Influence of Extender Oil on Properties of Solution Styrene-Butadiene Rubber Composites

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Abstract: Crosslink density of a rubber vulcanizate determines the chemical and physical properties, while bound rubber is an important factor to estimate reinforcement of a filled rubber compound. Extender oil is added to a raw rubber with very high molecular weight for improving processability of a rubber composite. Influence of extender oil on crosslink density, bound rubber formation, and physical properties of solution styrene-butadiene rubber (SSBR) composites with differing microstructures was investigated. Crosslink densities of non-oil-extended SSBR (NO-SSBR) vulcanizates were higher than those of oil-extended SSBR (OE-SSBR) ones. Bound rubber contents of NO-SSBR compounds were also greater than those of OE-SSBR ones. The experimental results could be explained by interfering of extender oil. The OE-SSBR vulcanizates had low modulus but long elongation at break, whereas the NO-SSBR ones had high modulus but short elongation at break. It was found that the crosslink densities affected the physical properties more than the bound rubber contents. The moduli increased with increase in the crosslink density irrespective of extender oil, while the elongation at break decreased. Each variation of the tensile strengths of NO-SSBR and OE-SSBR vulcanizates with the crosslink density showed a decreasing trend. Tear strength of the OE-SSBR vulcanizate increased with increase in the crosslink density, whereas variation of the tear strength of NO-SSBR vulcanizate with the crosslink density showed a weak decreasing trend.

Keywords: solution SBR, extender oil, crosslink density, bound rubber, physical property

Introduction

Characteristics of styrene-butadiene rubber (SBR) is determined by ratios of three components of styrene, 1,2-unit, and 1,4-unit. Solution SBR (SSBR) has higher 1,2-unit content than emulsion SBR (ESBR) and it also has various microstructures. Carbon black and silica are the most popular reinforcing fillers in rubber compounds.[1-9] One of common usages of SBR is manufacturing of tire tread and SSBR is usually used for silica-filled rubber compounds.[10-13] Silica has a number of silanol groups, which results in poor silica dispersion in a rubber compound.[14-16] Silane coupling agent is used for silica dispersion.[17,18] It is known that SSBR is good for silica dispersion and can improve both wet grip and rolling resistance.[19-22]

Crosslink density of a rubber vulcanizate determines the physical properties.[23-27] By increasing crosslink density, modulus, hardness, resilience, and abrasion resistance increase, whereas elongation at break, heat buildup, and stress relax-ation decrease. Bound rubber is an important factor to estimate rubber reinforcement. Mechanism and factors affecting the formation of bound rubber have been studied.[28-32] The filler-polymer interactions such as physical adsorption, chemisorption, and mechanical interaction lead to bound rubber formation. Polarity, microstructure, and molecular weight of polymer influence the level of bound rubber content. Models for bound rubber have been suggested and developed by several research groups.[33-41] Filler particles in a filled rubber compound are covered by an inner shell of tightly bound rubber and the outer region of loosely bound rubber. The complex filler-rubber units are connected by rubber filaments. In our previous work,[42] it was suggested that bound rubber was composed of core shell, primary layer, and secondary layer.

In a rubber industry manufacturing synthetic rubbers, oil is added to a raw rubber with very high molecular weight for improving processability of filled rubber compounds, which is called 'oil-extended rubber' and the oil is called 'extender oil'. Extender oil by swelling the polymer and by providing lubrication between rubber molecules softens the stiff rubber chains. Processing oils including extender oil assist in mixing

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operation, reduces compounding time, improve processability, and modify physical properties of the finished product.[43-46]

In the present work, silica/carbon black-filled SSBR compounds and vulcanizates with and without extender oil were prepared using commercial oil-extended SSBRs (OE-SSBRs) and non-oil-extended SSBRs (NO-SSBRs) with different microstructures (1,2-unit, 1,4-unit, and styrene contents). Bound rubber contents of total, core shell, primary layer, and secondary layer of the SSBR compounds were measured and crosslink densities of the SSBR vulcanizates were also measured. Influence of the extender oil on the bound rubber contents and crosslink density was investigated. Influence of the microstructures of SSBR on the bound rubber contents and crosslink density was also examined. Basic physical properties such as modulus, elongation at break, tensile strength, and tear strength of the SSBR vulcanizates were measured and influence of the bound rubber contents and crosslink density on the basic physical properties was investigated.

Experimental

Six oil-extended SSBRs (OE-SSBR1 – OE-SSBR6, M_w > 800,000) with different microstructures and five non-oil-extended SSBRs (NO-SSBR1 – NO-SSBR5, M_w < 700,000) with different microstructures were used. Oil contents of OE-SSBRs are described in Table 1. Microstructures (1,2-unit, 1,4-unit, and styrene contents) of SSBRs were analyzed by H-NMR according to ISO 21561:2005 (Styrene-butadiene rubber (SBR) - Determination of the microstructure of solution-polymerized SBR) and the results are summarized in Table 1. The SSBR compounds were composed of SSBR, silica, carbon black, silane coupling agent, antidegradants, pro-

Table 1. Microstructures of SSBRs Used in This Study

S-SBR	Extended oil content (phr)	Microstructure (mol%)		
		1,2-Unit	1,4-Unit	Styrene
OE-SSBR1	37.5	28.5	47.5	24.0
OE-SSBR2	37.5	30.4	45.9	23.7
OE-SSBR3	50.0	34.5	39.8	25.8
OE-SSBR4	37.5	36.5	43.7	19.9
OE-SSBR5	37.5	52.9	32.5	14.6
OE-SSBR6	37.5	54.3	30.9	14.8
NO-SSBR1	0	47.3	36.5	16.1
NO-SSBR2	0	48.3	40.5	11.2
NO-SSBR3	0	50.4	33.7	15.8
NO-SSBR4	0	54.0	33.9	12.1
NO-SSBR5	0	54.4	33.2	12.4

cessing oil, cure activators, and curatives. The SSBR compounds had the same formulation except for the SSBR type. Mixing for the master batch (MB) was performed using a Kneader type mixer and the final mixing (FM) was performed using a two roll mill. The SSBR vulcanizates were prepared by curing the compounds in a compression mold at 170ºC for 30 min.

Crosslink densities of the SSBR valcanizates were measured by a swelling method.[47-49] Organic additives in the samples were removed by extracting with THF and n-hexane for 3 and 2 days, respectively, and they were dried for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were then soaked in toluene for 2 days and the weights of the swollen samples were measured. The crosslink densities (X_c) were calculated using Flory–Rehner equation[50] (1)

$$X_c = -[\ln(1 - v_2) + v_2 + \chi v_2^2]/[V_1(v_2^{1/3} - v_2/2)] \quad (1)$$

where v_2 is the volume fraction of the crosslinked polymer, c is the interaction parameter between the polymer and solvent, V_1 is the molar volume of the swelling solvent. The v_2 is obtained by equation (2)

$$v_2 = (m_2/\rho_2)/[(m_2/\rho_2) + (m_1/\rho_1)] \quad (2)$$

where m_1 and m_2 are the solvent and specimen weights at equilibrium swelling, respectively, and ρ_1 and ρ_2 are the densities of swelling solvent and unswollen vulcanizate, respectively. Densities of toluene (ρ_1) and SBR (ρ_2) are 0.865 and 0.953 g/cm³, respectively. The V_1 is 106.3 cm³/mol. The interaction parameters of SBRs are dependent on their microstructures and it is not available to obtain the interaction parameters of various SBRs used in this study from literatures except for SBR with the styrene content of 23.5 wt%.[51,52] The χ value of 0.446 was employed.

Total bound rubber contents of the SSBR compounds were determined by extracting unbound materials such as ingredients and free rubbers (unbound rubbers) with toluene at room temperature for 6 days and with n-hexane at room temperature for 1 day. Then, they were dried at room temperature for 2 days. The weights of the samples before and after the extraction were measured and the bound rubber content (R_b) was calculated by the equation (3)

$$R_b(\%) = 100 \times \{W_{fg} - W_t[m_f/(m_f + m_r)]\}$$
$$/\{W_t[m_r/(m_f + m_r)]\} \quad (3)$$

where W_{fg} is the weight of filler and gel, W_t is the weight

of the sample, m_f is the fraction of the filler in the compound, and m_r is the fraction of the rubber in the compound.[53-55]

Primary layer bound rubber contents of the SSBR compounds were determined by extracting unbound materials and loosely bound rubber at 90°C and by following sonication. The samples were soaked in toluene for 6 days at 90°C in a convention oven. Then, the sonication treatment was carried out by sonicating a swollen rubber compound in toluene for 3 h at 45°C. And the samples were immersed in *n*-hexane at room temperature for 1 day and were dried for 2 days at room temperature. Weights of the dried samples were measured. The primary layer bound rubber contents were also calculated by the equation (3). Difference between the total and primary layer bound rubber contents is the secondary bound rubber content.

Core shell bound rubber contents of the SSBR compounds were measured by successive four procedures of the extraction at room temperature, ammonia bubbling, extraction at high temperature, and sonication for removing unbound materials and rubber chains except for rubber chains which are strongly connected and chemically bound to filler particles. Procedure to measure the core shell bound rubber content was as follows. (1) After soaking the samples in toluene at room temperature for 3 days, ammonia treatment was carried out by bubbling with ammonia gas in toluene for 1 day at room temperature. The ammonia treatment was described in detail in the previous work.[42] (2) The samples were soaked in new toluene for 2 days at room temperature. (3) The swollen samples in toluene were thermally treated at 120°C for 3 h in a heating block and sonication treatment was carried out for 3 h at 45°C. (4) The samples were immersed in *n*-hexane at room temperature for 1 day and were dried for 2 days at room temperature. Weights of the dried samples were measured. The core shell bound rubber contents were also calculated by the equation (3). When part of the sample was washed away during the experiment, the bound rubber contents were measured using thermogravimetric analyzer (TGA) to reduce the experimental errors.

Basic physical properties such as modulus, elongation at break, tensile strength, and tear strength of the SSBR vulcanizates were measured using a universal testing machine (UTM).

Results and Discussion

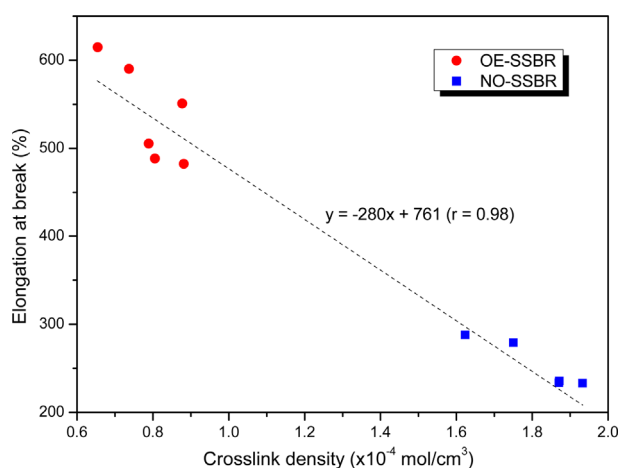Crosslink densities of the NO-SSBR vulcanizates are sig-

Table 2. Crosslink Densities of the SSBR Vulcanizates (×10^{-4} mol/cm^3)

Vulcanizate	Crosslink density
OE-SSBR1	0.806
OE-SSBR2	0.737
OE-SSBR3	0.655
OE-SSBR4	0.878
OE-SSBR5	0.881
OE-SSBR6	0.789
NO-SSBR1	1.750
NO-SSBR2	1.623
NO-SSBR3	1.933
NO-SSBR4	1.870
NO-SSBR5	1.871

nificantly greater than those of the OE-SSBR ones, irrespective of the microstructures (Table 2). Especially, crosslink density of the OE-SSBR3 vulcanizate with the most extender oil content is the lowest. This indicates that extender oil interferes in crosslinking reactions between rubber chains. There is no specific trend in relationship between the crosslink density and microstructure. Variations of the basic physical properties such as moduli, elongation at break, tensile strength, and tear strength were plotted as a function of the crosslink density (Figures 1, 2, 3, and 4, respectively). In general, moduli of rubber vulcanizates are proportional to the crosslink densities when the same formulation except the crosslink density is applied. Moduli of the NO-SSBR vulcanizates are greater than those of the OE-SSBR ones due to higher crosslink densities. Variations of the 100 and 300% moduli show
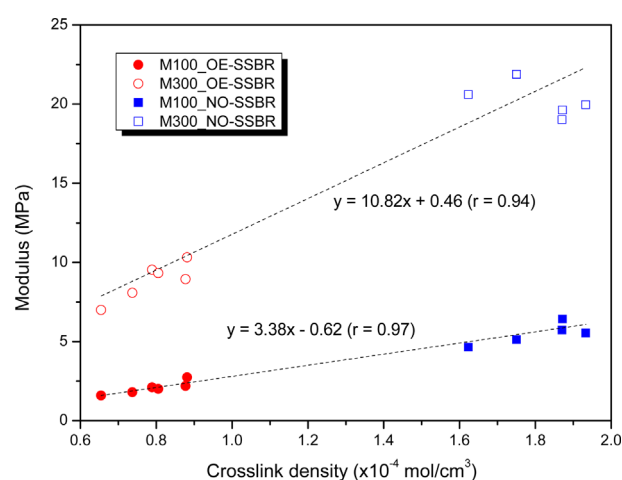
Figure 1. Variations of moduli of the SSBR vulcanizates with the crosslink density. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively. Solid and open symbols indicate 100 and 300% moduli, respectively.
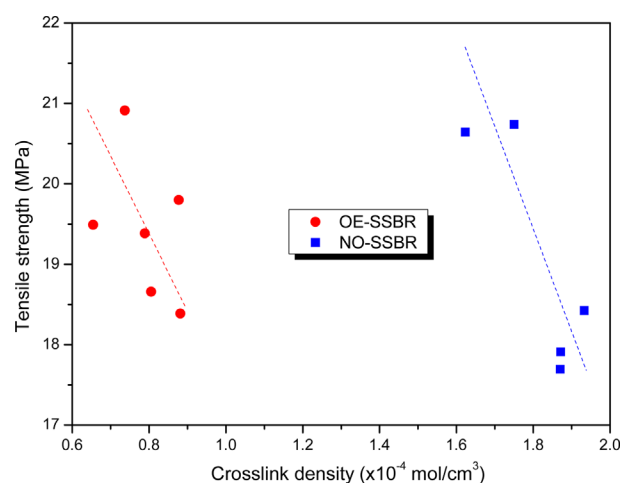
Figure 2. Variation of elongation at break of the SSBR vulcanizates with the crosslink density. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively.

Figure 3. Variation of tensile strength of the SSBR vulcanizates with the crosslink density. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively.

Figure 4. Variation of tear strength of the SSBR vulcanizates with the crosslink density. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively.

good increasing trends as shown in Figure 1. This means that crosslink densities of SSBR vulcanizates determine moduli irrespective of extender oil and microstructure.
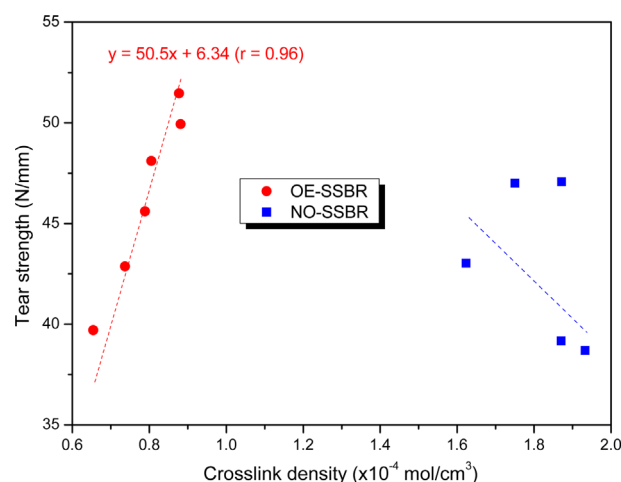
Elongation at break of a rubber vulcanizate is a physical property inversely proportional to crosslink density. Elongations at break of the NO-SSBR vulcanizates are lower than those of the OE-SSBR ones due to higher crosslink densities. Variation of the elongation at break shows a good decreasing trend as shown in Figure 2. This means that crosslink density of an SSBR vulcanizate determines elongation at break irrespective of extender oil and microstructure.

In general, tensile and tear strengths of a rubber vulcanizate increase and then decrease as the crosslink density increases. However, each variation of tensile strengths of the NO-SSBR and OE-SSBR vulcanizates shows a weakly decreasing trend with increase in the crosslink density although range of crosslink density variation is not wide and the maximum crosslink density is not enough high as shown in Figure 3. Varying region of tensile strength (17~21 MPa) is not also wide. The weak trends can be explained by reverse relation between modulus and elongation at break. The OE-SSBR vulcanizates have low modulus but long elongation at break, whereas the NO-SSBR ones have high modulus but short elongation at break. The weakly decreasing trends mean that the tensile strength variations are more affected by elongation at break rather than modulus.

Variations of tear strengths of the NO-SSBR and OE-SSBR vulcanizates with the crosslink density show reverse trends each other as shown in Figure 4. Tear strength of the

OE-SSBR vulcanizate linearly increases with the crosslink density, whereas the tear strength variation of NO-SSBR vulcanizates shows a decreasing trend. The good linear correlation between tear strength and crosslink density of the OE-SSBR vulcanizates seems like to follow the modulus variation. This may be due to high molecular weight of OE-SSBRs or slipping effect by extender oil.
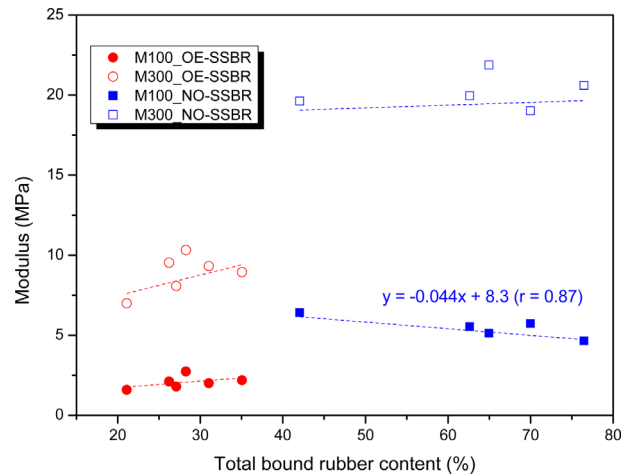
Various types of bound rubber contents (total, core shell, primary layer, and secondary layer) of the SSBR compounds were measured and the results were summarized in Table 3. Total, core shell, primary layer bound rubber contents of the NO-SSBR compounds are much greater than those of the OE-SSBR compounds. This indicates that extender oil pre-

Table 3. Bound Rubber Contents of the SSBR Compounds (%)

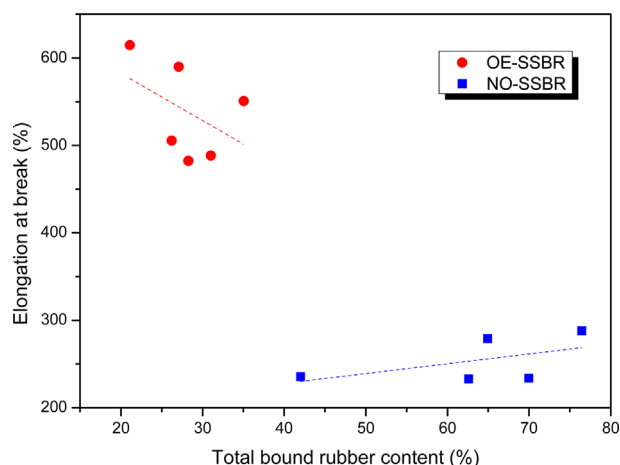| Compound	Bound rubber content			
	Total	Core shell	Primary layer	Secondary layer
OE-SSBR1	31.0	17.3	21.8	9.2
OE-SSBR2	27.1	11.9	14.6	12.4
OE-SSBR3	21.1	14.9	17.2	3.9
OE-SSBR4	35.0	19.0	28.4	6.6
OE-SSBR5	28.3	14.3	21.6	6.7
OE-SSBR6	26.2	17.0	20.2	6.0
NO-SSBR1	64.9	44.1	48.3	16.6
NO-SSBR2	76.5	45.8	57.4	19.1
NO-SSBR3	62.6	33.7	43.9	18.7
NO-SSBR4	70.0	48.8	58.4	11.6
NO-SSBR5	42.0	26.3	34.7	7.4

Figure 5. Variations of moduli of the SSBR vulcanizates with the total bound rubber content. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively. Solid and open symbols indicate 100 and 300% moduli, respectively.

vent formation of bound rubber by intercalating between rubber chain and filler particle. However, the secondary layer bound rubber contents show different trends from the other bound rubber types. Secondary layer bound rubber content of the OE-SSBR2 compound (12.4%) is larger than those of the NO-SSBR4 and NO-SSBR5 compounds (11.6 and 7.4%, respectively) although total bound rubber content of the former is much lower than those of the latters. And secondary layer bound rubber content of the OE-SSBR1 compound (9.1%) is larger than that of the NO-SSBR5 compound. Total bound rubber is composed of core shell, primary layer, and secondary layer. Significant formation of the secondary layer of the OE-SSBR2 compound is appeared more clearly by using fraction of the bound rubber type of total bound rubber. Fractions of secondary layer of total bound rubber of the OE-SSBR1, OE-SSBR2, NO-SSBR4 and NO-SSBR5 compounds are 0.30, 0.46, 0.17, and 0.18, respectively. The NO-SSBR3 compound has the most secondary layer fraction of the five NO-SSBR compounds, and its value is 0.30. Common microstructural characteristics of OE-SSBR1 and OE-SSBR2 is low 1,2-unit content, high 1,4-unit content, and relatively high styrene content. Hence, it seem like that 1,4-unit and styrene unit are favorable for formation of secondary layer bound rubber. For the NO-SSBR compounds, secondary layer bound rubber contents of NO-SSBR1, NO-SSBR2, and NO-SSBR3 compounds are greater than those of the NO-SSBR4 and NO-SSBR5 ones. 1,2-Unit contents of NO-SSBR1, NO-SSBR2, and NO-SSBR3 are lower than the NO-SSBR4 and NO-SSBR5.

Bound rubber contents of a filled rubber compound are used as a factor of reinforcement. Variations of the basic

physical properties were plotted as a function of the bound rubber content (Figures 5~10). It can be expected that modulus of a filled rubber vulcanizate will be increased by increasing the total bound rubber content since reinforcement of a rubber compound generally increases as the total bound rubber content increases. However, the moduli variations with the total bound rubber content do not show clear trends (Figure 5). The 300% modulus variation on the whole shows a weakly increasing trend with the total bound rubber content. For 100% modulus variations, 100% modulus of the OE-SSBR vulcanizate on the whole increases with increases in the total bound rubber content whereas that of the NO-SSBR vulcanizate on the whole decreases. Decreasing trend of 100% modulus of the NO-SSBR vulcanizate might be due to the crosslink density. The NO-SSBR sample with high total bound rubber content has low crosslink density. Order of total bound rubber contents of the NO-SSBR compounds is NO-SSBR2 > NO-SSBR4 > NO-SSBR1 > NO-SSBR3 > NO-SSBR5, while that of crosslink densities of the NO-SSBR vulcanizates is NO-SSBR3 > NO-SSBR5 > NO-SSBR4 > NO-SSBR1 > NO-SSBR2. Hence, 100% moduli of the NO-SSBR vulcanizates can be significantly affected by the crosslink density. Due to higher crosslink densities of the NO-SSBR vulcanizates, moduli of the NO-SSBR vulcanizates are greater than those of the OE-SSBR vulcanizates.

It can be expected that elongation at break of a filled rubber vulcanizate will be decreased by increasing the reinforcement level related to total bound rubber content. Varia-
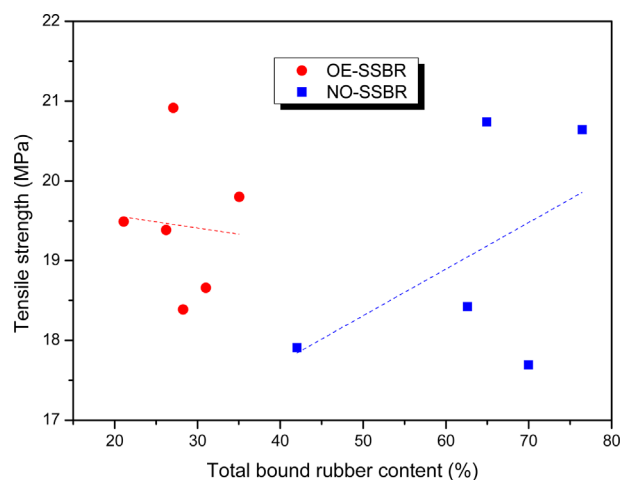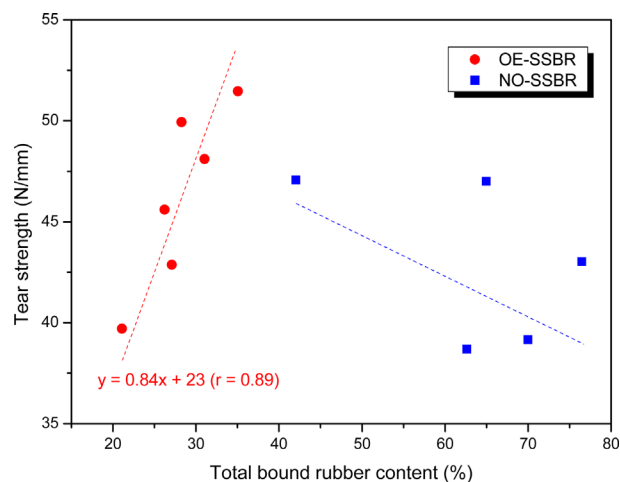
Figure 6. Variation of elongation at break of the SSBR vulcanizates with the total bound rubber content. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively.

Figure 8. Variation of tear strength of the SSBR vulcanizates with the total bound rubber content. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively.

tion of elongation at break of the OE-SSBR vulcanizates does not show a specific trend, whereas elongation at break of the NO-SSBR vulcanizates slightly increases with increase in the total bound rubber content as shown in Figure 6. The increasing trend of NO-SSBR vulcanizates can be also due to the crosslink density. The NO-SSBR sample with high total bound rubber content has low crosslink density as discussed above. Hence, elongations at break of the NO-SSBR vulcanizates are more influenced by the crosslink density not the bound rubber content.

Figure 7 shows variation of the tensile strength with the total bound rubber content but it does not show any specific

Figure 7. Variation of tensile strength of the S-SBR vulcanizates with the total bound rubber content. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively.

trend. This means that the total bound rubber content does not significantly affect tensile strengths of the SSBR vulcanizates. Figure 8 shows variation of the tear strength with the total bound rubber content. Like the tear strength variation with the crosslink density (Figure 4), tear strength of the OE-SSBR vulcanizate linearly increases with the total bound rubber content, whereas the tear strength variation of NO-SSBR vulcanizate shows a weakly decreasing trend. The weak trend of tear strength variation of NO-SSBR vulcanizate could be due to semi-reverse relationship between crosslink density and total bound rubber content as discussed previously. However, there is no relationship between crosslink density and total bound rubber content of the OE-SSBR samples as follow. Order of total bound rubber contents of the OE-SSBR compounds is OE-SSBR4 > OE-SSBR1 > OE-SSBR5 > OE-SSBR2 > OE-SSBR6 > OE-SSBR3, while the crosslink density order is OE-SSBR5 ~ OE-SSBR4 > OE-SSBR3 > OE-SSBR6 > OE-SSBR2 > OE-SSBR3.

Variations of the basic physical properties of SSBR vulcanizates were plotted as a function of the each part bound rubber content (primary layer, secondary layer, and core shell bound rubber contents). The basic physical property variations with the each part bound rubber content showed worse relationships than that with the total bound rubber content except for the modulus variation. The modulus variations with the primary layer and secondary layer bound rubber contents show similar trends to the variations with the total bound rubber content as shown in Figure 9. Figure 10 shows the modulus variations with the core shell bound rubber con-
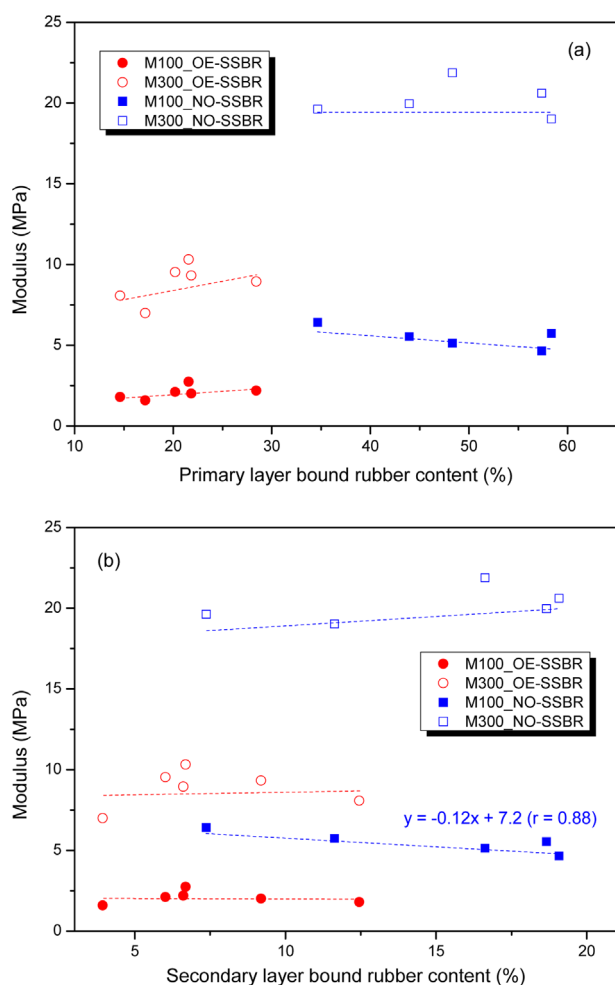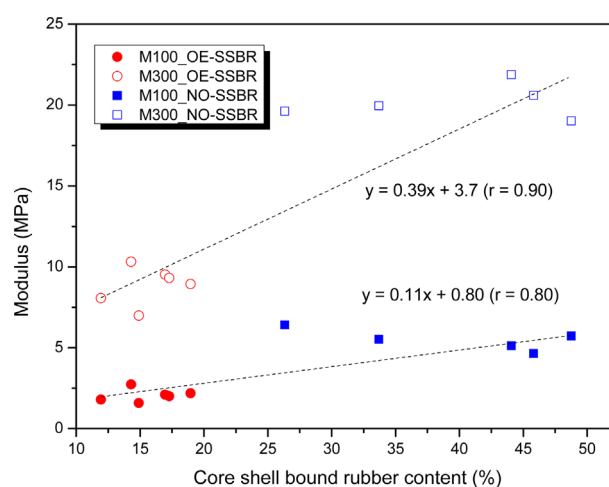
Figure 9. Variations of moduli of the SSBR vulcanizates with the primary layer (a) and secondary layer (b) bound rubber content. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively. Solid and open symbols indicate 100 and 300% moduli, respectively.

tent, and it shows a good relationship. There is one specific trend in Figure 10. The moduli on the whole increase with increase in the core shell bound rubber content. This indicates that the core shell bound rubber content influences the moduli.

Conclusion

Crosslink densities of the NO-SSBR vulcanizates are significantly greater than those of the OE-SSBR ones, irrespective of the microstructures, due to interference in crosslinking reactions by extender oil. Total, core shell, and primary layer bound rubber contents of the NO-SSBR compounds are much greater than those of the OE-SSBR compounds due to extender oil although OE-SSBRs have higher molecular

Figure 10. Variations of moduli of the SSBR vulcanizates with the core shell bound rubber content. Squares and circles denote non-oil-extended (NO-) and oil-extended (OE-) SSBR vulcanizates, respectively. Solid and open symbols indicate 100 and 300% moduli, respectively.

weights than NO-SSBRs. It was found that 1,4-unit and styrene unit are more favorable for formation of secondary layer bound rubber than 1,2-unit. Moduli of the NO-SSBR vulcanizates were greater than those of the OE-SSBR ones, while elongations at break of the formers were smaller than those of the latters. Moduli of the SSBR vulcanizates linearly increase with increase in the crosslink density irrespective of oil extension, while the elongation at break decreases. Each tensile strength variations of OE-SSBR and NO-SSBR vulcanizates shows a weakly decreasing trend with increase in the crosslink density. Tear strength of the OE-SSBR vulcanizate linearly increases with the crosslink density, whereas the tear strength variation of NO-SSBR vulcanizate shows a decreasing trend. The basic physical property variations with the each part bound rubber content (primary layer, secondary layer, and core shell bound rubber contents) did not show good trends compared to that with the total bound rubber content except for the modulus variation. The moduli increase with increase in the core shell bound rubber content, which indicates that the core shell bound rubber content influences the moduli.

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