# Phase Control of BR/SBR Blends by Silica Particles

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**Abstract** A phase control of butadiene rubber (BR)/styrene-butadiene rubber (SBR) blends was examined by using silica particles. The phase structure of the blends was qualitatively evaluated from transmission electron microscope (TEM) observation and temperature dependence of mechanical tan $\delta$ . It was found that the temperature dependence of tan $\delta$  was dependent on the size of agglomerate formed by silica particles in the blend. The vulcanized blends with small agglomerates showed a single tan $\delta$  peak suggesting a pseudo-miscible state. The vulcanized blends with large agglomerates showed two tan $\delta$  peaks corresponding to the  $T_g$ s of BR and SBR. The mutual dissolution of BR and SBR phases above the UCST line where the vulcanization was carried out might be disturbed by large agglomerates formed by silica particles in the blends.

**Keywords** Phase control, BR/SBR blend, Silica, tan $\delta$ , TEM, Agglomerate, Affinity.

#### Introduction

Silica has been recognized as an effective filler for rubber reinforcement. Silica has many silanol groups on the surface of the particles. Thus an affinity of silica with rubber depends on the chemical structure of rubber molecules, which influences on the dispersion of silica particles in rubber matrix. Further, silica particles easily form a secondary structure such as aggregates and agglomerates by the hydrogen bonding formed between the silanol groups. During the mechanical mixing of silica with rubber, the agglomerates are partly broken by the mechanical shear followed by the re-construction of the secondary structure in the rubber matrix. The destruction and re-construction of the agglomerates are repeated during the mechanical mixing, finally well dispersed silica particles exist in the rubber matrix. We reported that there existed entrapped rubber phase in the secondary structure which developed in the silica filled rubber composites<sup>1</sup>). This indicates that the formation of secondary structure is accompanied by the incorporation of rubber molecules into the structure. The entrapped rubber molecules might be partly released when the structure is destroyed by the mechanical shear.

A new concept of compatibility of polymer blends by using rigid nano-particles, instead of the conventional organic compatibilizer has been proposed<sup>2–7)</sup>. Two kinds of mechanism were proposed to explain the improved compatibility by the fillers. The one is the thermodynamics of interactions near the surface of fillers<sup>8–11)</sup>. The other one is an increase of viscosity in the polymer–polymer–filler ternary system<sup>3,12)</sup>.

In this study, the characteristics for silica which were described by the formation and destruction of secondary structure of silica particles in the rubber matrix were applied to the control of phase structure of butadiene rubber (BR)/styrene butadiene rubber (SBR) blends. The phase diagram of BR/SBR blend is the upper critical solution temperature (UCST) type<sup>13)</sup>. At room temperature, the blend is immiscible independent of blend ratio. When the vulcanization for the blend was carried out above the homogenization temperature around 150°C (i.e. above the UCST line), the immiscible blends are expected to turn to homogeneous one, and simultaneously the crosslink between BR and SBR molecules proceeds, which suppresses the phase separation below the UCST line. When silica filled BR or SBR was mixed with SBR or BR, the immiscible-miscible transition in the rubber phase is accompanied by the migration of silica aggregates and/or agglomerates which involved BR or SBR molecules. Also the affinity of silica for BR might be different from that for SBR. Thus, the immiscible-miscible transition might be affected by the existence of silica particles in the blend. These suggest that we can control the phase structure of silica filled vulcanized BR/SBR blend by the utilization of proper silica and controlling the mixing conditions for silica filled BR/SBR blend.

## **Experimental**

#### Materials

The raw rubbers used were styrene-butadiene rubber (SBR; Nipol 1502,  $T_g = -52^{\circ}$ C; Nippon Zeon Co., Japan) and high *cis* butadiene rubber (BR; Nipol 1220,  $T_g = -100^{\circ}$ C; Nippon Zeon Co., Japan). The silicas used were precipitated silica (AQ; Nipsil AQ; Nippon Silica, Japan) and fumed silica (A-50, Aerosil 50; Nippon Aerosil, Japan).

#### Mixing

The mechanical blend was carried out around  $70^{\circ}$ C by using Banbury mixer (Laboplastomill 50MR; Toyo Seiki, Japan). The blend ratio of rubber was fixed to be 50/50 by weight. Thus, the mixing temperature of  $70^{\circ}$ C was below the UCST line. The silica content in the rubber blends was also fixed to be 25 g per 100 g of rubber (25 phr). Two different mixing methods were utilized for the sample preparation. The first was that the silica was mixed with BR. Then the master-batch was mixed with SBR (method I). The second was that the silica was incorporated into SBR first, then the master-batch was mixed with BR (method II). Details of the mixing are shown in Figure 1. The composites obtained were seated on a roll followed by the vulcanization at 160°C for 30 min.

#### Measurements

Dynamic mechanical tests of vulcanized samples were carried out on a dynamic visco-elastometer (Rheovibron DDV-II-EP; Orientic, Japan) under a fine strain amplitude and frequency of 110 Hz.

Transmission electron microscopy (TEM) observations were carried out by using transmission electron microscope (Hitachi H-9000, NAR type; Hitachi, Japan) with an accelerated voltage of 200 kV.

#### **Results and Discussion**

#### 1. Temperature dependence of $tan \delta$

The phase structure of the blends was evaluated from the temperature dependence of mechanical tan $\delta$  and transmission electron microscope (TEM) observation. Figure 2 shows the temperature dependence of tan $\delta$  for unfilled blends with different sulfur contents. The unvulcanized (sulfur content=0 phr) blend showed two tan $\delta$  peaks around -90°C and -35°C. The peak temperatures for the lower and higher temperature sides



#### \*N-Cyclohexyl-2-benzo thiazolyl sulfenamide

Figure 1. Mixing method for silica filled BR/SBR blend (left: method I, right: method II).



Figure 2. Temperature dependence of  $\tan \delta$  for the blends with different sulfur contents.



Figure 3. Temperature dependence of  $\tan \delta$  for A-50 filled vulcanized blends.



**Figure 4.** Temperature dependence of  $\tan \delta$  for AQ filled vulcanized blends.



**Figure 5.** Temperature dependence of  $\tan \delta$  for AQ filled vulcanized blends from method II under different mixing times.

corresponded to the glass transition temperature  $(T_a)$  of BR and SBR, respectively (see Experimental). With increasing the sulfur content, the two peaks were observed to approach each other. At the sulfur content of 2 phr, the vulcanized blend showed only one  $tan\delta$  peak around -60°C indicating that the BR/SBR blend changed from immiscible to miscible state by the vulcanization. It is reported that the blend of BR/SBR shows an upper critical solution temperature (UCST) phase diagram<sup>13)</sup>. Thus, a chemical bonding developed between BR and SBR molecules by the vulcanization at 160°C where miscible state was achieved, might suppress the de-mixing below the binodal line, resulted in the appearance of pseudomiscible state for the vulcanized blends. The data also suggest that the sulfur content of 2 phr is enough to fix the phase structure by the vulcanization which was developed

around the vulcanization temperature of 160°C. Hereafter the sulfur content in all samples was fixed to be 2 phr.

Figure 3 shows the temperature dependence of  $\tan \delta$  for fumed silica (A-50) filled vulcanized blends prepared from both methods I and II. Both samples showed a similar temperature dependence of  $\tan \delta$  in which only one  $\tan \delta$ peak was observed, similar to that for unfilled vulcanized blend. The results indicate that the chemical bonding between BR and SBR molecules are well developed even in the existence of fumed silica.

Figure 4 shows the temperature dependence of  $\tan \delta$  for precipitated silica (AQ) filled vulcanized blends prepared from both methods I and II. The  $\tan \delta$ —temperature relation for the sample from method I was similar to that for unfilled and A-50 filled vulcanized blends as shown in Figures 2 and 3. On the other hand, the sample from

method II showed two  $\tan \delta$  peaks indicating that the miscibility of the blend was quite low. It is generally accepted that the silica with large amounts of silanol groups which have an acidic character interrupts the vulcanization in the existence of an accelerator which has a basic character<sup>14)</sup>. However, such behavior was negligibly small in the AQ filled vulcanizates since the blend from method I showed a single tan $\delta$  suggesting the well developed chemical crosslink between BR and SBR by the vulcanization. These results clearly indicate that the phase structure of silica filled vulcanized BR/SBR blends is affected by the sort of silica and the conditions for mixing. The appearance of two tan $\delta$  peaks in the blend from method II suggests that the mutual dissolution of BR and SBR phases above the UCST line was disturbed by the AQ, and the mixing time of 3 min was not enough to achieve the mutual dissolution.

Figure 5 shows the temperature dependence of  $\tan \delta$  for the AQ filled vulcanized blends prepared from method II. As was shown in Figure 1, the mixing time for most of the samples was fixed to be 3 min. Thus, the data shown in Figures 3 and 4 were for the samples with mixing time of 3 min. In Figure 5, the mixing time was extended up to 10 min. At a short time of mixing around 3 min, the blend showed two  $\tan \delta$  peaks. With increasing the mixing time further, the  $\tan \delta$  peaks were observed to approach each other and the sample with the mixing time of 10 min showed only one  $\tan \delta$  peak around  $-50^{\circ}$ C.

It is well known that the dispersion of silica particles in rubber matrix depends on the chemical structure of rubber molecules and the number of silanol group on silica particle. At a given rubber molecule, the smaller the number of silanol group, the better the dispersion of silica particle that could be achieved<sup>15)</sup>. The number of silanol group for the AQ was larger than for the A- $50^{11}$ . Thus, we can expect a better dispersion for the A-50 than for the AQ in the rubber matrix. We reported that a part of rubber molecules was entrapped in the silica agglomerates in the silica filled rubber composites. Further, the amount of entrapped rubber increased with increasing the agglomerate size<sup>1)</sup>. At the initial stage of the mechanical mixing of silica with rubber, a secondary structure (agglomerate and aggregate) is formed by the hydrogen bonding between silanol groups on silica particles. However, the structure is not strong enough against the mechanical shear in the rubber matrix, resulting in the partial destruction of the structure by the mechanical shear. The broken structure can re-construct during the mechanical mixing. Such processes might be repeated during the mechanical mixing. A part of the entrapped rubber might be released during the destruction of the secondary structure. Thus, it is reasonable to infer that the secondary structure formed by silica particles has an important role on the control of phase structure of silica filled unvulcanized BR/SBR blends.

# 2. TEM observation

Figure 6 shows TEM images of the AQ filled BR and SBR vulcanizates. The sample preparation for the observation is as follows; the vulcanized composites were cured again in melted sulfur (~150°C) for 24 h. At this stage, the structure change might be negligible since the structure of the samples had been fixed by the vulcanization which had been done at 160°C. The hardened samples were easily cut into ultra thin films (<100 nm) at room temperature by microtome. The thin films were stuck onto the TEM grids. A similar technique was utilized for the TEM observation for A-50 and AQ filled vulcanized blends of which results are shown in Figures 7 and 8. It is seen that the dispersion of silica particle was better in SBR than in BR. The results indicate that the affinity of silica with SBR is better than that with BR.

Figure 7 shows TEM images for A-50 filled vulcanized blends from both methods I and II. It can be seen that the silica particles are well dispersed in the rubber matrix, independent on the conditions for the mixing. This is reasonable since the number of silanol groups was quite small for the A-50.

Figure 8 shows the TEM images for AQ filled vulcanized blends from both methods I and II. The dispersion of silica particles in the rubber matrix was poor compared with that for the A-50 filled samples shown in Figure 7 with this tendency more prominent in the sample from method II which showed two tan $\delta$  peaks (see Figure 4). For the AQ filled BR/SBR blend from method II, the AQ was mixed with the SBR. At this stage, a part of the SBR was entrapped in the silica agglomerates. Then the master-batch was mixed with the BR. The blend of the BR and SBR is basically immiscible around the mixing temperature of 70°C which suggests that the size of each BR and SBR phase is large enough to show an individual  $T_a$ . During the mixing of the master-batch with the BR, a part of the entrapped SBR was dispersed in both BR and SBR phases due to the destruction of the agglomerates. However, the affinity of silica with BR is poor compared with SBR. Thus, the migration of silica agglomerates from SBR to BR might not be preferable, resulting in the poor dispersion of silica particles as well as the entrapped rubber phase in the BR phase. On the other hand, for the



**Figure 6.** TEM images for AQ filled BR vulcanizate (left) and AQ filled SBR vulcanizate (right).



Figure 7. TEM images for A-50 filled vulcanized blends (left: method I, right: method II).



Figure 8. TEM images for AQ filled vulcanized blends (left: method I, right: method II).



**Figure 9.** TEM images for stained AQ filled vulcanized blends (left: method I, right: method II).

blends from method I, the master batch is a AQ filled BR. The affinity of AQ with BR is lower than with SBR. Thus, the migration of AQ in the master batch to the SBR proceeds smoothly during the mixing of master batch with the SBR, resulting in the better dispersion of AQ and entrapped rubber phase in the SBR phase. We examined the staining of the samples used for Figures 7 and 8 by OsO4 to get information on the phase structure of rubber matrix. However, the stained samples showed little information on the phase structure probably due to the utilization of hardened samples. Thus, another sample preparation for TEM observation was examined to get information on the structure of rubber phase of the blends. The AQ filled vulcanized blends were immersed in a methyl methacrylate (MMA) with 1 wt% of benzoyl peroxide for 1 h. At this stage, the vulcanized blends were slightly swollen by MMA. Then the MMA with vulcanized blends was polymerized at 60°C for 24 h. The

polymerized MMA with blends were easily cut into ultra thin films at room temperature by microtome. The thin films were stained by  $OsO_4$  vapor for 24 h.

Figure 9 shows the TEM images of stained AQ filled vulcanized blends from methods I and II. The bright colored phase corresponds to SBR domain. The dark colored phase corresponds to silica agglomerates and BR domain. The gray colored zone was also recognized in the two images. The phase might correspond to the pseudo-miscible phase of BR and SBR. Although we observed large agglomerates in AQ filled vulcanized blend (see Figure 8), such agglomerates were not recognized in Figure 9. As described, the rubber phases around the agglomerates were swollen state. Thus, most parts of the agglomerates might be covered with swollen rubber phases. However, we can see a part of agglomerates within a swollen rubber phases as a dark colored SBR phases

around silica (dark colored dot) with a large size in the sample from method II. On the other hand, such structures were less prominent in the sample from method I. The existence of gray colored phase in the sample from method I suggests that a high level of pseudo-miscibility was achieved in the sample from method I in accordance with  $\tan \delta$  results.

As can be seen, the blend from method II has large SBR domain around silica. This suggests that large amounts of SBR which are entrapped by large silica agglomerates can't dissolve easily into the BR phase even above the binodal line. As a result, the vulcanization proceeded within the SBR or BR phase, showing two tan $\delta$  peaks corresponding to the  $T_v$ s for SBR and BR.

## Conclusions

Silica filled vulcanized BR/SBR blends were prepared by using two kinds of silica and two different mixing methods. Based on the temperature dependence of mechanical tan $\delta$  and TEM observation, following conclusions were derived;

- 1. The agglomerate size of silica particles in the BR/SBR blends was larger for precipitated silica AQ than for fumed silica A-50.
- 2. The agglomerate size of AQ in the BR/SBR blends was dependent on the conditions for mixing, the size was larger for, method II than for method I. This was explained by the difference of affinity of AQ with BR or SBR.
- 3. The mutual dissolution of BR and SBR phases above

the UCST line was disturbed by the silica, which was most prominent in the blends in which large silica agglomerates were developed.

#### References

- Sawanobori J., Ono S., Ito M.: Jpn. J. Polym. Sci. Technol., 57, 356 (2000).
- Ferreiro V., Douglas J. F., Amis E. J., Karim A.: *Macromol.* Symp., 167, 73 (2001).
- Wang Y., Zhang Q., Fu Q.: Macromol. Rap. Commun., 24, 231 (2003).
- del Rio C., Ojeda M. C., Acosta J. L.: *Eur. Polym. J.*, **36**, 1687 (2000).
- 5) Voulgaris D., Petridis D.: Polymer, 43, 2213 (2002).
- Kim S. W., Jo W. H., Lee M. S., Ko M. B., Jho J. Y.: *Polymer*, 42, 9837 (2001).
- Gelfer M. Y., Song H. H., Liu L., Hsiao B. S., Chu B., Rafailovich M., Si M.: J. Polym. Sci. B, 41, 44 (2003).
- 8) Nesterov A. E., Lipatov Y. S.: Polymer, 40, 1347 (1999).
- Lipatov Y. S., Nesterov A. E., Ignatova T. D., Nesterov D. A.: *Polymer*, 43, 875 (2002).
- Nesterov A. E., Lipatov Y. S., Ignatova T. D.: *Eur. Polym. J.*, 37, 281 (2001).
- Lipatov Y. S., Shumsky V. F., Rosovitsky V. F., Getmanchuk J. P., Kvitka N. A.: J. Appl. Polym. Sci., 47, 941 (1993).
- 12) Zhan Q., Yang H., Fu Q.: Polymer, 45, 1913 (2002).
- Ougizawa T., Inoue T., Kammer H. W.: *Macromolecules*, 18, 2089 (1985).
- 14) Choi S. S., Park B. H., Song H.: Polym. Adv. Technol., 15, 122 (2004).
- Suzuki N., Yatsuyanagi F., Ito M., Kaidou H.: J. Appl. Polym. Sci., 86, 1622 (2002).