

Improvement of the Filler Dispersion in Silica-Filled SBR Compounds Using Low Molecular Weight Polybutadiene Treated with Maleic Anhydride

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Maleic Anhydride로 처리된 저분자량 폴리부타디엔을 이용한 실리카로 보강된 SBR 배합물에서 충전제 분산성 향상

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ABSTRACT : Influence of low molecular weight polybutadiene (liquid PB) treated with maleic anhydride on properties of a silica-filled SBR compounds was studied. Silica dispersion was improved by adding liquid PB. The liquid PB treated with maleic anhydride (liquid MAPB) was found to be more effective for the improvement of silica dispersion than the liquid PB without maleic anhydride (liquid NPB). Viscosity of the SBR compound decreased by adding the liquid PB. The crosslink density decreased with increase of the liquid PB content and the cure rate became slower with increasing the liquid PB content. Considering the experimental results, it was believed that addition of small amount of the liquid PB (less than 5 phr) was desirable to improve properties of silica-filled SBR compounds.

요 약 : Maleic anhydride로 처리된 저분자량 폴리부타디엔 (액상 PB)이 실리카로 보강된 SBR 배합물의 특성에 미치는 영향을 연구하였다. 실리카 분산은 액상 PB의 첨가에 의해 향상되었다. Maleic anhydride가 포함된 액상 PB가 maleic anhydride가 포함되지 않은 액상 PB보다 실리카 분산성 향상에 더 효과적임을 알 수 있었다. SBR 배합물의 점도는 액상 PB가 첨가됨에 따라 감소하였다. 가교밀도는 액상 PB의 함량이 증가함에 따라 감소하였고 가황 속도는 느려졌다. 실험 결과를 고려하면, 5 phr 이하의 소량으로 액상 PB를 첨가함으로써 실리카로 보강된 SBR 배합물의 특성을 향상시킬 수 있을 것으로 사료된다.

Keywords : silica compound, silica dispersion, low molecular weight polybutadiene, maleic anhydride

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I. Introduction

Silica has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds.^{1,2} Since intermolecular hydrogen bonds between hydroxyl groups on the silica surface are very strong, it can aggregate tightly.^{2,3} Its property can cause a poor dispersion of silica in a rubber compound. Thus, for a silica-filled rubber compound, the filler dispersion is a critical problem to solve in order to make good compounds. A good dispersibility in a silica-filled rubber compound improves tensile strength, elongation at break, abrasion resistance, and fatigue resistance.⁴ Dispersibility of filler in a rubber compound is very important. In order to improve the dispersibility, various processing aids are used in mixing of a rubber compound.⁵⁻⁸ A rubber compound with a poor filler dispersion will have worse physical properties than that with a good one.

The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. The adsorption of curatives by silica results in delay of the scorch time and reduction of the crosslink density. In general, a silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface.⁹⁻¹¹ The silane coupling agent reacts with silanol on the surface of silica and a siloxane bond is formed. The silane molecule is bound to the silica surface.

In the previous works,¹²⁻¹⁵ we reported that properties of a silica-filled styrene-butadiene rubber (SBR) compound were improved by adding acrylonitrile-butadiene rubber (NBR) or low molecular weight polybutadiene (liquid PB). NBR has nitrile groups (-CN). The basic nitrile groups makes hydrogen bonds with silica and the filler dispersion is improved. The adsorbed NBR molecules on the

silica surface prevent adsorption of curatives. SBR consists of the four components of styrene, *cis*-1,4-, *trans*-1,4-, and 1,2-units. The 1,2-unit is more interactive with silica than the other components.¹⁶⁻¹⁸ Polybutadiene can have three different components of *cis*-1,4-, *trans*-1,4-, and 1,2-units. Liquid PB with high content of the 1,2-unit improves the filler dispersion in silica-filled SBR compounds.^{14,15}

In general, less polar rubber molecules become compatible with polar materials by treating with maleic anhydride.¹⁹⁻²⁰ In the present work, we study the improvement of the filler dispersion in silica-filled SBR compounds using liquid PB treated with maleic anhydride. We believe that the maleic anhydride may help to improve the silica dispersion. The liquid PBs having 0, 10, and 20 wt% of maleic anhydride content were used.

II. Experimental

The compounds were made of SBR, liquid PB (3, 6, and 9 phr), silica, silane coupling agent (Si69, TESPT), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Ricon131, Ricon131MA10, and Ricon130MA20 of Sartomer Co. were employed as liquid PB. The maleic anhydride contents of Ricon131, Ricon131MA10, and Ricon130MA20 are 0, 10, 20 wt%, respectively. Average molecular weights (M_n) are 4500, 5000, and 3100, respectively. The 1,2-unit contents are the same (28%). Z175 (pH = 6.9, BET = 175 m²/g) of Kofran Co. was used as silica. The formulations were given in Table 1.

Mixing of the compounds was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for the 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. The MB compounds were prepared as follow. (1) SBR was loaded into the mixer and premixed for 0.5 min. (2) The silica, silane coupling agent, and liquid PB were com-

Table 1. Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8	9	10
SBR1500 ^{a)}	100.0	97.0	96.0	91.0	97.0	96.0	91.0	97.0	96.0	91.0
Ricon131 ^{b)}	0.0	3.0	6.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0
Ricon131MA10 ^{c)}	0.0	0.0	0.0	0.0	3.0	6.0	9.0	0.0	0.0	0.0
Ricon130MA20 ^{d)}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	6.0	9.0
Z175 ^{e)}	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
Si69 ^{f)}	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
HPPD ^{g)}	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS ^{h)}	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4

a) SBR1500: styrene-butadiene rubber with 23.5% of styrene content

b) Ricon131: liquid polybutadiene copolymer (1,2-unit content = 28%, 8600 of $M_n = 4500$)

c) Ricon131MA10: liquid polybutadiene copolymer (maleic anhydride content = 10%, 1,2-unit content = 28%, $M_n = 5000$)

d) Ricon130MA20: liquid polybutadiene copolymer (maleic anhydride content = 20%, 1,2-unit content = 28%, $M_n = 3100$)

e) Z175: silica (pH = 6.9, BET = 175 m²/g)

f) Si69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)

g) HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine

h) TBBS: *N*-tert-butyl-2-benzothiazole sulfenamide

pounded into the rubbers for 2.0 min. (3) The ingredients (cure activators and antidegradants) were mixed for 2.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min. Mooney scorch time of the compound was measured at 125 °C with a Mooney viscometer MV 2000 of Alpha Technologies. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at 180 °C. The vulcanizates were prepared by curing at 160 °C for 40 min. Physical properties of the vulcanizates were measured with a universal testing machine (Instron 6021).

III. Results and Discussion

Surface of the vulcanizate was observed with scanning electron microscopy to determine the level of the silica dispersion. Figure 1 shows the SEM photographs. Figure 1(a) is the surface of the vulca-

nize without the liquid PB and Figures 1(b)-(d) are the surfaces of the vulcanizates containing 3 phr of the liquid PBs with the different maleic anhydride contents. The compounds containing the liquid PB have better silica dispersion than that without the liquid PB. Especially, the compounds containing the liquid PB treated with maleic anhydride show the excellent filler dispersion. This can be explained with the interaction of maleic anhydride group with silica. The maleic anhydride group can make a hydrogen bond with the silanol group of silica. Due to the interaction, the liquid PB molecules treated with maleic anhydride will be located around the silica surface and then the silica dispersion will be improved.

Figures 2-4 show variations of the rheocurves with the liquid PB content. The minimum and maximum torques (T_{min} and T_{max} , respectively) decrease with increasing the liquid PB content, irrespective of the liquid PB type. The decreased

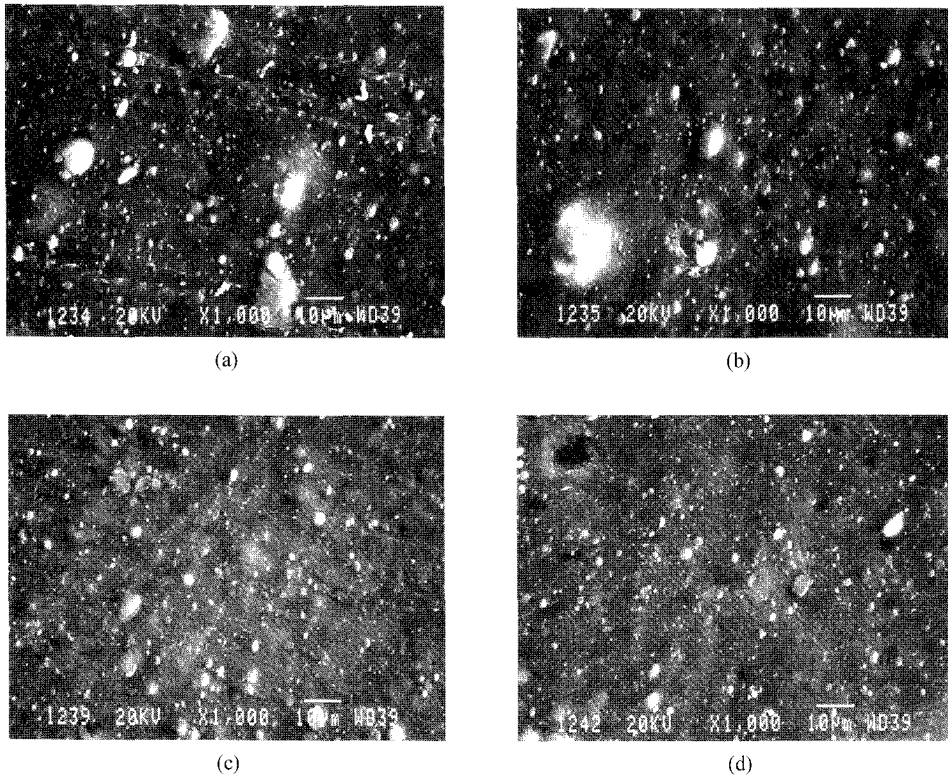


Figure 1. Scanning electron microscopy (SEM) photographs ($\times 1000$) of the vulcanizate surfaces. (a) the vulcanizate without liquid PB, (b) the vulcanizate containing 3 phr of Ricon131, (c) the vulcanizate containing 3 phr of Ricon131MA10, and (d) the vulcanizate containing 3 phr of Ricon130MA20.

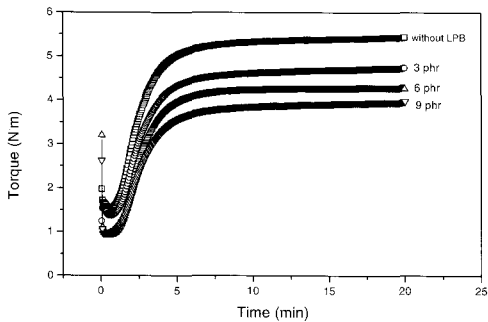


Figure 2. Rheocurves of the compounds containing Ricon131 at 180°C . Squares, circles, up-triangles, and down-triangles indicate the liquid PB contents of 0, 3, 6, and 9 phr, respectively.

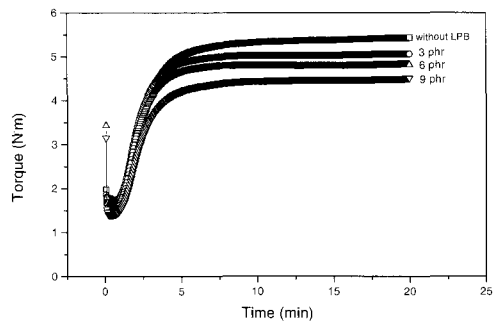


Figure 3. Rheocurves of the compounds containing Ricon131MA10 at 180°C . Squares, circles, up-triangles, and down-triangles indicate the liquid PB contents of 0, 3, 6, and 9 phr, respectively.

T_{\min} can be explained with the improved filler dispersion. The filler dispersion is improved by adding the liquid PB as discussed previously.

Rheocurves of the compounds containing 3 phr of the liquid PB were plotted together in Figure 5 to compare the rheological behaviors during the

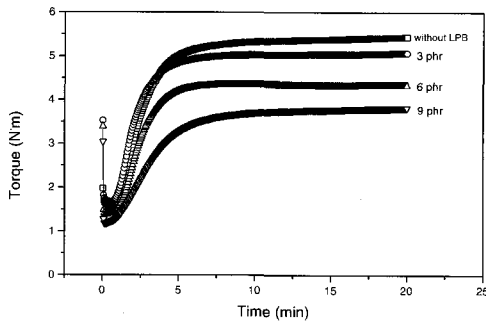


Figure 4. Rheocurves of the compounds containing Ricon130MA20 at 180°C. Squares, circles, up-triangles, and down-triangles indicate the liquid PB contents of 0, 3, 6, and 9 phr, respectively.

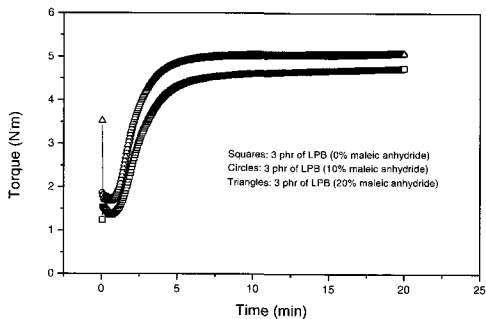


Figure 5. Rheocurves of the compounds at 180°C. Squares, circles, and triangles indicate the compound containing 3 phr of Ricon131, the compound containing 3 phr of Ricon131MA10, and the compound containing 3 phr of Ricon130MA20, respectively.

vulcanization of the compounds containing the same content of the liquid PBs with the different maleic anhydride contents. The rheocurves of the compounds containing the liquid PBs treated with maleic anhydride (liquid MAPB) of 10 and 20 wt% are nearly the same, but the rheocurve of the compound containing the liquid PB without maleic anhydride (liquid NPB) shows different behaviors compared to the compounds containing the liquid MAPB.

The delta torque (ΔT) is the difference between the maximum and minimum torques ($\Delta T = T_{\max} - T_{\min}$). The ΔT is correlated closely with the crosslink density since the torque in a rheocurve is increased by crosslinking reactions. Figure 6 gives variation

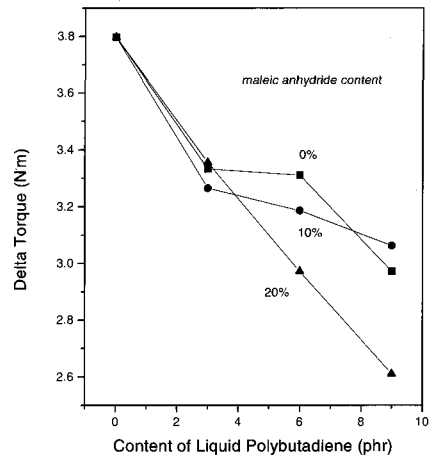


Figure 6. Variations of the delta torque at 180°C with the liquid PB content. Squares, circles, and triangles indicate the compounds containing Ricon131, Ricon131MA10, and Ricon130MA20, respectively.

of the ΔT with the liquid PB content. The ΔT decreases with increase of the liquid PB content. This can be explained by the big difference in molecular weights between SBR and liquid PB and by prevention of crosslink formations between the SBR molecules or between the SBR molecule and silica by the liquid PB. Crosslinks between long polymer chains are more efficient to increase the crosslink density than those between short chains. Lots of the liquid PB molecules will be located around silica since the liquid PB is more mobile than the SBR chain. Thus, the liquid PB molecules prevent the SBR chains from contacting with silica so crosslinking reactions between the SBR and silica will be reduced. The liquid PB molecules between the SBR chains will also prevent the crosslinking reactions between the SBR chains.

Variation of the Mooney scorch time (t_5) with the liquid PB content was plotted in Figure 7. The t_5 means the time taken for the viscosity to reach from the minimum point to increase of 5 MU (Mooney Unit). The t_5 becomes slower as the liquid PB content increases. This can be explained by the difference in mobility between SBR and liquid PB and the prevention of crosslink formations between the

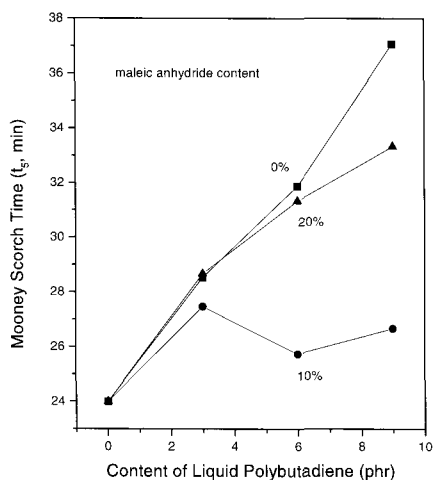


Figure 7. Variations of the Mooney scorch time (t_s) at 125°C with the liquid PB content. Squares, circles, and triangles indicate the compounds containing Ricon131, Ricon131MA10, and Ricon130MA20, respectively.

SBR chains or between the SBR and silica by the liquid PB. Long chain molecule moves slower than short one and sulfur crosslinking reactions occur faster in less mobile long chains than in more mobile short chains. The t_s of the compound containing the liquid MAPB is faster than that of the compound containing the liquid NPB. This implies that maleic anhydride group participates in vulcanizing reaction. A rubber compound with an accelerated sulfur cure system contains stearic acid, zinc oxide, cure accelerator, and sulfur. Stearic acid reacts with zinc oxide to form zinc stearate by dehydration. Zinc stearate reacts with sulfur and cure accelerator to form zinc complex.^{21,22} This complex accelerates crosslinking reaction so that the scorch time and cure rate become faster. Polar materials in a rubber compound react as a ligand of zinc complexes. The maleic anhydride groups in the liquid PB can role as a ligand. The zinc complexes activated by the maleic anhydride groups can react fast and the crosslinking reactions will be also proceeded fast. The t_s of the compound containing the liquid PB treated with 20 wt% maleic anhydride is slower than that of the compound containing the liquid PB treated with 10 wt% maleic anhydride. This may

be due to the difference in the molecular weight distribution. The compound containing the liquid PB treated with 20 wt% maleic anhydride has lower molecular weight distribution than the compound containing the liquid PB treated with 10 wt% maleic anhydride. Lower molecular weight liquid PB is more mobile than higher molecular weight one and the number of molecules of the former is larger than that of the latter for the same weights. Thus, the liquid PB treated with 20 wt% maleic anhydride prevents the crosslinking reactions more than than the liquid PB treated with 10 wt% maleic anhydride since the former is more mobile the latter and the number of molecules of the former is larger than that of the latter for the same weights.

Physical properties of a rubber vulcanizate cured by accelerated sulfur cure system depend on the crosslink density.²³ Modulus is a proportional property to the degree of crosslink density, while elongation at break is an inversely proportional property to the degree of crosslink density. Figure 8 shows variation of the 100% modulus with the liquid PB content. For the vulcanizates containing the liquid PB without maleic anhydride, the modulus decreases linearly with increase of the liquid PB con-

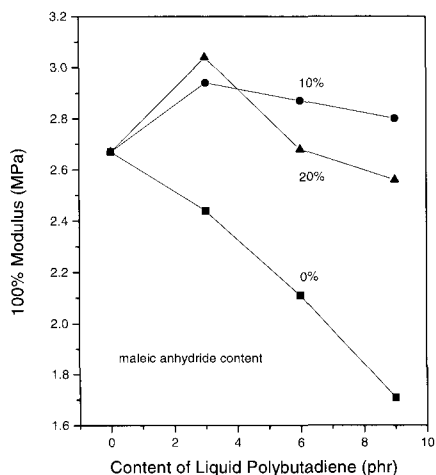


Figure 8. Variations of the 100% modulus with the liquid PB content. Squares, circles, and triangles indicate the vulcanizates containing Ricon131, Ricon131MA10, and Ricon130MA20, respectively.

tent. This is due to the decreased crosslink density. However, the variations of the vulcanizates containing the liquid MAPB show the different trends. For the vulcanizates containing the liquid MAPB, the 100% modulus increases and then decreases as the liquid PB content increases. The moduli of the vulcanizates containing the liquid PB of 3 and 6 phr are higher than that of the vulcanizate without the liquid PB. This is a very surprising result because the crosslink density decreases with increase of the liquid PB content as shown in Figure 6. This can be explained with the highly improved silica dispersion by adding the liquid MAPB. Improvement of the silica dispersion by the liquid MAPB was discussed previously (Figure 1). When the vulcanizates contain 6 and 9 phr of the liquid PB, the modulus of the vulcanizate containing the liquid PB treated 10% maleic anhydride is higher than that of the vulcanizate containing the liquid PB treated 20% maleic anhydride. This is because crosslink density of the former is higher than that of the latter when they contain 6 and 9 phr of the liquid PB as shown in Figure 6.

Figure 9 shows variation of the 300% modulus with the liquid PB content. For the vulcanizates containing the liquid NPB, the modulus decreases linearly with increase of the liquid PB content as similar to the 100% modulus variation. This is also due to the decreased crosslink density. For the vulcanizates containing the liquid MAPB, the 300% moduli of the vulcanizates containing the liquid PB of 3 phr are higher than that of the vulcanizate without the liquid PB. This can be also explained with the highly improved silica dispersion by adding the liquid MAPB. When the vulcanizates contain 6 and 9 phr of the liquid PB, the modulus of the vulcanizate containing the liquid PB treated 10% maleic anhydride is higher than that of the vulcanizate containing the liquid PB treated 20% maleic anhydride. This phenomenon is also observed at the 100% modulus. This may be also due to the higher crosslink density of the vulcanizate containing the liquid PB treated 10% maleic anhydride as shown

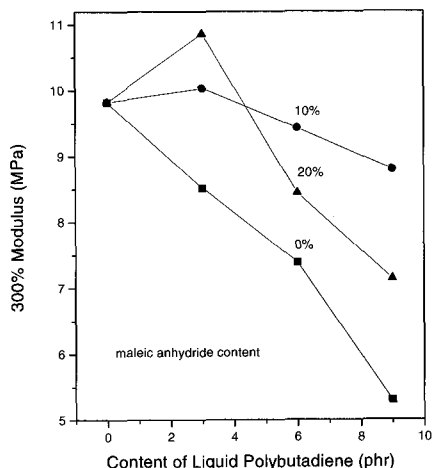


Figure 9. Variations of the 300% modulus with the liquid PB content. Squares, circles, and triangles indicate the vulcanizates containing Ricon131, Ricon131MA10, and Ricon130MA20, respectively.

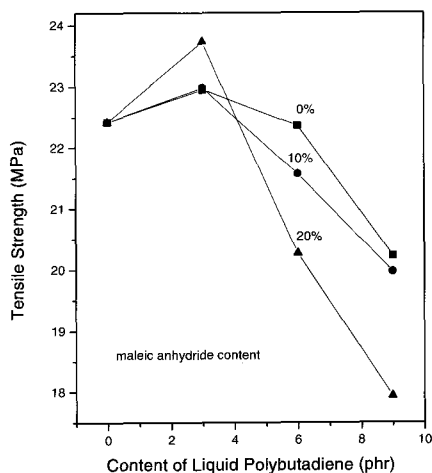


Figure 10. Variations of the tensile strength with the liquid PB content. Squares, circles, and triangles indicate the vulcanizates containing Ricon131, Ricon131MA10, and Ricon130MA20, respectively.

in Figure 6.

Figure 10 shows variation of the tensile strength with the liquid PB content. The tensile strength increases at 3 phr of the liquid PB and then decreases as the liquid PB increases. The elongation at break becomes longer as the liquid PB increases irrespective of the liquid PB type as shown in Figure

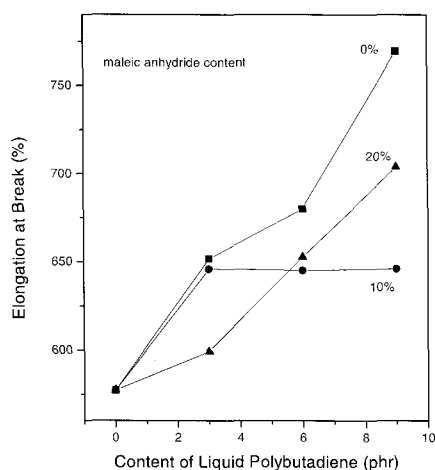


Figure 11. Variations of the elongation at break with the liquid PB content. Squares, circles, and triangles indicate the vulcanizates containing Ricon131, Ricon131MA10, and Ricon130MA20, respectively.

11. This is because the crosslink density decreases as the liquid PB content increases. The higher tensile strength at 3 phr of the liquid PB can be explained with the improved silica dispersion.

IV. Conclusions

By adding liquid PB to a silica-filled SBR compound, the filler dispersion was improved. Especially, the maleic anhydride-treated liquid PB was more efficient to improve the silica dispersion compared to the untreated liquid PB. The maleic anhydride groups can make hydrogen bonds with silanol bonds on the silica surface. The crosslink density decreased with increase of the liquid PB content. For the compounds containing the maleic anhydride-treated liquid PB, the modulus of the vulcanizate containing the liquid PB was higher than that of the vulcanizate without the liquid PB though the former had lower crosslink density than the latter when the liquid PB content was 3 and 6 phr. It was recommendable that small amount of the maleic anhydride-treated liquid PB was added to a silica-filled compound to improve the filler dispersion.

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