Journal of Technical Education Science No.55 (12/2019)
Ho Chi Minh City University of Technology and Education

OPTIMIZATION OF NANOSILICA FABRICATION TECHNOLOGY PROCESS AND ITS APPLICATION IN RUBBER COMPOSITE MATERIAL PRODUCTION

Le Minh Tai
Ho Chi Minh City University of Technology and Education, Vietnam

Received 16/5/2019, Peer reviewed 24/5/2019, Accepted for publication 30/6/2019

ABSTRACT

Rice husk (RH), an inexpensive waste material, was used to produce nanosilica that was then applied to fabricate composite with natural rubber. The optimization of process parameters on the weight of nanosilica using the Taguchi method was performed. Experimental specimens were then made to confirm optimum values for each process parameter. The results indicated that the weight of the optimal nanosilica was improved to 7.9 g with addition of NaOH concentration of 5M and stirring time of 5h from only 10 g of original rice husk. The structural properties of nanosilica were studied by scanning electron microscope. The results of mechanical tests exhibit improvements of tensile strength and elongation by 52.5% and 20.4%, respectively, at 6.0 pphr (part per hundred of rubber) nanosilica as compare to those of the pure polymer specimen. Morphologies of the fracture surface of resulting nanocomposites observed by a field emission scanning electron microscope (FESEM) showed good adhesion between the filler and the resin.

Keywords: *Rice husk; Natural Rubber; Nanosilica; Taguchi method; Nanocomposite.*

1. INTRODUCTION

In recent years, the technology of nanostructure materials is developing at an astonishing speed and is being applied extensively to many materials and system [1]. Polymer/ nano-filler composites have received intense attention become a core focus of nanoscience and nanotechnology [2]. The reinforcement of polymers recently using nano fillers such as silica, clay, carbon nanotube, etc., where dispersion of nanoparticle is better than micro fillers [3].

Natural rubber (NR) with excellent chemical and physical properties has been widely used in various areas [4]. The raw NR is usually reinforced with antiageing agents [5] and inorganic fillers [6] before it is manufactured to products, as its poor ageing resistance and mechanical properties generally could not meet the requirements of applications.

Nanosilica (SiO_2) is produced as an industrial scale to support a growing number of commercial products. It is a high porosity material and has a large high surface area with microstructure network [7]. The nanosilica was used as filler in natural rubber to reinforce its mechanical properties [8], morphological behaviours, and also reduces the cost of natural rubber [9].

Rice husk (RH), a by-product of the multistage processing of rice, is an excellent source of high-grade silica [10]. The presence of silica in RH has been known since 1938 [11], ever since several efforts on preparation of silica from RH by researchers have been known internationally [12].

Many industries have employed the Taguchi method [13] to improve product design and process performance. It has been applied widely in engineering analysis to optimise performance characteristics through the setting of design parameters.

The emphasis of this paper is to optimize the conditions for the preparation of highly purified rice husk ash (RHA), of which nanosilica is then extracted, and to study its properties. Also, the impact of SiO_2 on the mechanical properties and morphology of natural rubber matrix have been investigated.

2. MATERIALS AND METHODS

2.1. Materials

NR used in this study are Standard Vietnamese Rubber was supplied by Dong Nai rubber company. Nanosilica (Figure 1) was fabricated by using precipitation method from rice husk. Zinc oxide, stearic acid, N-cyclohexyl-2-benzothiazyl sulfonamide (CBS) N-isopropyl-N-phenyl-p- phenylenedi amine (IPPD) and sulphur were supplied by Tin Phu company.

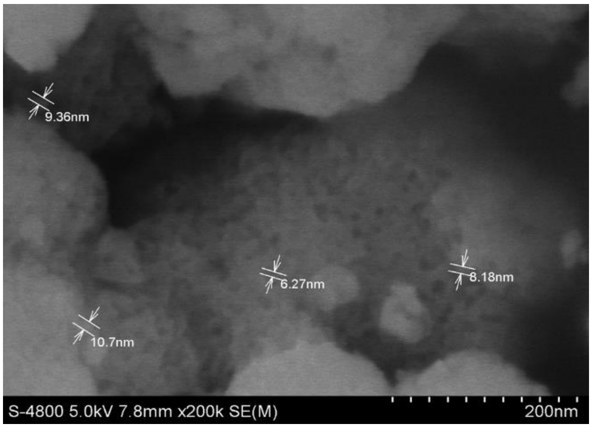


Fig. 1 *SEM image of nanosilica*

2.2 Taguchi method for optimization of process parameters of nanosilica production

2.2.1 Selection of control factors

Control factors are the design parameters which primarily affect the output of the weight of SiO_2. Two control factors on this study, NaOH concentration and stirring time were considered in three levels. A list of the control factors and their levels for mixing parameters are shown in Table 1.

Table 1. *Control factors and levels of process parameters.*

Symbol	Factor	Level		
A	NaOH concentration (M)	3	4	5
B	Stirring time (hour)	3	4	5

2.2.2 Orthogonal array

The number of orthogonal arrays (OA) suggested by the Taguchi method for two factors and three levels is 9 experimental trials. To execute the experimental plan, an L9 the orthogonal array was employed since it is the most suitable array for the conditions being investigated, and the standard $L_9(3^2)$ OA was listed in Table 2.

Table 2. *$L_9(3^2)$ orthogonal array*

Run	A	B
1	1	1
2	1	2
3	1	3
4	2	1
5	2	2
6	2	3
7	3	1
8	3	2
9	3	3

2.2.3 Data analysis

Since the objective of this study is to obtain the highest value of weight, then the larger the better S/N ratio was selected to measure quality characteristics using the Taguchi method, which is defined as:

$$S/N\ (dB) = -10 \log \left(\frac{1}{n} \sum_{i=1}^{n} \left(\frac{1}{y_i} \right)^2 \right) \qquad (1)$$

where n is the number of repeated experiments for each combination of control factors, and y_i are the measured weight of nanosilica at its repeating experiment.

Table 3*. Means of Weight*

Run	A	B	Mean of Weight (g)	S/N ratio
1	3	3	2.12	11.30
2	3	4	3.65	16.02
3	3	5	4.28	17.40
4	4	3	5.41	19.44

Run	A	B	Mean of Weight (g)	S/N ratio
5	4	4	6.23	20.66
6	4	5	7.0	21.67
7	5	3	7.29	22.03
8	5	4	7.62	22.41
9	5	5	7.9	22.72
Average			5.72	19.29

2.3. Preparation of Nanocomposite

Natural rubber was compounded with nanosilica filler at 0-10 pphr. The dispersion of nanosilica in the natural rubber matrix was conducted by a sonication method, and a high-speed shear mixer was used for mixing the curing agent and resin. The compounds were vulcanized into test sheets using a hot press moulding machine at 160^0C with respective cure time and the pressure of 1000 psi. Table 4 shows the function of materials used and its loading.

***Table 4**. Rubber formulation and its functions*

Materials	pphr	Functions
Natural rubber	100	elastomer/matrix
Zinc Oxide	5	Activator
Stearic axide	2	Activator
nanosilica	0-2-4-6-8-10	Filler
CBS	1	Accelerator
IPPD	2	Anti-oxidants
Sulphur	2.5	Crosslink agent

2.4 Characterizations

2.4.1 Tensile Test

For tensile test, the specimen with 2 ± 0.2 mm thickness was cut using dumb-bell die following ASTM D 412-D. The test was carried out at 500 mm/min and the gauge length was 50 mm. Five samples were tested for each set of conditions using the Instron 5566 (Figure 2) under ambient condition 24 ± 2^0C and the humidity of 52%. Tensile strength, elongation at break were averaged and reported.

***Fig. 2** Tensile Tester of INSTRON 5566 – CN 2081*

2.4.2 Scanning elecontron microscopy

Scanning elecontron microscopy (SEM) has been used to study the morphology of the samples prepared. The tensile fracture surface of the samples were tested with acceleration voltage 10 kV and magnification 50X using Zeiss scanning electron microscope, type Supra 35 VP.

3. RESULTS AND DISCUSSION

3.1 Results from Taguchi analysis

The weight of nanosilica was measured in each of three trials. The effect of the process parameters [based on $L_9(3^2)$ OA] on the weight of nanosilica is shown in Table 3. According to the measured results, the highest mean value and *S*/*N* ratio of the weight of nanosilica achieved were 7.9 g and 22.72 dB, respectively. Compared to the initial combination (trial no. 1), the mean values were increased by approximately four times. This condition confirmed that the process parameters selected significantly improved the weight of nanosilica. Improving the weight using an efficient method is the main issue of this study.

***Table 5.** Mean S/N ratios for weight*

Parameter	Level 1	Level 2	Level 3	Effect	Rank
A	14.91	20.59	22.39	7.48	1
B	17.59	20.36	20.60	3.01	2

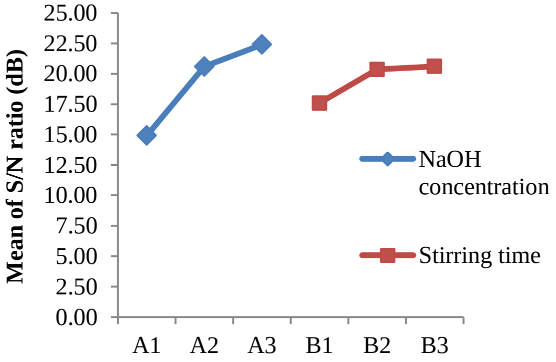


***Fig. 3** Effect of parameters on weight of nanosilica*

The mean of the *S*/*N* ratio for every control factor is represented in Table 5. Table 5 shows the effect of each parameter on the weight of the nanosilica. The effects of control factors on the *S*/*N* ratio and with their corresponding levels are shown in Figure 3. Since a higher *S*/*N* ratio means better quality characteristics (i.e., higher weight), the optimal combination of control factor levels obtained were A_3B_3.

3.2 Confirmation experiment

A confirmation experiment is the final step used by the Taguchi method to examine quality characteristics. Figure 3 shows the optimal levels of control factors determined as A_3, B_3 and used as an additive model to predict the S/N ratio obtained by the confirmation experiment. The examination model shows that the total effect, resulting from two factors, is equal to the summation of every individual effect. Since all factors used provided significant influences on the S/N ratio, predictions can be calculated as:

$$\varphi_{predict} = \zeta + (A_3 - \zeta) + (B_3 - \zeta) \qquad (2)$$

where ξ is mean value of total S/N ratio, and A_3, B_3 are the S/N ratio on each significant level.

$\zeta = 19.29$ as shown in Table 3

$$\varphi_{predict} = \zeta + (A_3 - \zeta) + (B_3 - \zeta)$$

$$\varphi_{predict} = 19.29 + (22.39 - 19.29)$$

$$+ (20.60 - 19.29) = 23.70 \text{ (dB)}$$

$\varphi_{predict}$ value (23.70 dB) shows close value compared to the optimal combination obtained which was 22.72 dB, meaning that the additive model is suitable to predict the value of optimal combination levels (A_3B_3). Table 6 shows that the mean of the weight of the nanosilica for initial combination (A_1B_1) and the optimal combination (A_3B_3) were 2.12 g and 7.9 g, respectively. Compared to the initial combination, the mean of the weight was increased by approximately four times.

***Table 6.** Comparison of the weight of nanosilica*

	Level	Mean of weight (g)	Mean of S/N for weight (dB)
Initial combination	A_1B_1	2.12	11.3
Optimal combination	A_3B_3	7.9	22.72

3.3 Results and analysis from fabrication and characterization

3.3.1. Tensile test

Tensile strength and elongation at break were shown in Table 7. The results showed that, tensile strength increased with increasing nanosilica content up to 6.0 pphr. Hence, the optimum loading of nanosilica filler is chosen at 6.0 pphr.

***Table 7.** Mechanical properties of rubber vulcanizates*

Nanosilica (pphr)	Tensile Strength (MPa)	Elongation at Break (%)
0	19.54	815.42
2	20.5	890.75
4	23.11	950.54
6	29.8	981.77
8	22.03	880.86
10	18.15	820

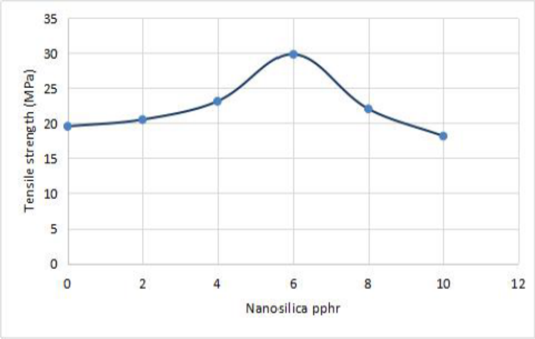


***Fig. 4** The effect of nano silica on tensile strength of recipe*

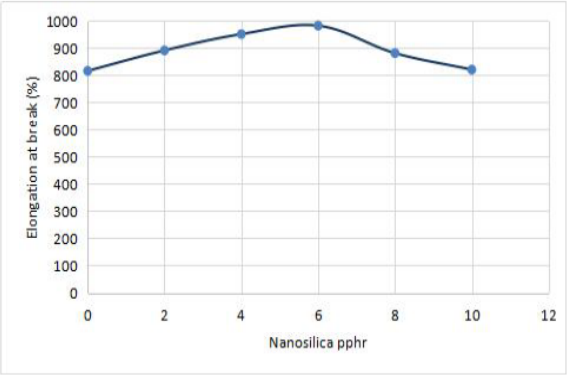


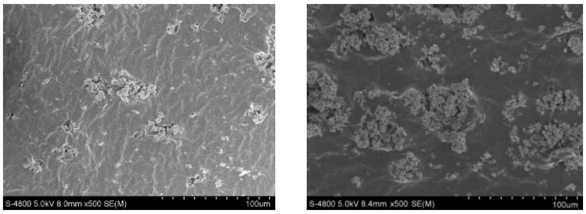
***Fig. 5** The effect of nano silica on elongation property of recipe*

Addition of small quantity of nano silica (less than 6.0 pphr) shows an increase in the tensile strength. As the concentration increases, tensile strength decrease (Figure 4). Such behavior can be explained that in case of small quantities, particles will be filled the spaces between rubber chains, thus gave a rigid structure with better tensile strength (29.8 MPa). While in high quantities of nano silica aggregate occurs in rubber matrix, this weakening the bond between chains and decrease the tensile strength.

The elongation property increases with the addition of small quantities of nanosilica at less than 6.0 pphr (Figure 5), because the diffusion of very fine nano silica through the rubber chains and support the rubber chains so enhanced stretching which reflect on elongation. As an increase the quantities of nano silica reduced the elongation property. This is due to the rubber is highly stretching so that when very fine particles fill the spaces, it will restrict the movement of chains and then decrease elongation property.

3.3.2. Scanning Electron Microscopy

Figure 6 showed the fracture surface of compounds without filler was smooth compared to compounds with 6.0 pphr of nanosilica filler. The pattern indicated that the fracture surface was many layers because of the strong interfacial adhesion. It means that 6.0 pphr of nanosilica have a good interaction between matrix-filler and filler-filler.



(a) (b)

***Fig. 6** Tensile fracture specimens filled with nanosilica at differents loading: a (2.0 pphr), b (6.0 pphr) with acceleration votage 10KV*

4. CONCLUSIONS

Optimization of the process parameters on the weight of nanosilica using the Taguchi method was performed. Characterization of the mechanical properties of natural rubber composite reinforced by nanofiller (SiO_2) was also conducted by using a tensile test. Morphologies of the fracture surface of resulting nanocomposites were observed by a FESEM. The results are as follows:

The Taguchi analysis indicated that NaOH concentration, stirring time were the control factors having decisive roles for the weight of nanosilica.

This research indicated that the weight of resulting optimal nanosilica was improved by up to 7.9 g with the NaOH concentration of 5 M and stirring time of 5 h from only 10 g of original rice husk. In addition, with the SEM images of the tensile fracture surface of SiO_2/NR composite, a good adhesion between the nanosilica and the resin can be observed.

The composites containing a natural rubber and differing amounts of the filler (nanosilica) were successfully synthesised by a hot press casting technique. It can be concluded that vulcanizates containing 6.0 pphr of nanosilica fillers give better overall mechanical properties and short optimum cure time. Better filler dispersion and strong interfacial adhesion has contributed for better mechanical properties. At 6.0 pphr of nanosilica is optimum percent which gives better tensile strength, and elongation at break give 29.8 MPa and 981.77 % respectively.

The novelty of the current study expected that the experimental results will lead to the offering of a low-cost, high-strength and sustainable material for applications in the industry of automobile’s tire manufacturing.

ACKNOWLEDGMENTS

The study was supported by Science and Technology Incubator Youth Program, managed by the Center for Science and Technology Development, Ho Chi Minh Communist Youth Union, the contract number is “No. 01/ HĐ-KHCN-VƯ”

REFERENCES

[1] M. Choolaei, The effect of nanosilica on the physical properties of oil well cement, Materials Science and Engineering: A 538 (2012) 288-294.

[2] P.B. Sarawade, Production of low-density sodium silicate-based hydrophobic silica aerogel beads by a novel fast gelation process and ambient pressure drying process, Solid State Sciences, 12 (2010) 911-918.

[3] S. Jacob, Reinforcing effect of nanosilica on polypropylene–nylon fibre composite, Materials Science and Engineering: B, 168 (2010) 245-249.

[4] K. Sanguansap, T. Suteewong, P. Saendee, U. Buranabunya, and P. Tangboriboonrat, Composite natural rubber based latex particles: a novel approach, Polymer, 46 (2005) 1373-1378.

[5] J. K. Kurian, N. R. Peethambaran, K.C. Mary, and B. Kuriakose, Effect of vulcanization systems and antioxidants on discoloration and degradation of natural rubber latex thread under UV radiation, Journal of Applied Polymer Science, 78 (2000) 304-310.

[6] H. H. Cai, S. D. Li, T. G. Rian, H. B. Wang, and J. H. Wang, Reinforcement of natural rubber latex film by ultrafine calcium carbonate, Journal of Applied Polymer Science, 87 (2003) 982-985.

[7] M. J. van Bommel and A. B. de Haan, Drying of silica aerogel with supercritical carbon dioxide, Journal of Material Science, 29 (1994) 943-948.

[8] J. H. Chen, Interfacial enhancement of nano-SiO_2/polypropylene composites, Composites Science and Technology, 69 (2009) 252-259.

[9] O. H. Lin, Z. A. Mohd Ishak, and H. M. Akil, Preparation and properties of nanosilica-filled polypropylene composites with PP-methyl POSS as compatibiliser, Materials & Design, 30 (2009) 748-751, 2009.

[10] Real, C, Alcala, MD, Criado, JM: Preparation of silica from rice husks. J. Am. Ceram. Soc. 79 (1996) 2012.

[11] Martin, JI: The desilification of rice hull and a study of the products obtained. Lousiana State University, MS thesis (1938)

[12] Yalçin, N, Sevinç, V: Studies on silica obtained from rice husk. Ceram. Int. 27 (2001) 219.

[13] Ross, S.H. Taguchi Techniques for Quality Engineering, 2nd ed., (1996) McGraw-Hill, New York.

Corresponding author:
Le Minh Tai
Ho Chi Minh City University of Technology and Education
Email: tailm@hcmute.edu.vn