The effect of nanostructured silica synthesis temperature on the characteristics of silica filled natural rubber composite

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Abstract. The processing, curing, mechanical, and morphological characteristics of natural rubber (NR) filled with nanostructured silica (NS) were discussed in this paper. NS was synthesized at 60-90°C using bagasse ash as raw material. NR was mixed with NS using Haake Rheomix equipped with roller rotors. Curing kinetics of NR compounds was studied using the data obtained from a moving die rheometer. Lower compounding temperature and lower compound viscosity were observed with increasing silica synthesis temperature. Highest bound rubber content and modulus at break were found at natural rubber filled with silica synthesized at 70°C. The state-of-mix of the filler was found to increase with increasing silica synthesis temperature. The curing curve obtained showed that the vulcanization kinetics follow autocatalytic model.

1. Introduction
About 60% of world rubber production is used in tire manufacturing. Silica addition into tire compound is widely known to improve the tire rolling resistance [1]. Silica is made through three synthesis routes: precipitation of an aqueous sodium silicate solution (precipitated silica), high-temperature hydrolysis of silicon tetrachloride (fumed silica), and hydrolysis of tetraethylorthosilicate [2,3]. The primary particle diameters of precipitated silica and fumed silica range between 10-80 nm and 5-20 nm, respectively. Smaller primary particle size of fumed silica provides a higher level of reinforcement, but its expensive price limits its use only for silicone rubber and other specialty synthetic rubber. Sodium silicate produce more refined and uniform particle size along with the higher silica concentration than tetraethylorthosilicate [4]. As a reinforcing filler for natural rubber (NR), 15 phr (parts per hundred rubber) silica gives the composite a tensile strength of 27 MPa [2].

Many researchers have tried to use biomass-based silica as a rubber filler. Huabcharoen et al. [5] studied the effect of acid treatment of bagasse ash on the mechanical properties of NR composite. The authors reported that the optimum bagasse ash concentration was 15 phr. Higher bagasse ash decreased the mechanical properties of rubber composites. Zeng et al. [6] modified rice husk ash using a rare earth coupling agent. The modified ash was used as a NR filler by the latex process. The highest tensile strength of 25.96 MPa was obtained at 4 wt% ash content and then dropped to 18.42 MPa at 10 wt% ash
content. Other researchers also found that purification and/or surface modification only gave biomass ash a role as a semi-reinforcing filler [7–9].

Boonme et al. [4] synthesized silica nanoparticle from bagasse ash by the sol-gel method. The average diameter of the particles obtained was 90 nm. The silica obtained has a high filler-filler interaction and non-homogeneous dispersion in the NR matrix thus gave a negative effect on the mechanical properties of composites at a concentration of 10 phr. Jembere & Fanta [10] applied a xerogel from rice husk ash as a replacement of commercial precipitated silica. At a xerogel level of 12 phr, the increase in tensile strength obtained was only 17.5% compared to the unreinforced rubber matrix. Filler agglomeration was the main problem of the small optimum silica concentration and/or mechanical properties in some of the studies above. Commercial rubber products require a silica concentration of 15-100 phr to fulfill the targeted mechanical properties. Agglomeration at high silica levels needs to be minimized by using silica with sufficient reinforcing properties and the addition of a coupling agent [2].

According to our previous work, nanostructured silica (NS) from bagasse ash has the potential as a rubber reinforcing filler at high silica loading. We found lower water content (as silanol) and higher primary particle size of the nanostructured silica with increasing synthesis temperature [11,12]. Filler polarity affects filler dispersion and filler primary particle size influences the surface area that interacts with the rubber. This study was aimed to extend our previous findings on the use of nanostructured silica from bagasse ash as a reinforcing filler in NR. To the best of our knowledge, no report has yet described in detail the influence of silica synthesis temperature on the processing, curing, mechanical, and morphological characteristics of NR/NS composite.

2. Materials and methods
NS was synthesized using bagasse ash as raw material at 60, 70, 80, and 90°C. NR was mixed with NS using Haake Rheomix equipped with roller rotors. NS was synthesized and mixed with NR according to previously published methods as can be seen from Figure 1 [12].

Vulcanization kinetics was studied at 140, 150, and 160°C on a Gotech 3000A moving die rheometer (MDR) according to ASTM D2084-01. Mechanical properties of the vulcanizate were determined using samples with a thickness of 2 mm obtained by compression molding at a temperature of 150°C under a pressure of 14.7 MPa. Mooney viscosity of the compound was measured by a Mooney shearing disk viscometer (MonTech MV3000) according to ASTM D 1646. Mooney viscosity was reported as ML (1+ 4), 100°C. Bound rubber content (BRC) was calculated using the relation [13]
\[
\%BRC = \frac{W_{fg} - W_{\left(\frac{m_f}{m_f + m_p}\right)}}{W_{\left(\frac{m_f}{m_f + m_p}\right)}} \times 100
\]  

where \(W\) and \(W_{fg}\) were the weight of the sample before and after immersion in toluene, respectively. \(m_f\) and \(m_p\) were the weight of silica and rubber in the uncured mix, respectively.

Morphology of the vulcanizate was characterized using an optical microscope (Arcs Video Measuring System) with a 112.5 magnification factor. The fraction of agglomerates area was determined using imageJ software. The stress-strain behavior of the vulcanizate was monitored according to ASTM D 412-06 with dumbbell-shaped samples using a universal testing machine (Tinius Olsen H25K).

3. Results and discussion
The incorporation of NS into NR was performed in a Haake 3000P Rheomix. The torque and compounding temperature in the internal mixer during mixing process was recorded. From Figure 2, it can be seen that the first torque peak curve represents the natural rubber mastication process. The parts for the fast torque increase to the second and third peaks value represent the incorporation of nanostructured silica into the natural rubber. Higher silica synthesis temperature produces shorter incorporation time due to lower surface area and water content [12]. Afterward, a slow decrease in torque values represents the dispersion of the silica [14]. Lower torque and lower compounding temperature are observed with increasing silica synthesis temperature. The torque is proportional to the viscosity of the blends [15]. Lower viscosity could be attributed to the higher dispersion state of filler in rubber [16]. According to Sholeh et al. [12], higher synthesis temperature produces silica with lower surface area, thus resulting in the decrease of the shear force and friction, which results in a substantial decrease in compounding temperature [14].

Fluctuating trend of the torque is attributed to difficulty in incorporating the second portion of the filler (7th min). At synthesis temperature of 60°C, the second portion of the filler was pushed upward to about three-quarter the height of the hopper’s neck. This can be explained as follows. The lower the synthesis temperature, the greater the water content (more polar) [12]. Friction between the silica loaded with the rubber became smaller, resulting in slippage due to differences in polarity between the filler and the elastomer.

![Figure 2. Torque and compound temperature during mixing.](image)
Table 1 shows the effect of silica synthesis temperature on Mooney viscosity. It can be seen that Mooney viscosity decreases with increasing synthesis temperature. A lower viscosity means higher processability [17]. According to Ryu et al. [16], viscosity reduction is due to better dispersion. Sholeh et al. [12] reported that higher synthesis temperature produces silica with lower water content, thus resulting in a decrease of the surface polarity. Silica with lower surface polarity gives a better rubber-filler interaction, which leads to an improvement in the dispersion state.

The results in Table 1 reveal that bound rubber content increases with increasing synthesis temperature from 60°C to 70°C and then decrease from 70°C to 90°C. Although bound rubber content is proportional to the level of filler dispersion, the result doesn’t show the opposite trend to Mooney viscosity. It seems that from 70°C to 90°C, the decrease of bound rubber content with increasing synthesis temperature is attributed to the decreasing surface area of the silica [12].

| Synthesis temperature, °C | Mooney viscosity, MU | Bound rubber content, % |
|--------------------------|---------------------|------------------------|
| 60                       | 30.5                | 33.05                  |
| 70                       | 29.4                | 36.95                  |
| 80                       | 20.8                | 31.75                  |
| 90                       | 16.7                | 27.20                  |

Figure 3 shows images results from the optical microscope. NS agglomerates appear as luminous spots, while the area of well-dispersed silica is shown in black color. It is clear from Figure 3 that the number of visible agglomerates become much smaller with the higher synthesis temperature, thus means better silica macrodispersion. This result corroborate the Rheomix and Mooney viscosity data. The image in Figure 3 was transformed into a black and white image with a given threshold using ImageJ software, then the fraction of agglomerates area was obtained by dividing the total area of agglomerate with a diameter larger than 5 μm by the image area [18]. The calculation result is depicted in Figure 4. According to the classification by Waddell et al. [19], excellent silica dispersion is achieved at agglomerate area less than 2%.

![Figure 3](image_url)

**Figure 3.** Optical images (1395 mm x 1052 mm) obtained by Arcs video measuring system. NS synthesis temperature (a) 60°C, (b) 70°C, (c) 80°C, and (d) 90°C.

To explore the curing behavior of NR/NS compound, the curing characteristics were studied at different vulcanization temperatures. Figure 5 shows curing curves of NR/NS composite at 140, 150, and 160°C. It is clear that vulcanizing curves exhibited three distinct regions. The first region is induction period that provided a time for the compound to easily flow to fill the mold or through a die. Uncrosslinked compound in this region provides the lowest torque on the rheograph. The second region is the curing reaction period during which the crosslinking of rubber is formed. The torque rises towards the maximum value in this region. The third region is the overcure region that happens as an equilibrium or reversion cure behaviors [20]. Equilibrium behavior is shown by a relatively constant torque while reversion cure behavior is shown by a slow decrease in torque values. Shorter induction and curing
reaction region are observed with increasing vulcanization temperature. Reversion begins to appear at a vulcanization temperature of 150°C for compounds filled with silica synthesized at 60 and 70°C (Figure 4(a) and (b)). At 160°C, significant reversion is detected for all compounds. It is well known that NR is susceptible to degradation at high temperature due to its chemical structure.

The percentage of reversion (%R) at 600 min is defined as [21]:\[ %R = \frac{M_H - M_{600}}{M_H - M_L} \times 100 \] where \( M_H \), \( M_L \), and \( M_{600} \) are the maximum torque, minimum torque, and torque at 600 s, respectively. The calculation result of %R is shown in Table 2. It can be seen from Table 2 that %R is found to increase with decreasing synthesis temperature. According to Kok [22], silanol group on silica surface can react with zinc oxide (activator) to form zinc silicate. These reactions can reduce the efficiency of the formation of the zinc-accelerator complex, believed to be responsible for the desulphuration reaction. Lower synthesis temperature produces silica with higher surface area and silanol content [12], thus could resulting in an increase of the zinc silicate formation, which results in an increase in %R.

Detailed curing characteristics at a vulcanization temperature of 160°C are given in Table 2. It shows that scorch time (\( t_{92} \)) increases with increasing synthesis temperature from 60 to 80°C and then decreases from 80°C to 90°C. Both state-of-mix of the filler and silanol content affect on scorch time [2,16]. Based on the silica dispersion result above, scorch time should increase from synthesis temperature 60 to 90°C. However, it is clear from Figure 4 that silica synthesized at 90°C only gives a slightly better silica macrodispersion than silica synthesized at 80°C. Thus it is believed that scorch time at synthesis temperature 80°C is longer than 90°C because the effect of higher silanol content is more dominant. The curing time (\( t_{90} \)) shows a similar trend as scorch time.

The dependence of minimum torque and maximum torque on silica synthesis temperature is also illustrated in Table 2. Compounds having higher silica synthesis temperature give lower minimum torque and higher maximum torque. The result of minimum torque is in line with the result from Mooney viscosity test. The trend of \( M_H \) and \( M_H-M_L \) show that higher silica synthesis temperature gives stiffer vulcanizate and higher crosslink density, respectively.

Vulcanization kinetics model is used to predict the degree of cure at any time-temperature history. The torque obtained from the rheometer is believed to be proportional to the crosslink density of the rubber. Thus the degree of curing (\( \alpha \)) can be obtained from the torque values obtained from rheometer using the relation [20]:\[ \alpha = \frac{M_L}{M_H-M_L} \]
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Figure 5. Curing curve of NR/NS composite at different curing temperatures: NS synthesis temperature (a) 60°C, (b) 70°C, (c) 80°C, and (d) 90°C.

| Synthesis temp, °C | $t_{52}$, s | $t_{90}$, s | $M_L$, Nm | $M_H$, Nm | $M_{H-M_L}$, Nm | $M_{600}$, Nm | %R  |
|-------------------|-------------|-------------|-----------|-----------|----------------|--------------|-----|
| 60                | 38          | 106         | 0.47      | 4.38      | 3.91           | 3.92         | 11.6|
| 70                | 49          | 117         | 0.44      | 4.46      | 4.02           | 4.11         | 8.69|
| 80                | 53          | 120         | 0.29      | 4.74      | 4.46           | 4.40         | 7.68|
| 90                | 49          | 109         | 0.26      | 4.87      | 4.61           | 4.60         | 5.92|

where $M_t$ are the torque values at time $t$. An appropriate kinetic model to describe vulcanization reaction is the autocatalytic reaction model. The follow relationship is assumed [20,23]:

$$\frac{da}{dt} = k \alpha^m (1 - \alpha)^n$$  \hspace{1cm} (4)

Where $k$, $m$ and $n$ denote the rate constant, reaction orders of autocatalytic reaction, and reaction orders of non-autocatalytic reaction, respectively. The parameters $k$, $m$ and $n$ were determined using nonlinear regression analysis, and the results are shown in Table 3. The fitted curves are illustrated in Figure 6. A comparison between the experimental and the model curves was made. Autocatalytic reaction is indicated by the increasing of the reaction rate with the degree of curing and passes through a maximum [23]. The experimental conversion rate values were closely fitted with the model for all samples. It is clear that the rate constant value is increasing with the increase in curing temperature and silica synthesis temperature. Higher synthesis temperature produces silica with lower surface area and
silanol content [12], thus could resulting in a decrease of the zinc silicate formation, which results in an increase in $k$. The rate constant follows the Arrhenius equation below:

$$k = A e^{-E/RT}$$

where $A$ and $E$ are pre-exponential factor and the activation energy, respectively. The calculation result is shown in Table 3.

Table 3. Kinetic parameters of NR/NS composites.

| $T_{\text{synthesis}}, ^\circ\text{C}$ | $T_{\text{curing}}, ^\circ\text{C}$ | $k$, s$^{-1}$ | $m$ | $n$ | $E$, J/mol | $A$, s$^{-1}$ | $R^2$ |
|--------------------------------------|-----------------------------------|--------------|-----|-----|------------|--------------|------|
| 60                                   | 140                               | 0.0350       | 0.836 | 1.93 | 5.66.10$^4$ | 5.27.10$^5$ | 0.937|
|                                      | 150                               | 0.0611       | 0.870 | 1.56 |            |              |      |
|                                      | 160                               | 0.0746       | 0.832 | 1.25 |            |              |      |
| 70                                   | 140                               | 0.0318       | 0.946 | 1.48 | 7.68.10$^4$ | 1.73.10$^6$ | 0.959|
|                                      | 150                               | 0.0648       | 1.00  | 1.56 |            |              |      |
|                                      | 160                               | 0.0891       | 0.899 | 1.36 |            |              |      |
| 80                                   | 140                               | 0.0326       | 0.876 | 1.74 | 7.20.10$^4$ | 4.40.10$^7$ | 0.956|
|                                      | 150                               | 0.0639       | 0.968 | 1.67 |            |              |      |
|                                      | 160                               | 0.0856       | 0.860 | 1.30 |            |              |      |
| 90                                   | 140                               | 0.0347       | 0.800 | 1.65 | 8.06.10$^4$ | 5.69.10$^6$ | 0.965|
|                                      | 150                               | 0.0720       | 0.934 | 1.77 |            |              |      |
|                                      | 160                               | 0.102        | 0.844 | 1.36 |            |              |      |

Figure 6. Reaction rate versus degree of curing: NS synthesis temperature (a) 60°C, (b) 70°C, (c) 80°C, and (d) 90°C.
Uniaxial tension experiments on a NR/NS composite was conducted to obtain the stress-strain curve. It can be seen from Figure 6 that higher synthesis temperature produces stiffer vulcanizate. This result agrees well with maximum torque obtained by rheometer. However, the modulus at break doesn’t follow the same trend with $M_H/M_L$. It is obvious that modulus at break increases with increasing synthesis temperature from 60 to 70°C and then decreases from 70°C to 90°C. The detrimental effect on modulus at break at higher synthesis temperature may be attributed to the higher primary particle diameter of the nanostructured silica [11].

The experimental stress-strain curve was fitted to the Ogden constitutive model as follow [24]:

$$\sigma_1 = \frac{2\mu}{A} \left[ \lambda^{A-1} - (\frac{\lambda}{2})^{A-1} \right]$$

where $\sigma_1$, $\lambda$, $\mu$, and $A$ are the uniaxial stress, stretch in the loading direction, shear modulus, and strain hardening exponent, respectively. Material constants can be determined using a nonlinear regression analysis and the results is shown in Table 4. Figure 7 illustrates that the experimental stress-strain values were closely fitted with Ogden model for all samples.

| Table 4. Ogden constants evaluated from uniaxial tensile stress versus strain response of NR/NS composite. |
|-------------------------------------------------|------------------|------------------|------------------|------------------|
| parameter                                      | Synthesis temperature, °C |
|                                                | 60               | 70               | 80               | 90               |
| $\mu$, MPa                                      | 0.976            | 1.13             | 1.27             | 1.21             |
| $A$                                             | 2.88             | 2.81             | 2.77             | 2.89             |

4. Conclusion

Compounding of NR with NS synthesized at four different temperatures was conducted in an internal mixer. Higher silica synthesis temperature produced shorter incorporation time, lower torque, lower compounding temperature, and lower Mooney viscosity, thus higher processability. Highest bound rubber content was found at NR filled with NS synthesized at 70°C. Images results from the optical microscope revealed that all vulcanizates had excellent NS dispersion with the best state-of-mix was found at NS synthesized at 90°C. Rheometer data showed that scorch time increased with increasing synthesis temperature from 60 to 80°C and then decreased from 80°C to 90°C. Higher silica synthesis temperature gave stiffer vulcanizate, higher crosslink density, and lower percent reversion. However, modulus at break decreased from 70°C to 90°C attributed to the higher primary particle diameter of the
nanostructured silica. The experimental curing and stress-strain curve value were closely fitted with autocatalytic and Ogden model, respectively.

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