 85:15, 70:30)

the modulus of the compounds. The Gary Day states that the macro-structural differences between the polymers mean that the modulus values vary with strain. A high molecular weight induces high tensile strength and elongation<sup>5</sup>. On the other hand, in some SBRs, such as E-SBR, S-SBR1 and FS-SBR1, no significant change in the 300 % modulus was observed with increasing BR content. This might be because the high molecular weight of SBR overwhelms the BR content. Therefore, there is no significant change in the physical properties.

**$T_g$  (glass transition temperature) by DMA (dynamic mechanical analysis):** The  $T_g$  value of rubber is one of the key factors to consider when designing a compound.  $T_g$  is related to the brittle point of the compound at low temperatures and is dependent on the microstructure of the polymer<sup>6</sup>.

Fig. 3(a) shows the  $T_g$  values of the mixed rubber compounds with various types of SBRs. The  $T_g$  range of the SBR 100 phr compound was -6.5 to -13.2 °C. The  $T_g$  values of the compounds tend to decrease with increasing BR due to the low  $T_g$  of BR. On the other hand, the relationship between  $T_g$  and BR loading did not show the same trend for all polymer-based compounds. For example, referring to Fig. 3(b), the  $\Delta T_g$  to  $\Delta BR$  ratio was lower for E-SBR than for S-SBRs and FS-SBRs.  $\Delta T_g/\Delta BR$  was somewhat different based on the microstructure of the raw polymer. This means that  $\Delta T_g/\Delta BR$  of the high styrene polymer compound is lower than that of the high vinyl polymer compound. According to A. Yoshioka *et al.*<sup>7</sup> the  $T_g$  values of SBR/BR compounds depend on the compatibility of SBR and BR. This compatibility is related to the microstructure of the polymer, such as the presence of styrene, vinyl and *cis* and *trans* butadiene units. The high number of butadiene units in SBR means it can be mixed easily with BR, leading to high compatibility between SBR and BR. In contrast, there was no large difference in  $\Delta T_g/\Delta BR$  when comparing S-SBRs with FS-SBRs. This means that functionalization of the polymer is not related to the  $T_g$  shift with increasing BR.

**tan  $\delta$ :** In the tyre industry, tan  $\delta$  at 0 and 70 °C are used to predict the index of wet traction and the rolling resistance of a tyre, respectively. The basic theory behind these parameters is related to the hysteresis of the compound by continuous deformation of the sample. During the rolling of tyres, the frequency of the material is *ca.*  $10^1$ - $10^2$  Hz, whereas the temperature of the tread compound is *ca.* 60-70 °C. Therefore,

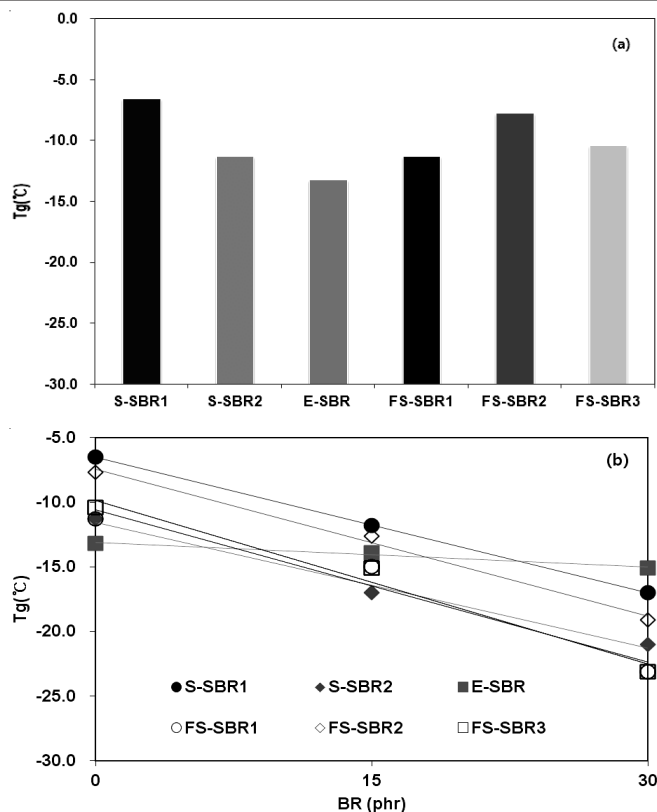


Fig. 3. (a) Glass transition temperatures with various types of SBRs (S-SBR1, S-SBR2, E-SBR, FS-SBR1, FS-SBR2, FS-SBR3, 100 phr compound); (b) Glass transition temperatures with various SBR/BR ratios (SBR:BR = 100:0, 85:15, 70:30)

the rolling resistance of the tyre can be predicted by measuring the ratio of the storage and loss moduli. On the other hand, during the braking of tyres, the frequency of the material is increased by *ca.*  $10^5$  Hz at 40 °C<sup>8</sup>. According to the Williams-Landel-Ferry (WLF) equation, this frequency can be replaced by the temperature condition. Therefore, the traction can be predicted by measuring the frequency under low-temperature conditions<sup>9,10</sup>.

Fig. 4 shows tan  $\delta$  at 0 °C with increasing BR ratio in the SBR/BR compounds. The tan  $\delta$  at 0 °C decreased with increasing BR content. On the other hand, depending on the polymer type, the ratio of  $\Delta \tan \delta$  at 0 °C to  $\Delta BR$ , which is described by the slope shown in Fig. 4, was different. The slopes of the polymer compounds with high styrene contents, including S-SBR2 and E-SBR, were relatively low compared to those of compounds with high vinyl contents (S-SBR1, FS-SBR1 and FS-SBR2). This suggests that the functionalization of S-SBR does not play a significant role in shifting tan  $\delta$  at 0 °C with increasing BR content. The compatibility of SBR and BR affects tan  $\delta$  at 0 °C and  $T_g$ , because tan  $\delta$  at 0 °C is affected significantly by  $T_g$ , as shown in Fig. 4(b).

Fig. 5 presents the rolling resistance prediction parameter, tan  $\delta$  at 70 °C. The tan  $\delta$  values at 70 °C of the FS-SBRs are lower than those of the S-SBRs and E-SBR. Functionalization of the polymer can help increase the interaction between the polymer and silica filler, resulting in better silica dispersion<sup>11</sup>. From this point of view, functionalization of the polymer has a beneficial effect on the filler dispersion, which leads to a lower tan  $\delta$  at 70 °C. On the other hand, there was no significant

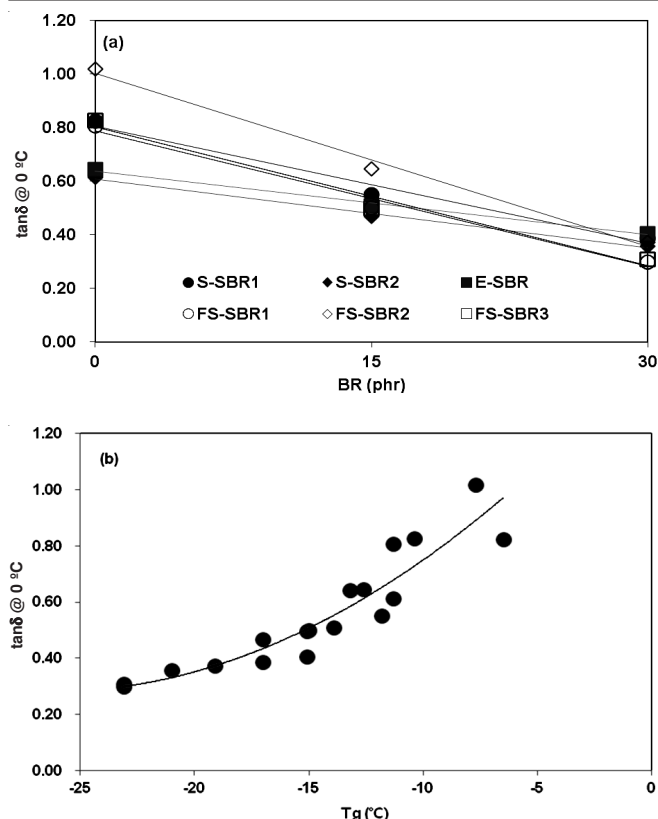


Fig. 4. (a)  $\tan \delta$  at 0 °C (prediction index for wet traction) with various SBR/BR ratios (SBR:BR = 100:0, 85:15, 70:30); (b) Relationship between  $\tan \delta$  at 0 °C and  $T_g$  (glass transition temperature)

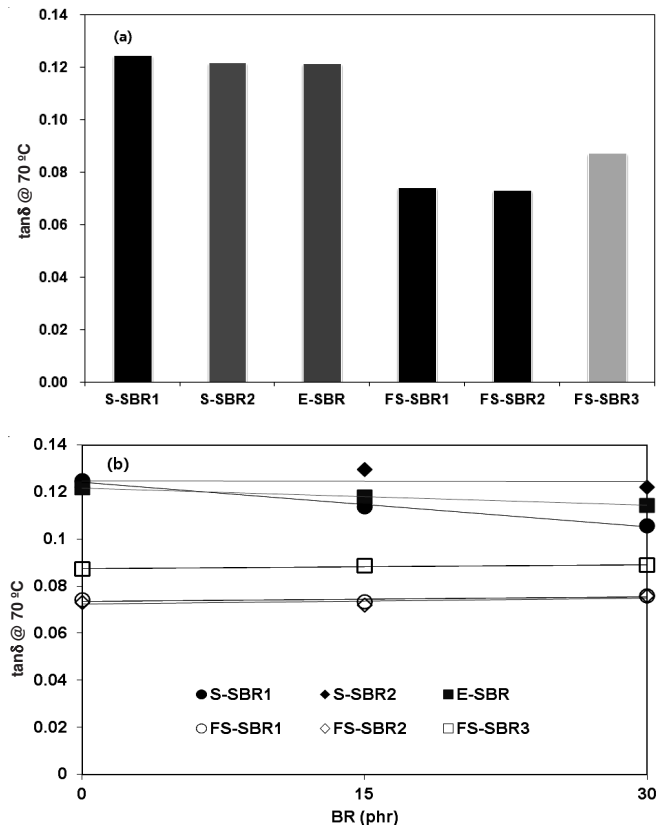


Fig. 5. (a)  $\tan \delta$  at 70 °C with various types of SBRs (S-SBR1, S-SBR2, E-SBR, FS-SBR1, FS-SBR2, FS-SBR3, 100 phr compound); (b)  $\tan \delta$  at 70 °C with various SBR/BR ratios (SBR:BR = 100:0, 85:15, 70:30)

change in  $\tan \delta$  at 70 °C with increasing BR content in the SBR/BR compound. Only two types of polymer, S-SBR1 and E-SBR, showed a slight change in  $\tan \delta$  at 70 °C with increasing BR content. This shows that an increase in BR content mainly affects the  $T_g$  and  $\tan \delta$  values at 0 °C. In contrast, the  $\tan \delta$  at 70 °C is not determined by the SBR/BR ratio, but by the SBR type.

**Dynamic mechanical analysis (DMA) and Payne effect:**

Fig. 6 shows the dynamic mechanical analysis curves for the different SBR types. Generally, functionalized S-SBRs showed high  $\tan \delta$  peaks, whereas the others showed relatively lower ones. This means that the functionalization of the polymer improved its reactivity with silica, leading to better dispersion.

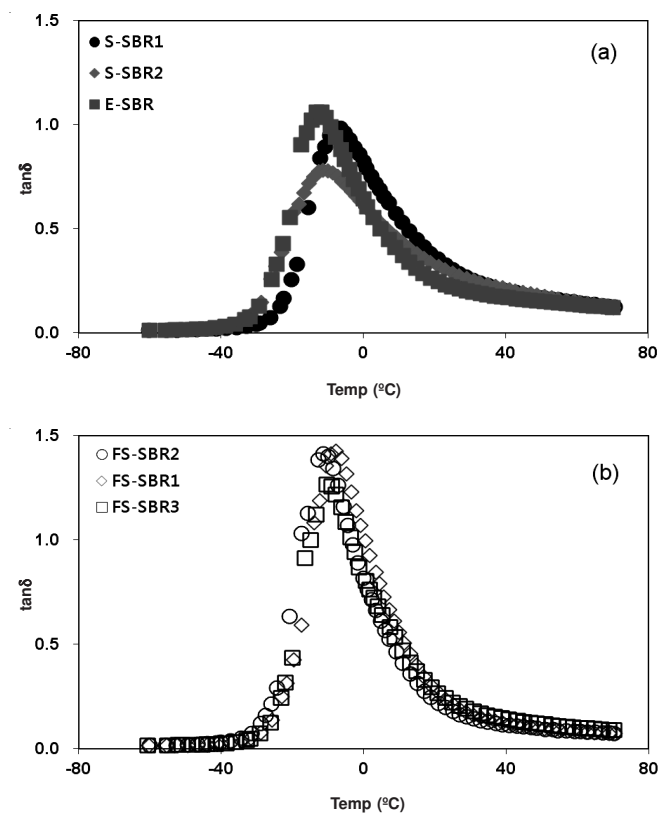


Fig. 6. (a) Dynamic mechanical analyses with non-functionalized SBRs (S-SBR1, S-SBR2, E-SBR, 100 phr compound); (b) Dynamic mechanical analysis with functionalized SBRs (FS-SBR1, FS-SBR2, FS-SBR3, 100 phr compound)

To determine the degree of silica dispersion, the Payne effect (also known as the Fletcher-Gent effect) was examined for different SBR types. Payne<sup>4</sup> suggested that the change in modulus with increasing strain of the sample was related to the filler dispersion. Reuvekamp *et al.*<sup>3,12</sup> explained the silica dispersion by measuring the modulus of the compound in the region of very low strain. In this low-strain area, the interaction between the filler particles was stronger than that between polymer and filler, whereas the opposite was true in the high-strain area. Therefore, with this mechanism, the filler dispersion can be predicted by measuring the dynamic modulus of the low-strain area, as shown in Figs. 7(a) and 7(b). Fig. 7 shows the Payne effect of the silica-filled compound for different SBR types. As predicted by  $\tan \delta$  at 70 °C, functionalized SBRs, such as FS-SBR1, FS-SBR2 and FS-SBR3,



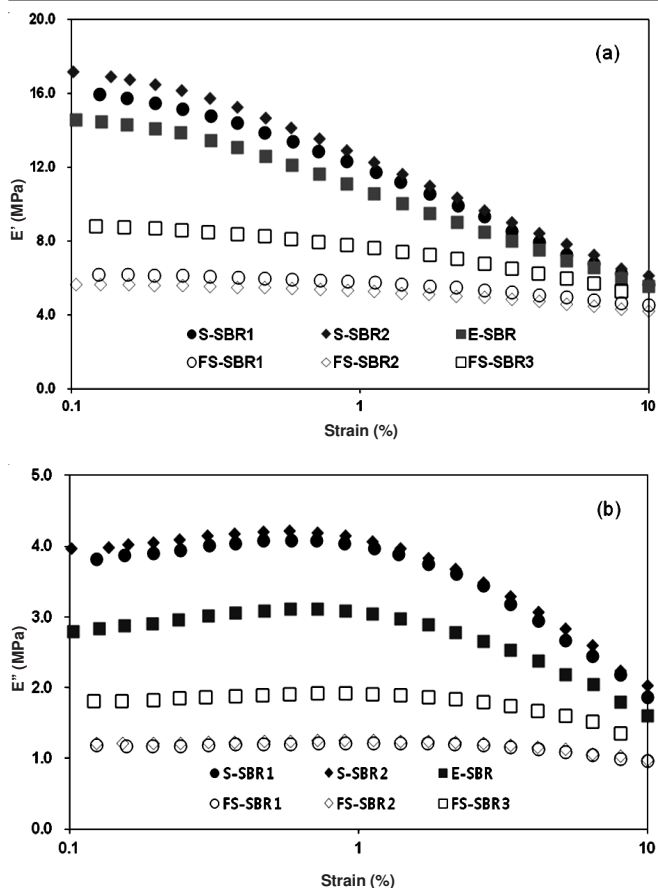


Fig. 7. (a) Storage modulus ( $E'$ ) with various strain ratios in the SBR 100 phr compound; (b) Loss modulus ( $E''$ ) with various strain ratios in the SBR 100 phr compound

showed lower moduli in the low-strain area. This means that the functionalization of SBR is beneficial for filler dispersion. Moreover, there were no significant differences in  $\tan \delta$  between S-SBRs and E-SBR. Therefore, the high vinyl content of S-SBR is not the key factor in the improvements in filler dispersion.

**Fatigue:** Fatigue is one of the basic properties to be considered in the design of compounds and is relevant to the cut-and-chip phenomenon of tyres under field conditions<sup>13</sup>. For example, a tyre tread with low fatigue properties can be cut and chipped easily under severe road conditions. High 'tensile strength  $\times$  elongation' compounds have better cut/chip performance<sup>13</sup>. Fig. 8 shows the cut growth length determined by a DMFC (Demattia Flex Crack) test in compliance with the 'tensile strength  $\times$  elongation'. In this figure, a shallow slope of the graph means that the compound has high fatigue resistance, whereas a steep slope means it is easily cut and chipped through deformation. The tests showed that the cut growth lengths of FS-SBRs were relatively high compared to those of non-functionalized SBRs, such as S-SBR1, S-SBR2 and E-SBR, as shown in Fig. 8(a). According to the slopes of the graphs, FS-SBR1 and FS-SBR2 are also the weakest compounds in terms of the cut growth length with various physical properties. Therefore, when designing the tread compound for tyres by applying each polymer, the tensile strength and elongation are carefully targeted considering the cut growth length.

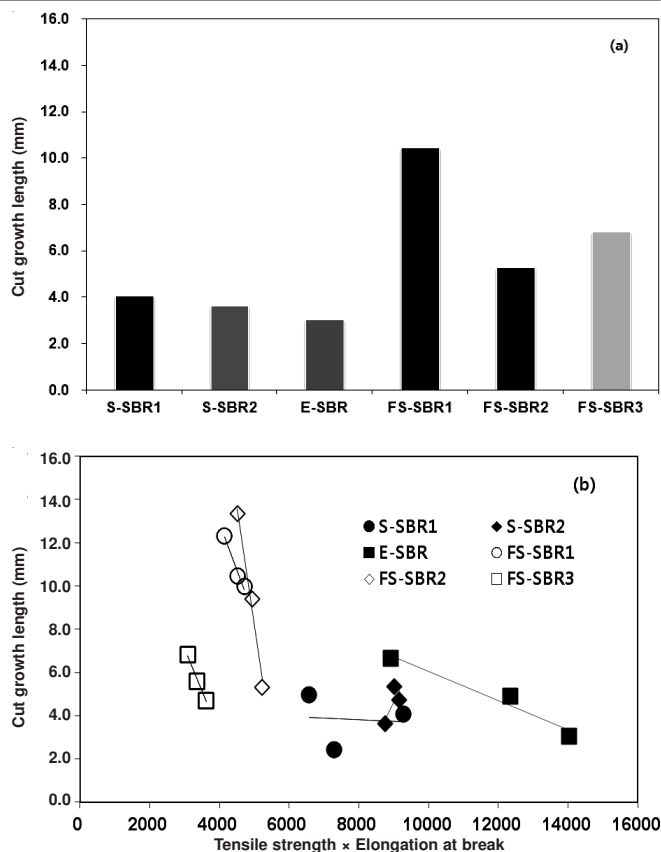


Fig. 8. (a) Cut growth length determined using a DMFC (Demattia flex crack) tester with various types of SBRs; (b) Cut growth length determined using a DMFC (Demattia flex crack) tester with various SBR/BR ratios (SBR:BR = 100:0, 85:15, 70:30)

## Conclusion

Several tests were conducted to determine the effect of the SBR type (including microstructure) and its functionalization on the properties of the compound. From the test results, the following conclusions can be made:

(1) The cure rate ( $T_{40}$ ) determined by the MDR test decreased with increasing BR content. Among the six types of polymer, the cure rate sensitivity was greater in the FS-SBRs than in the S-SBRs and E-SBR with increasing BR content.

(2) The 300 % modulus tends to decrease with increasing BR content in some polymer types, such as FS-SBR2 and FS-SBR3.

(3) The viscoelastic properties, such as the change in  $T_g$  and  $\tan \delta$  at 0 °C with the BR content, which indicates that the compatibility between the SBRs and BR is a critical factor in determining the viscoelastic properties. This is related to the microstructures of the polymers and has little to do with their functionalization. On the other hand, the FS-SBRs show a low  $\tan \delta$  at 70 °C and a high  $\tan \delta$  peak. This might be related to the degree of silica dispersion.

(4) According to the results of the Payne effect tests, the FS-SBRs show better silica dispersion than the S-SBRs and E-SBR. The functionalization of SBR is believed to assist in the dispersion of silica through its interaction with the end chain of the polymer.

(5) Among the six types of polymers, FS-SBR1 and FS-SBR2 showed high cut growth lengths, which is in agreement

with their physical properties (tensile strength  $\times$  elongation). Therefore, when designing special compounds with low hysteresis, the fatigue properties must be considered carefully and the tensile strength and elongation must be maintained to support fatigue.

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