Effect of Silane Treatment on Hybridized Use of Short Cellulose Fibers and Silica Particles for Natural Rubber Reinforcement

Lopattananon, Natinee^{*1}/Jitkalong, Dolmalik^{*1}/Seadan, Manus^{*2}/Sakai, Tadamoto^{*3}

Processability, swelling and tensile properties of natural-rubber-based hybrid composites prepared by mixing short cellulose fibers and fine silica particles of equal contents with total loading of 20 phr using a two-roll mill were analyzed. Their properties were compared with those of natural rubber reinforced with single filler (silica or cellulose fiber) and corresponding unfilled natural rubber. The tensile test showed the reinforcing effect of both single filler system and hybrid filler system in relation to natural rubber. The tensile modulus and tensile strength of hybrid composites generally laid between those of fiber-reinforced and silica-reinforced natural rubber composites, whereas the elongation at break of hybrid composites was equal to that of single filler reinforcement system. The Mooney viscosity of silica-filled compound was much higher than that of unfilled natural rubber and short fiber-filled compounds, and was significantly reduced when hybridized fillers were used. Furthermore, a silane coupling agent, Si 69, was used to modify the surface properties of cellulose fibers and silica particles. Three microscopic evaluation techniques, that is, elemental X-ray mapping (EDX), 3 D microfocus X-ray scanning, and N-ARC methods were applied to investigate the filler dispersion/mixing effects. It was found that both of the fillers were more homogeneously dispersed in the hybrid composites, and the affinity between the fillers and natural rubber was improved after the silane treatment. The results from this work suggested that the better dispersion of short cellulose fiber/silica hybrid fillers had great advantages in rubber processing, and allowed for equal or higher composite strength compared to a simply silica-filled composite system.

Key words : Silica/Cellulose fiber/Natural rubber/Composites/Processability/Dispersion/Silane treatment

1. Introduction

Natural rubber is one of the most widely used elastic materials across a broad spectrum of industries. With its high mechanical strength, excellent compression set, good resilience, abrasion resistance and vibration dampening properties, it is widely used for rubber products, especially for automobile tire applications. In general rubber compounding, the addition of various kinds of fillers is indispensable for reinforcement, processing and production cost. Among fillers, particulate silica is the most suitable reinforcing alternative to carbon black in rubber compounding. It is mainly used in compounds designed to be translucent or colored products and to reinforce,

significantly mechanical strength and related properties such as hardness and abrasion resistance.¹⁾ However, compared to carbon black-filled rubber compounds, the modulus of silica-reinforced rubber is relatively lower.²⁾ Unlike carbon black, silica does not disperse well in general rubber compounds due to their polar silanol surface groups (-SiOH). These specific functional groups are not compatible with the non-polar rubber matrix and cause easily the tight aggregation/agglomeration of silica particles. The interaction between silica particles also induces higher compound viscosity and inferior processability.³⁾ In addition, the agglomerated silica was reported to serve as flaws or defects within the rubber network, which reduces the strength of rubber.⁴⁾ Therefore, in common practice, the silica fillers are generally used with a silane coupling agent to improve filler dispersibility in rubber compounds^{1),5)} and to enhance rubber reinforcement.⁶⁾

Plant-based cellulose fibers have been strongly expected as potential reinforcement to plastic products because they are strong, biodegradable and easily process-

^{*1} Prince of Songkla University
Pattani, 94000, Thailand
lnatinee@bunga.pn.psu.ac.th

^{*2} Silpakorn University
Nakhon Pathom, 73000, Thailand

^{*3} Shizuoka University
3-3-6 Shibaura, Minato, Tokyo, 108-0023, Japan
Received Dec. 28, 2010.

able, as well as renewable.⁷⁾ Owing to unique characteristics of silica fillers and cellulose fibers, their combination should provide beneficial effects to rubber compounding and reinforcement. In tire tread applications, the use of cellulose fiber in silica-reinforced rubber has been applied to improve certain properties such as processability, dimensional stability and mechanical balance between abrasion resistance and rolling characteristics.^{8)~9)} The tire tread compound reinforced with precipitated silica and short cellulose fibers is also used for enhancing ice traction on icy road.¹⁰⁾ In our previous work, we studied the effect of hybridized ratio of short cellulose fiber and silica on the processing properties and mechanical performance of natural rubber-based composites.¹¹⁾ In this research work, we aimed to examine the processing properties and reinforcement of natural rubber combined with short cellulose fiber/fine silica filler, in which both fillers were treated with a silane coupling agent for the surface affinity increase. Furthermore, in this study we also investigated the influence of silane treatment on filler dispersion or mixing state of hybridized cellulose fiber and silica in the natural rubber matrix. For this purpose, we employed three different analytical techniques, that is, X-ray silicon mapping, 3D micro-focused X-ray scanning technique (developed at Shimadzu) and a surface polishing technique, so-called N-ARC method (developed at Nissan ARC) for better understanding of the mixing process in natural rubber reinforced with short cellulose fibers and fine silica particles.

2. Experimental

2.1 Materials

Natural rubber (STR 5 L) was obtained from Thavorn Industry (Thailand). Cellulose fibers (ARBOCEL[®] B 00), obtained from soft wood, were manufactured by JRS (Germany). The cellulose fibers are very short with average length of 120 μm and diameter of 20 μm , respectively (Figure 1). They contain native cellulose, which is a hydrophilic glucan polymer consisting of a linear chain of 1, 4-anhydroglucose units containing alcoholic hydroxyl groups (-OH) as shown following.

Precipitate silica (Ultrasil[®] VN 3 GR) was manufactured by United Silica (Siam) (Thailand). They have average particle size and specific surface area of 10-40 nm and 210 m²/g, respectively. Silane coupling agent used was Si 69, bis (triethoxysilylpropyl) tetrasulfide (JJ-Degussa). The structure of Si 69 is given as follows ;

Zinc oxide (Global Chemical), stearic acid, sulfur, N-tert-butyl-2-benzothiazyl sulphenamide (TBBS) (Bayer Thai), 2, 2, 4-trimethyl-1, 2-dihydroquinoline (TMQ) (Flexsys) and diethylene glycol (DEG) were used as rubber additives. Acetone used was AR-grade and used as received.

2.2 Fabrication of natural rubber-based composites

Natural rubber, silica, cellulose fiber and other rubber additives were compounded at room temperature using a laboratory two-roll mill (150 x 300 mm). The formulation of the natural rubber-based composites is given in Table 1. Natural rubber was firstly masticated for 1 min, and added with other ingredients according to the time schedule given in Table 2. Finally, the natural-rubber-based composites were passed through the roll-mill for 7 times keeping the direction for each pass constant to ensure the fiber alignment and uniform dispersion of fillers. In this study, the total amount of fillers was fixed at 20 phr. For preparation of the hybrid filler composites, the silica and cellulose fiber were pre-mixed at ratio of 10/10 phr/phr and added with DEG (8 wt% of filler). They were also pretreated with acetone solution of Si 69 (2 wt % of filler) using the procedure outlined by Lopattananon and co-workers.¹¹⁾ For comparison unfilled natural rubber compounds were also prepared with the same procedure. The rubber compounds were then vulcanized by hot-pressing at 150°C for respective optimal cure times obtained from oscillating disc rheometer (ODR) test at 150°C.

2.3 ODR measurements

Cure characteristics of the rubber compounds were measured using Oscillating Disc Rheometer, ODR 2000 (Monsanto Co., Ltd). The measurement was performed at 1 arc degree and 150°C in accordance with ASTM D-2084-81.

Fig.1 Typical SEM photomicrograph of ARBOCEL[®] B 00 showing fiber-like structure.

Table 1 Formulation of short cellulose fiber/silica hybrid filler reinforced natural rubber composite

Ingredients	Parts per hundred of rubber(phr)
Natural rubber (STR 5 L)	100
Stearic acid	1
Zinc oxide	5
TMQ	1
TBBS	0.7
DEG	1.6
Sulfur	2.5
Cellulose fiber/silica	0/20, 10/10 and 20/0

Table 2 Compounding steps of short cellulose fiber/silica hybrid filler reinforced natural rubber composites

Step of mixing	Time (min)
Masticate natural rubber	2
Add stearic acid	1
Add zinc oxide	1
Add TMQ, TBBS	2
Add fillers	7
Add sulfur	2
Sheet out (7 times)	5

2.4 Mooney viscosity (ML(1+4), 100°C) measurements

Mooney viscosity of the rubber compounds was measured using a Mooney Viscometer (SPRI Ltd.), in accordance with ASTM D 1646-94. The test was performed at temperature of 100°C. The samples were pre-heated for 1 min, and Mooney viscosity was then recorded with a total testing time of 4 min.

2.5 Swelling test

Crosslink density was determined using a swelling test. The method was carried out in accordance with ASTM D 471-98. The vulcanizates (10 mm x 10 mm) were accurately weighted and swollen in a mixture of toluene/isooctane (70/30% v/v) at room temperature (30 ± 2°C) until equilibrium, which took 48 h. Thereafter, the specimens were removed from the solvent and blotted lightly with filter paper to remove excess solvent from the surfaces, and weighted. The weight of the specimen before (Q_0) and after solvent immersion (Q_s) was used to determine the swelling ratio ;

$$\text{swelling ratio} = \frac{Q_s - Q_0}{Q_0} \quad (1)$$

2.6 Tensile measurements

The tensile test used dumb-bell shaped test specimens, which were cut from the vulcanized rubber sheet. The test was performed with Hounsfield Tensometer model H 10 KS (Hounsfield Test Equipment), in accordance with ASTM D 412-98. The specimens were stretched at room temperature (25 ± 2°C) with extension rate of 500 ± 50 mm/min. The average tensile properties for each cellulose fiber/silica reinforced natural rubber hybrid

composite were determined from 5 specimens.

2.7 Filler dispersion analyses

Morphological properties of short cellulose fibers were examined by scanning electron microscope (JEOL, model JSM-6510 LA). The fiber surfaces were sputter-coated with a thin layer of gold to avoid electrical charging during the examination. The EDX silicon mapping of hybrid composites was performed with Oxford EDS system (Energy Dispersive X-ray Spectroscopy) attached to the SEM microscope (JOEL, model JSM-5800 LV). The 3 D Microfocus X-ray CT Device (Shimadzu SMX-160 CTS Labo 6, Shimadzu) was used to study the dispersion of silica. The maximum X-ray source output voltage, image solution, and minimum focus size were 35 kV, 512 x 512 pixel and 0.4 μm, respectively. The dispersion of cellulose fiber/silica hybrid filler in the rubber matrix was studied by using N-ARC method developed by Nissan ARC.¹²⁾ At first, the fractured cross-section of each hybrid composite was ground with abrasive paper disc (No. 120 to 1000), and polished with fine Al₂O₃ powder to obtain the ultrafine polished surface. Finally, the N-ARC treated surface was examined using an optical microscope (Nikon Eclipse L-300).

3. Results and Discussions

3.1 Processing properties

The cure characteristics obtained from ODR test (M_L , M_{IH} , T_{s1} and T_{c90}) and Mooney viscosity (ML(1+4), 100°C) of unfilled natural rubber, simply filled and hybridized filling composites are given in Table 3, respectively. The total filler content of each composite was 20 phr, and the hybrid composite contained silica/cellulose fiber ratio of 10/10 phr/phr. Minimum torque (M_L) is closely related to rubber compound viscosity. From Table 3, it was seen that M_L of the unfilled compound increased with the addition of single filler. At the given filler loading, the M_L of the cellulose fiber compound was lower than that of the silica filled-compound. This viscosity difference was explained by the fact that the fibers have much larger size than the silica particles, and thus lower surface area, which resulted in less viscosity thickening effect. When the untreated silica/cellulose fiber hybrid filler was added to rubber, the M_L was not different from that of silica filled compound, but the M_L decreased significantly after the silane surface treatment due to the improved affinity between filler-rubber matrix and better dispersion (later discussed in 3.4).

In addition, Mooney viscosity, as an index of rubber compound viscosity after compounding, is given in Table 3. It should be noted that the use of single filler brought about the increase of the minimum torque (M_L) determined from the rheometer cure curve, but the Mooney viscosity of rubber compound was noticeably reduced with the incorporation of cellulose fibers, where the silica

Table 3 Comparison of cure characteristics (ODR Test) and Mooney viscosity of unfilled natural rubber and different filler reinforced-natural-rubber composites with total filler loading of 20 phr.

Materials	M_L (dN-m)	M_H (dN-m)	T_{sl} (min)	T_{c90} (min)	(ML (1 + 4), 100°C)
Unfilled natural rubber	4.21	18.91	11.49	17.80	30
Fiber composite	4.80	27.30	5.50	10.50	15
Untreated hybrid filler composite	5.70	23.80	5.50	12.50	25
Si 69 treated hybrid filler composite	3.17	26.26	8.60	13.97	20
Silica composite	5.70	26.30	3.80	10.80	42

allowed considerably high viscosity of the compound. The difference in viscosity changes in the fiber compounding system might be explained by the differences in test parameters performed with the ODR and Mooney viscosity tests, i.e. temperature. The Mooney viscosity of unfilled rubber system was normally dropped after compounding due to the reduction of molecular weight caused by mechanical shear, that is, the rupture of rubber chains.¹³⁾ In the presence of silica, the strong filler-filler interaction may generally induce the large viscosity increase. However, it was clear that the simply fiber-reinforced rubber showed much lower Mooney viscosity than the simply silica-reinforced one. Furthermore, the hybridized addition of fibers together with silica lead to much lower compound viscosity compared with the simply silica-reinforced one. From the earlier work of Bai and Li¹⁴⁾, it was also reported that the partial replacement of silica with microcrystalline cellulose in the styrene-butadiene rubber/polybutadiene blends reduced re-aggregation of silica particles during compounding due to the interaction between short fiber and silica. The Mooney viscosity of hybrid composite decreases further when the silane treatment was applied (Table 3). This result indicated that the Si 69 treated hybrid filler provided better mixing process as later discussed. The maximum torque (M_H) is considered as a modulus related index for cured rubber composites.¹⁵⁾ The results showed that the addition of fillers permits the increase of the stiffness of the cured natural rubber due to the insertion of rigid filler into soft rubber, which restricted the mobility of rubber chains.¹⁶⁾ It was also considered that the M_H was independent to any filler systems, such as single filler or hybridized filler (Table 3). Nevertheless, the M_H of the hybrid filler composite increased with Si 69 modification because of the increase in crosslink formation as reported in our previous study.¹¹⁾ Scorch time (T_{sl}) and optimum cure time (T_{c90}) are also closely related to the times both at onset of curing/cross-linkage reaction and at 90% of the cure completion, respectively. Obviously, the scorch and cure times of filled-natural rubber composites were significantly inferior to those of unfilled natural rubber vulcanizates. Similar observations was reported for natural rubber composites.¹⁷⁾ The reinforcement of natural rubber by adding cellulose fibers re-

Fig. 2 Swelling ratio of unfilled natural rubber and different filler reinforced-natural rubber composites with total filler of 20 phr

sulted in longer scorch time (T_{sl}) than that of simply silica-reinforced natural rubber. Furthermore, it is also interesting to note that the hybrid filler-reinforced rubber showed the noticeable increase of scorch time when Si 69 treatment was used. This increase was probably due to the improvement in filler dispersion¹⁸⁾ and also due to the increase in steric hindrance for cross-linking by the presence of bulky groups (triethoxysilylpropyl groups) in long chain Si 69.¹⁹⁾ The hybrid filler composites with the silane treatment also showed longer cure time (T_{c90}) than that of corresponding hybrid composites without the silane treatment. The increase in scorch time would prevent premature cure during compounding and processing using injection molding, extrusion etc.

Basically, the processing operation for cured rubber requires three main steps, i.e., compounding, shaping and vulcanization to obtain the finished products. From our results it was suggested that the use of short cellulose fiber/silica hybrid fillers treated with a silane coupling agent improved various rubber processing properties in the following ways ; (1) lower compound viscosity and (2) fasten curing step, leading to shorter processing time.

This would allow the processing operation simpler by means of reducing overall energy consumption for processing.

3.2 Swelling properties

Figure 2 compares the swelling ratios of different composite types and corresponding natural rubber vulcanizates. Swelling ratio of the vulcanizate, which is inversely related to crosslinking density²⁰⁾, was reduced when cellulose fiber and silica were used for each filler composite system. This was due to the increase in crosslink density and filler-rubber interactions. Compared with the fiber-reinforced rubber, the drop in swelling ratio for the silica-filled vulcanizates was much greater. It was considered that the significant drop in case of silica-filled composites was mainly due to greater filler-rubber interaction, judging from the report that the filler with much smaller particle size has larger surface area and leads to greater filler-rubber interaction.²¹⁾ From Figure 2, it can also be seen that the swelling ratios of composites containing silica solely and untreated hybrid filler showed the same values. On the other hand, the swelling ratio of the hybrid composites was clearly reduced when

Si 69 treated hybrid fillers were combined with. This result implied that the level of the crosslink density of the silane-treated hybrid composite was higher than that of the untreated hybrid one.

3.3 Tensile properties

Figure 3 shows stress-strain curves for various types of natural rubber composites compared with corresponding unfilled natural rubber. It is obvious that the all types of natural rubber composites showed similar stress-strain curve typical of natural rubber vulcanizates, where the strain-induced crystallization of natural rubber was not affected after 400% elongation. However, the stress increase of the rubber composites at elongation of less than 300% was mainly due to the filler reinforcement. This resulted from the increase of crosslink density and filler-rubber interaction as shown by the swelling test (Fig. 2). It is also evident that the load at any given elongation was the higher for the Si 69 treated composites.

Fig. 3 Representative stress-strain curves of unfilled natural rubber and different filler reinforced-natural rubber composites with total filler of 20 phr

Fig. 4 Modulus at 100% elongation of different filler reinforced-natural rubber composites with total filler of 20 phr

Fig. 5 Tensile strength of different filler reinforced-natural rubber composites with total filler of 20 phr

Fig. 6 Elongation at break of different filler reinforced-natural rubber composites with total filler of 20 phr

Figures 4–6 show the tensile properties of each natural rubber composite reinforced with short cellulose fiber, silica and 10/10 hybrid filler under the conditions with and without the surface treatment, respectively. It was obvious that the modulus (Figure 4) and tensile strength (Figure 5) of the untreated hybrid composite laid between those of individually filler-reinforced natural rubber, but both properties were improved when the surface treatment using Si 69 was applied. The improvement levels of the modulus and tensile strength were about 15% and 25%, respectively.

Generally, the mechanical properties for a reinforced

rubber composite is crucially influenced by the filler dispersion and filler-rubber adhesion.^{1), 5), 22)} The Si 69 silane used in this work was bi-functional polysulfidic organosilane that has ability to bond with both of the cellulose fiber and silica surfaces by interacting with hydroxyl (-OH) and silanol functional groups as reported in our previous study.¹¹⁾ Thus, the pretreatment of fiber and silica with Si 69 rendered their surfaces less polar, giving better affinity between cellulose fiber/silica and natural rubber. The enhanced affinity led to better fiber/silica dispersion and increased the adhesiveness between the hybrid fiber/silica and the natural rubber matrix,

Fig. 7 X-ray silicon mapping images of (a) untreated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite and (b) Si 69 treated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite

Fig. 8 3 D micro-focus X-ray scanning images of (a, b) untreated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite (taken from one and three dimensional observations, respectively) and (c, d) Si 69 treated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite (taken from one and three dimensional observations, respectively)

thereby improving rubber reinforcement. The elongation at break of hybrid natural rubber composite was equal to those of single filler composites (Figure 6). However, the elongation at break of hybrid composites treated with Si 69 was slightly decreased. The reason is considered that the silane treatment caused stiffening effect to the hybridized filler composite.

3.4 Filler dispersion

The dispersion of silica filler in the hybrid composites with and without silane treatment was macroscopically evaluated using the X-ray silicon mapping as shown in Figure 7. The variation in brightness over the background represented the localized distribution of silicon element across the sample surfaces. The greater brightness in the images indicated higher silicon concentration. From Figure 7, it is observed that the brightness due to particulate silica aggregate/agglomeration apparently was densely packed and not evenly distributed over the surface without silane treatment (Figure 7 (a)), and furthermore the aggregation/agglomeration decreased with the silane treatment (Figure 7 (b)).

To investigate the effects of the silane treatment on the silica dispersion more in detail, we carried out 3 D microfocus X-ray scanning analysis to acquire three-dimensional silica distribution in the hybrid composites

Fig.9 Volume distribution of silica agglomerates in (a) untreated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite and (b) Si 69 treated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite

with and without Si 69 treatments. The results are shown in Figure 8. From Figure 8(a) – (b), it was seen that the images concerning the spatial distribution of silica particles showed a lot of silica agglomerates in the untreated hybrid composites. At the same time, the silane modification clearly enhanced the dispersion level by reducing the extent of silica agglomeration as shown in Figure 8(c) – (d). In this work, we also estimated the particle volume of agglomerates from the 3 D microfocus X-ray data to obtain the spatial particle-volume distribution of hybridized silica in the untreated and Si 69 treated hybrid filler reinforced natural rubber composites. These results are shown in Figure 9. In this Figure, x-axis shows the volume of silica agglomerates and y-axis shows count number of particles. X-axis shows each agglomerate volume three-dimensionally calculated from 3 D X-ray measurement data. Therefore, in this Figure the largest agglomerate in the pictures (Fig. 8) corresponds to the data positioned at the end of right side of X-axis.

Fig.10 Optical photomicrographs of N-ARC treated surfaces of (a) untreated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite and (b) Si 69 treated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite

The right end of particle volume (x-axis) corresponds to silica agglomerate size of approximately 50–80 μm , whereas the left end is roughly around 1–2 μm of particle size as detectable limit. On comparing the histogram of untreated and Si 69 treated composites, it was obvious that the relative amount of agglomerate, in particular larger ones, was much higher for the untreated hybridized silica reinforced natural rubber. This observation is well in line with the previously obtained elemental maps (Figure 7). However, it should be note that the silicon mapping and 3 D microfocus X-ray images only provide the direct information for the silica dispersion in the hybrid filler composites.

To confirm the dispersion state of the hybridized filler reinforced composites which contained short cellulose fiber, the N-ARC method was carried out. Figure 10 shows the comparison of the optical photomicrographs on the fractured surfaces of the untreated and treated hybrid composites, which were treated by N-ARC polishing method. The thin and long-shaped structure with dimension less than original fiber length (120 μm) was part of cellulose fibers in each composite. The spherical-like

particles having several microns and more in size were silica agglomerates. It was visibly seen that the untreated fibers were aggregated, and the agglomerated silica particles were not uniformly dispersed over the rubber surface (Figure 10(a)). The relatively large agglomerates due to interaction between short fiber and silica were also observed for the hybrid composite with and without the silane treatment (Figure(10 a) – (b)). When the untreated hybrid composite was compared with the treated one, the fiber aggregates were less in number, and the silica agglomerates were much homogeneously dispersed across the Si 69 modified surface (Figure 10 (b)). Furthermore, Figure 11 shows the comparison with higher magnification and better contrast to observe the difference in dispersion between short cellulose fibers and silica particles. In these Figures, cellulose fibers located over the fractured surface were chemically dyed such as Iodine-Potassium Iodine solution only to obtain better contrast between cellulose fibers on the polished specimen surface and silica particles. From these optical microscope observations, larger agglomerations was formed with the mixture of silica particles and cellu-

Fig. 11 Higher magnification and contrast photomicrographs of N-ARC treated surfaces of (a, c) untreated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite and (b, d) Si 69 treated 10/10 cellulose fiber/silica hybrid filler reinforced natural composite

lose fibers in case of the untreated composite, but in case of the Si 69 treated composite the disentanglement between silica-silica, fiber-fiber and silica-fiber was accelerated and more homogeneous dispersion was obtainable.

Based on the observations obtained from various microscopic methods, we concluded that the quality of hybrid filler dispersion increased with silane (Si 69) treatment due to greater surface affinity of Si 69 modified fiber/silica fillers to the natural rubber matrix. As a result, the rubber compound viscosity significantly decreased (Table 3), which thus greatly improved rubber processability, as well as the rubber reinforcement (Figure 3–5).

4. Conclusion

Short cellulose fiber and particulate silica were used as hybridized reinforcing fillers to prepare new natural rubber composites. The cellulose fiber and silica fillers and were also individually used for comparison. The hybridized use of both short fiber and particulate silica showed certain property improvements, such as higher 100% modulus, and lower Mooney viscosity when both simply silica-filled composites and unfilled natural rubber were compared with. However, the tensile strength of the hybrid filler composite was lower than that of the unfilled natural rubber and singly silica-filled composite. The elongation at break of the hybrid filler composite was not much different from those of the unfilled natural rubber and single filler composite. A silane (Si 69) coupling agent was used to modify both of the fiber and silica surfaces. As a result, the surface modification led efficiently to the increase of scorch time, and the reduction of compound viscosity of the hybrid filler-reinforced natural rubber. Furthermore, the tensile modulus and related strength of the hybrid filler composite were also increased with the silane treatment. The results of silicon X-ray mapping (EDX), 3 D microfocus X-ray scanning and N-ARC treatment showed that the Si 69-pretreated hybrid fiber/silica filler was more uniformly dispersed in the rubber matrix when the hybrid filler without Si 69 treatment was compared. This better filler dispersion was the main reason for the improvements in rubber compounding and reinforcement of hybridized composites. From the results presented in this study, the hybridized cellulose fiber/silica filler combined with Si 69 silane coupling agent can be synergistically used as more useful reinforcing substitute to particulate silica for the rubber reinforcement.

Acknowledgment

We are grateful to Mr. M. Natsuhara (Shimadzu, Tokyo, Japan) for technical support on 3 D Micro-focus X-ray scanning analysis.

References

- 1) Pal, P. K. and DE, S. K. : *Rubber Chem. Technol.*, **55**, 1370(1982)
- 2) Hashim, A., Kawabata, N. and Kohjiya, S. : *J. Sol. Gel. Sci. Technol.*, **5**, 211(1995)
- 3) Wolff, S., Görl, U., Wang, M. J. and Wolff, W. : *Rubber J.*, **16**, 16(1994)
- 4) Eggers, H. and Schümmer, P. : *Rubber Chem. Technol.*, **69**, 253(1996)
- 5) Smits, V., Chevalier, P., Deheunynck, D. and Miller, S. : *Reinf. Plast.*, **55**, 37(2008)
- 6) Kraleovich, M. L. and Koeing, J. L. : *Rubber Chem. Technol.*, **71**, 300(1998)
- 7) Mohanty, A. M., Misra, M., and Drzal, L. T. : *Natural fibers, biopolymers, and biocomposites.*, CRC Press, New York, US(2005)
- 8) Kikuchi, N. : U. S. Patent, 5852097(1998)
- 9) Takase, K. : Japan Patent JP 2006 – 282790(2006)
- 10) Lucas, D., Agostini, G., Corvasce, F. G., Hunt, J. O. and Louis, O. : U. S. Patent, 5967211(1999)
- 11) Lopattananon, N., Jitkalong, D. and Seadan M. : *J. Appl. Polym. Sci.*, **120**, 3242(2011)
- 12) Kato, A. and Ishikawa, I. : *Plastics*, **44**, 56(1998)
- 13) Fries, H. and Pandit, R. R. : *Rubber Chem. Technol.*, **55**, 309(1982)
- 14) Bai, W. And Li, K. : *Composites A*, **40**, 1597(2009)
- 15) Teh, P. L., Ishak, Z. A. M., Hashim, A. S., Karger-Kocsis, J. and Ishiaku, U. S. : *Eur. Polym. J.*, **40**, 2513(2004)
- 16) Varghese, S., Kuriakose, B., Thomas, S. and Koshy, A. T. : *J. Adhesion Sci. Technol.*, **8**, 235(1994)
- 17) Lopattananon, N., Panawarangkul, K. Sahakaro and B. Ellis : *J. Appl. Polym. Sci.*, **102**, 174, (2006)
- 18) Dannenberg, E. M. : *Elastomerics*, **113**, 30(1981)
- 19) Poh, B. T. and Ng, C. C. : *Eur. Polym. J.*, **34**, 975(1998)
- 20) Sae-Oui, P., Sirisinha, C., Hatthapanit, K., Thepsuwan, U. : *Polym. Testing*, **24**, 439(2005)
- 21) Alipour, A., Naderi, G., Bakhshandeh, G. R., Vali, H., and Shokoohi, S. : *Intern. Polym. Proc.*, **26**, 48(2011)
- 22) Abdelmouleh, M., Boufi, S., Belgacem, M. N. and Dufresne, A. : *Compos. Sci. Technol.*, **67**, 1627(2007)

セルロース短繊維とシリカ粒子とを複合化して用いた 強化天然ゴムにおけるシラン処理の効果

Natinee Lopattananon・Dolmalik Jitkalong・Manus Seadan・酒 井 忠 基

セルロース短繊維とシリカ微粒子の添加量を総量で 20 phr に制御し、得られた天然ゴム系ハイブリッド複合材の引張り特性、膨潤特性、加工特性をそれぞれの強化剤を単独に添加した場合および天然ゴムだけの場合と比較した。その結果、ハイブリッド複合材の引張り弾性率と引張り強さはそれぞれの強化剤を単独で強化した場合の中間的な特性を示すものの、ムーニー粘度などゴムの加工特性を示す指標には複合化した強化剤の効果が大きく現れており、良好な加工特性の向上が認められた。さらに、この複合強化剤の表面をシラン処理すると、引張り特性および加工特性により大きな改善効果がみられた。そこで、EDX、3D マイクロフォーカス X-線 CT および N-ARC 法でこれらの複合強化剤の天然ゴムにおける分散状態に及ぼすシラン処理の効果を検討した。その結果、複合強化剤にシラン処理を施すとそれぞれの強化剤の分散が良くなっていることが確認できた。そして、天然ゴムの強化に対して、セルロース短繊維とシリカとを複合的に用いるだけでなく、複合強化剤にシラン処理を施すと得られる天然ゴム系ハイブリッド複合材の引張り特性や加工性を大きく向上できることが分かった。