Natural Rubber/In Situ Silica Nanocomposite of a High Silica Content

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By using *n*-hexylamine as a catalyst of sol–gel reaction of tetraethoxysilane in uncured natural rubber matrix, spherical silica particles of ca. 46 nm were homogeneously generated in situ at a high content, i.e., 71 parts per one hundred rubbers by weight. The mechanical properties of this soft nanocomposite were very unique comparing with those of conventional silica-filled one. Especially, hysteresis loss and permanent set of the former were much lower than those of the latter. The result will be a breakthrough for practical applications of in situ silica filling.

Reinforcement of rubber is one of the most important processes in rubber technology.[1] It results in a higher stress and improvement of various mechanical properties, such as tear, tensile strength, and wear. However, there are also disadvantages such as increases in hysteresis and compression set. It is well-known that the carbon black is the most effective reinforcing filler for rubber composites, although it always makes rubber products black-colored. As an alternative, silica is the other important filler in rubber industry. A problem of silica, however, is a poor dispersion in rubbery matrix because of the strong interaction between silica particles. Recently, in situ silica filling has been focused, because it is a processing for the preparation of new soft nano-composites.

In general, the sol–gel reaction of tetraethoxysilane (TEOS) takes place in two steps, the hydrolysis and the condensation reactions, to generate SiO_2 at lower temperature.[2] Up to now, the in situ silica reinforcement by sol–gel process in various rubbers is reported such as silicone rubber,[3] butadiene rubber,[4] styrene–butadiene rubber (SBR),[4b,5] natural rubber (NR),[6] latexes[7] of SBR and nitrile rubber. For practical applications of in situ silica filling, the sol–gel reaction of TEOS in uncured rubber matrix or rubber latex is preferable. However, the yield of silica in the uncured rubber was not high enough, i.e., less than ca. 45 parts per one hundred rubbers by weight (phr),[6c] which have restricted the use of in situ filling in rubber industry. Thus, an effective catalysis for high in situ silica filling is reported in this letter which ensured the unique characteristics of in situ silica-filled NR vulcanizate of 71 phr silica content.

NR was prepared into thin sheets of ca. 1 mm thickness on a two-roll mill and the sheets were swollen in TEOS at 40 °C for 1 h and at 25 °C for 16 h. The swollen NR sheets were immersed in aqueous solutions of amine. Among several amines tested (*n*-butylamine, *n*-hexylamine, *n*-octylamine, dipropylamine, and triethylamine), 0.064 mol/L aqueous solution of *n*-hexylamine gave the highest yield of homogeneous in situ silica particles at 40 °C for 72 h, which was 71 phr. The in situ silica content was determined by a thermogravimetry by heating up to 1000 °C at 10 °C/min under air. The generation of 71 phr of in situ silica in the uncured NR matrix has never been reported be-

Table 1. Recipe for rubber compounds in phr[a]

Sample code	NR-0	NR-71Si	NR-71VN
NR (RSS No. 1)	100	0	100
In situ silica-filled NR	0	171	0
Stearic acid	2.0	2.0	2.0
Active ZnO	1.0	1.0	1.0
N-cyclohexyl-2-benzothiazole sulfenamide	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5
Nipsil VN-3	0	0	71
Diethylene glycol	0	0	4.3
Curing time/min	16	9	16

[a]Part per hundred rubbers by weight

fore. Next, the masterbatch (in situ silica generated NR sheets) was mixed with cross-linking reagents (sulfur and curing reagents) by a conventional milling. The recipe is shown in Table 1. All ingredients except in situ silica were mixed on a two-roll mill at rt. Then, the rubber compound was molded into a sheet of ca. 1 mm thickness by pressing at 140 °C to obtain the vulcanizate (NR-71Si). As reference samples, unfilled NR vulcanizate (NR-0) and 71 phr of commercial silica (VN-3)-filled NR vulcanizate (NR-71VN) were prepared by a conventional method. For NR-71VN, diethylene glycol was added to decrease the negative effect of silica surface on curing reaction.

The hysteresis behaviors of NR-71Si and NR-71VN are displayed in Figure 1. The hysteresis measurements were carried out by repeating the stretching of ring-shaped sample up to 100% elongation, followed by retracting to the original starting point at 20 mm/min at rt. for five cycles. It is worth noting that the hysteresis loss and permanent set in stress–strain curves of
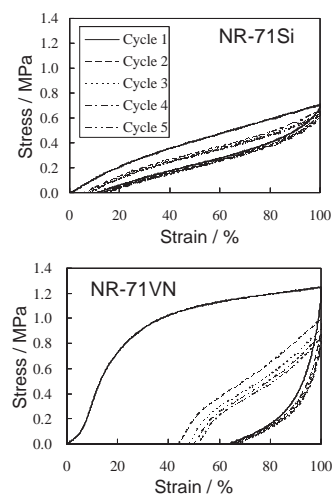

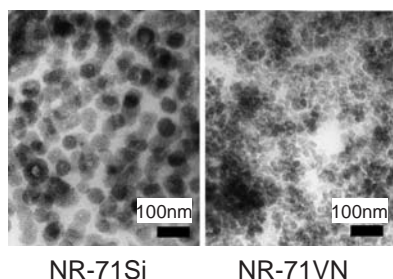**Figure 1.** Hysteresis curves of silica-filled NR vucanizates.

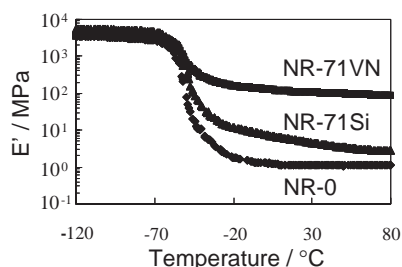**Figure 2.** TEM photographs of silica-filled NR vucanizates.

Figure 3. Temperature dependence of unfilled and silica-filled NR vucanizates.

NR-71Si were significantly smaller than those of NR-71VN at each cycle. Especially, the hysteresis loss of NR-71VN at the first cycle was much higher compared to the others. Since their network-chain densities were similar (7.60×10^{-5} mol/cm^3 for NR-71Si and 7.21×10^{-5} mol/cm^3 for NR-71VN), the difference is ascribed to the silica morphology in the NR matrix.

In Figure 2, photographs of transmission electron microscopy (TEM) of NR-71Si and NR-71VN are displayed. The TEM observation was conducted at accelerating voltage of 80 kV. Ultrathin samples were prepared using a microtome in liquid nitrogen. As shown in this figure, the in situ silica particles were homogeneously dispersed, whereas the much more aggregated structure of VN-3 was formed in the NR matrix. Such aggregated structure of VN-3 seems to have given rise to a pseudonetwork structure of silica particles, which resulted in the increase of hysteresis at the initial deformation for NR-71VN. In other words, the rubber vulcanizate mixed with VN-3 contained dual networks, i.e., beside a network by crosslinking it had additional one by VN-3. The pseudonetwork structure of conventional silica particles was broken by strain below 100%. The hysteresis for NR-71VN decreased much in the second cycle, and the difference in hysteresis seems to have been small after the third cycle. In contrast, the hysteresis between the first and second cycles for NR-71Si was not much different, and the stabilized curve was observed after the third cycle in this sample. The difference in hysteresis behaviors between NR-71Si and NR-71VN in the first cycle can be resulted of the stronger filler-filler interaction of conventional silica in NR-71VN.

This consideration is supported by results of dynamic mechanical analysis (DMA) for NR vulcanizates as shown in Figure 3. DMA was carried out at a frequency of 10 Hz and double strain amplitude of 0.1% at a heating rate of 2 °C/min. The storage modulus (E′) at rt of NR-71VN was much larger than that of NR-71Si, which indicates that the filler-filler interaction was significant to form a pseudonetwork. It maintains the net-work structure at the low strain amplitude to increase E′ in the rubbery region of NR-71VN. In the TEM observation for NR-71Si, it is also noted that the shape and size of generated in situ silica particles were a homogeneous sphere and ca. 46 nm of diameter, respectively. The diameter was larger than that of VN-3, ca. 19 nm as seen in Figure 2. Still, the size of in situ silica seemed to be relatively small in spite of the fact that it was produced in raw rubber.[4–6] The reason why *n*-hexylamine was the effective catalyst is not clear, but the results suggest that the amphiphilic property of the catalyst is the important factor to control the amount of in situ silica.

From this study, the in situ silica filling is concluded to be one of the choices for practical reinforcing fillers in rubber technology. The lower hysteresis and permanent set are desired in many applications, especially in the tire industry. NR is known to crystallize upon elongation, which observed after ca. 350% strain and influences much on tensile behaviors.[8] Thus, more detailed analysis on the high in situ silica filling in uncured rubber matrix and the effects of high filling of in situ silica on the mechanical properties and strain-induced crystallization of the vulcanizates will be reported in a near future.

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