Corn Cob Powder (CCP) Filled Natural Rubber (NR) Composites with Si69 as Coupling Agent: Effect of Si69 Content on Properties of the Composites

Sunan Saikrasun[a] and Supalak Attharangsan[a]*

Received June 20, 2021; Revised June 26, 2021; Accepted June 26, 2021; Published online: June 30, 2021

Abstract

Corn cob is an agro-waste produced in abundance annually in Thailand usually with little utilisation and incinerated for disposal. This study aims to employ corn cob in the form of corn cob powder (CCP) for usage as filler for natural rubber (NR) in bio-based composites, which in contrast to conventional fillers for NR, is sustainable. Altogether, coupling agent is an essential ingredient for the enhancement of adhesion between the polar lignocellulosic filler (CCP) and NR matrix. In this work, bis-(3-triethoxysilylpropyl) tetrasulphane (or Si69) was used as coupling agent for corn cob powder (CCP) filled natural rubber (NR) composites, which was varied from 0 to 5 phr, i.e. 0, 1, 1.5, 2, 3 and 5 phr. The effect of Si69 content on curing characteristics, tensile properties, fatigue life, morphology and rubber-filler interaction of the CCP filled NR composites was investigated. The results show that the listed mechanical properties are enhanced with increasing Si69 content up to an optimal of 2 phr due to the improved adhesion. However, there is no significant effect of Si69 content on the scorch time and cure time. Potential applications of this bio-composite include anti-slip pads, shockproof material and furniture rubber leg caps.

Keywords: Natural rubber; Corn cob; Composite; Silane; Mechanical properties

1. Introduction

Nowadays the subject of sustainable development and global warming is a significant determinant in the course of all kinds of development. In regards to polymer composites, the usage of bio-based materials appears to be a superior solution over petroleum-based materials owing to its advantages such as biodegradability, natural abundance, renewable character, recyclability, environmental safety, low density and cost (Kabir et al., 2012; Kengkhetkitet & Amornsakchai, 2014; Zhou et al., 2015).

Among the types of rubber, natural rubber (NR) is one of the most important and widely used in the rubber industry. Commercial NR has been only produced from a single species of tree – Hevea brasiliensis, commonly known as the Para rubber tree. Due to its excellent properties as compared to synthetic rubbers including high elasticity, resilience and toughness, the utilisation of NR as polymer matrix for creating composites has been a great interest for researchers. Nevertheless in practice, the addition of filler to NR is still necessary for the reinforcement of the properties of NR to suit its further usage. Carbon black and silica are the major reinforcing fillers for NR. Despite that these fillers are able to significantly enhance the properties of NR such as strength, stiffness and hardness, it is well acknowledged that they do not satisfy the concept of sustainable development, and rather contribute to global warming.

Over the past two decades, numerous academic and industrial research activities have paid attention to the employment of cellulose obtained from agricultural waste for use as filler of polymer composites. Various kinds of agricultural wastes such as pineapple leaf (Kengkhetkitet & Amornsakchai, 2014), kenaf fiber (Asyraf et al., 2021), pineapple leaf/kenaf fiber (Asim et al., 2018), wheat bran (Formela et al., 2016), bowstring hemp (Osabohien & Egboh ,2008), sisal fiber/oil palm (Jacob et al., 2004), rice husk (Maziad et al., 2009) have

[a] Creative Chemistry and Innovation Research Unit, Center of Excellence for Innovation in Chemistry, Department of Chemistry, Faculty of Science, Mahasarakham University, Mahasarakham 44150, Thailand
*Corresponding author email: sunan.s@msu.ac.th, supalak@msu.ac.th * Telephone number: 66-0808625559

been studied for their potentials as reinforcing filler. As Thailand is an agricultural country, the large amounts and varieties of agricultural wastes produced annually offers a broad selection of cellulosic materials for studies.

Corn cob (CC) is one interesting agro-waste that has not been studied much. Thailand has produced more than 4.5 million tons of corn for animal feed between the years 2019 to 2020 alone (Office of Agricultural Economics, 2021). The processing of corn into animal feed results in large quantities of CC as wastes, where some portions could be used for energy development, for instance as biomass or briquette fuel. However, the remaining portions of CC waste are usually disposed by incineration, which inevitably promotes air pollution and global warming. Therefore, this study focuses on taking advantage of CC as filler in NR.

Nonetheless, it is known that the limited compatibility between hydrophilic hydroxyl groups of lignocellulosic fillers and hydrophobic rubber matrix as well as poor dispersion quality of the fillers in the matrix are the main drawbacks of the use of these plant-based fillers. For these reasons, the mechanical properties of their composites are inferior and the usage of these materials as fillers is also limited. To overcome these problems, various chemical and physical approaches have been carried out to improve adhesion between the rubber and filler particles as well as the filler dispersion quality (Chanda et al., 2015; Fröhlich et al., 2005; Kabir et al., 2012; Lee et al., 2009).

Among those approaches, the use of coupling agents has been extensively utilised to improve the interfacial adhesion between filler particles and matrix since it is very effective and feasible in real practice. The coupling agents possess two reactive groups, where one reacts with the hydroxyl groups of the filler while the other reacts with the matrix. Thus, chemical bridges between the filler and matrix could be formed, leading to better mechanical properties of the composites. Among several kinds of coupling agents, silanes have been widely applied for lignocellulosic materials filled polymer composites (Xie et al., 2010) such as short natural-fiber reinforced polyethylene and natural rubber composites (Abdelmouleh et al., 2007), bamboo fiber filled NR composites3, poly(lactic acid) (PLA) bio-based composites (PLA/newspaper fibers/talc hybrid composites) (Huda et al., 2007).

In this study, bis-(3-triethoxysilylpropyl) tetrasulphane (or Si69) was used to improve the adhesion between CCP and NR matrix as well as the quality of filler dispersion. Si69 is an effective and extensively used coupling agent for composites that are filled with polar fillers such as silica. Likewise, CCP is a cellulosic material and also polar. Besides that, Si69 is in the form of a pellet, which makes it suitable for compounding. Hence, Si69 was selected to be used as the coupling agent in this study. Furthermore, the semi-efficient vulcanization system (semi-EV system) was also used in this study, so the quantities of all rubber additives applied were in correspondence with the semi-EV system, as shown in the formulation of composites (Table 1). The purpose of this work is to study the effect of Si69 content on curing characteristics, mechanical properties, rubber-filler interaction, and morphology of the composites as well as to optimize the quantity of Si69 for CCP filled NR composites.

2. Materials and Methods

2.1 Materials

STR 5L grade natural rubber was obtained from a supplier in Bangkok, Thailand. Corn cob was collected from cultivation areas in Khon Kaen Province, Thailand, while bis-(3-triethoxysilylpropyl) tetrasulphane (Si69) was supplied by Merck Co. Ltd., Thailand. Other chemicals used in the rubber composites such as zinc oxide, stearic acid, sulphur, N-cyclohexyl-2-benzothiazole sulphenamide (CBS) and N-isopropyl-N´-phenyl-p-phenylenediamine (IPPD) were all purchased from Bayer Co. Ltd., Thailand and used as received without further purification. Toluene was acquired from Merck Co. Ltd., Thailand.

2.2 Preparation of corn cob powder

The collected corn cob was first washed with tap water, chopped into small pieces and sun-dried for approximately three to five days. Once thoroughly dried, it was ground using food blender and then sieved with an Endicott's sieve. The resulting corn cob powder (CCP) was stored in an airtight container.

2.3 Preparation of CCP filled NR composites

The formulations of the CCP filled NR composites are presented in Table 1. The CCP was dried in an air oven at 105 °C for 24 h to expel moisture before use. Mixing was carried out using a laboratory-sized (160 mm×320 mm) two-roll mill maintained at approximately 70 °C according to ASTM D 3184. After mixing, all rubber composites were stored in plastic bags and kept in the freezer for at least 24 h before further tests.

2.4 Characterization

2.4.1 Determination of curing characteristics

The curing characteristics such as scorch time, cure time as well as maximum torque of the composites were evaluated at 150 °C using a Monsanto Moving Die Rheometer (MDR 2000). About 10 g of each rubber compound were used in this experiment.

2.4.2 Tensile test

The rubber composites were compression moulded at 150 °C in order to form 2 mm thick sheets according to the respective cure times determined by MDR 2000. Dumbbell-shaped samples were then cut out from the sheets. The tensile testing procedure was carried out according to ASTM D 412. The tensile properties in terms of tensile strength, elongation at break and modulus at 100% and 300% elongation were determined using a universal tensile testing machine (Instron 5567A) at room temperature (25±2 °C) with a crosshead speed of 500 mm/min along the grain direction. Five specimens were used for each test. The average of five specimens was reported for each tensile property.

2.4.3 Fatigue life measurement

The rubber composites were compression moulded at 150 °C according to their respective cure times to form rectangular sheets of 22.9×7.6×0.15 cm with beaded edges. Individual dumbbell samples were then cut out at right angles to the grain using a BS type E dumbbell cutter. The fatigue life of the rubber composites was performed using Monsanto Fatigue to Failure Tester at 25±2 °C. The samples were subjected to repeat cyclic strain at 100 rpm with an extension ratio of 1.61. Six specimens were used to measure the fatigue life of all composites. The fatigue life in kilocycle (kc) for each sample was calculated as the Japanese Industrial Standard (JIS) average, which was obtained from the four highest values recorded using the formula (1):

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C+D) \quad (1)$$

where A is the highest value followed by B, C and D.

2.4.4 Rubber-filler interaction measurement

Swelling test with toluene employed as the liquid medium was also used to investigate the rubber-filler interaction of the composites. Each test piece of dimension 30mm × 5mm × 2mm was weighed (recorded as original weight) and immersed in a glass vessel containing toluene (30 ml). The vessels were kept in the dark at 25 °C until equilibrium swelling was achieved,

Table 1. The compound formulation of CCP filled NR composites with the Si69 as a coupling agent

Ingredient	Loading (phr*)
NR (STR 5L)	100
CCP	10
Zinc oxide	1.5
Stearic acid	1.5
CBS	1.9
IPPD	2.0
Sulphur	1.6
Si69	0, 1, 1.5, 2, 3, 5

* phr: parts per hundred of rubber

which took 72 hours. The specimens were then taken out from the vessels and wiped with tissue paper to remove the excess toluene on the surface of the samples. The swollen specimens were reweighed (recorded as swollen weight). After weighing, the test pieces were dried in an air oven at 60 °C until constant weight could be obtained (recorded as dried weight). The Lorenz and Parks (Lorenz & Parks, 1961) equation (2) has been applied to determine the rubber-filler interaction.

$$\frac{Qf}{Qg} = ae^{-z} + b \quad (2)$$

where Q is defined as grams of toluene uptake per gram of rubber hydrocarbon. In our study, the Q is calculated by equation (3).

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100/\text{Formula weight}} \quad (3)$$

The subscripts f and g in equation (2) refer to filled and gum rubber composites, respectively. Z is the ratio of weight of filler to rubber hydrocarbon in the rubber composites, while a and b are constants. The higher the Qf/Qg values, the lower the extent of interaction between the filler and the rubber matrix.

2.4.5 Scanning electron microscopy

The morphological study of the tensile fracture surfaces of the CCP filled NR composites were evaluated using scanning electron microscope (FESEM, ZEISS SUPRA 35 VP). The test specimens were mounted on aluminium stubs and sputtered with a thin layer of gold to eliminate electrostatic charging during testing.

3. Results and discussion

3.1 Curing characteristics

The effect of Si69 loading on the scorch time (t_{s2}) and the cure time (t_{90}) of CCP filled NR composites is shown in Figure 1. It was found that for a fixed content of CCP at 10 phr, both curing properties changed very slightly with the increase of Si69. There were no significant differences in the scorch time and the cure time. According to Poh and Ng (Poh & Ng, 1998) for temperature higher than 140 oC, the scorch time is virtually independent of Si69 concentration since thermal energy at high temperature is sufficient to overcome the activation energy of vulcanization. In this experiment, the rubber compounds with various quantities of Si69 were vulcanized at 150 oC. At this temperature, the thermal energy supplied is high enough to easily overcome the activation energy of vulcanization. Hence, a significant effect of Si69 on the scorch time could not be observed. Yan et al. (Yan et al. 2004) also reported similar results that at high temperatures, the dependence of the scorch time on the Si69 concentration is less significant.

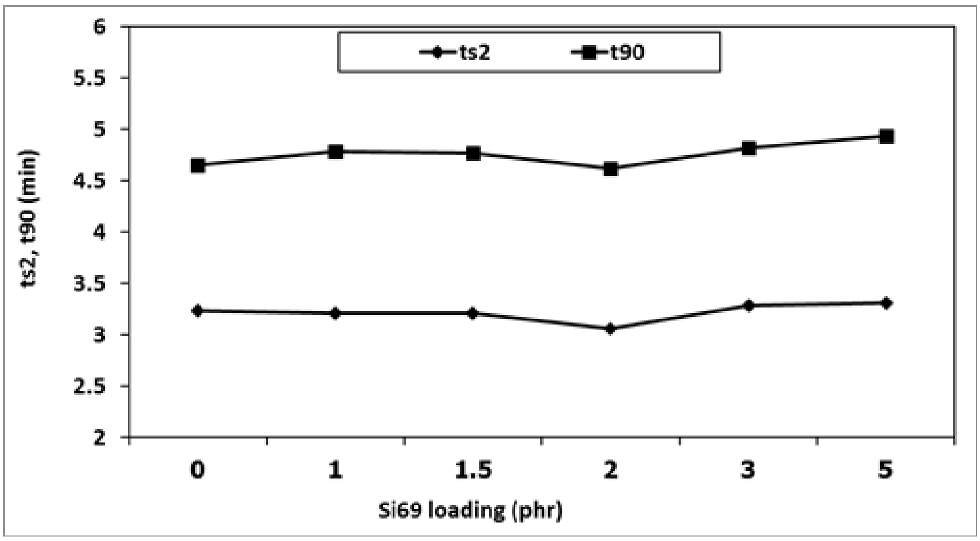

Figure 1. Effect of Si69 loading on scorch time (t_{s2}) and cure time (t_{90}) of the CCP filled NR composites

Figure 2 presents the influence of Si69 loading on maximum torque of the CCP filled NR composites. It can be seen that the maximum torque increased continuously with increasing Si69 loading. Since the maximum torque is a measurement of stiffness or shear modulus of the fully vulcanized sample, the stiffness of the rubber composites increases with the increment in formation of crosslinks during curing process. Thus, this result indicates that Si69 content could enhance the degree of crosslink density of the NR composites. This observation may be mainly attributed to sulphur atoms in Si69 molecules as shown in Figure 3. As each Si69 molecule has four sulphur atoms, higher Si69 loading provides a greater number of sulphur atoms for vulcanizing reaction. This phenomenon is known as "sulphur contribution effect". Accordingly, a greater degree of crosslink density can be achieved with increasing Si69 content, which consequently leads to higher values of maximum torque.

In addition, the role of Si69 as coupling agent in the improvement of the adhesion between CCP particles and NR also imparts the increase of the maximum torque of the NR composites. Generally, better interaction between the filler and rubber matrix leads to a

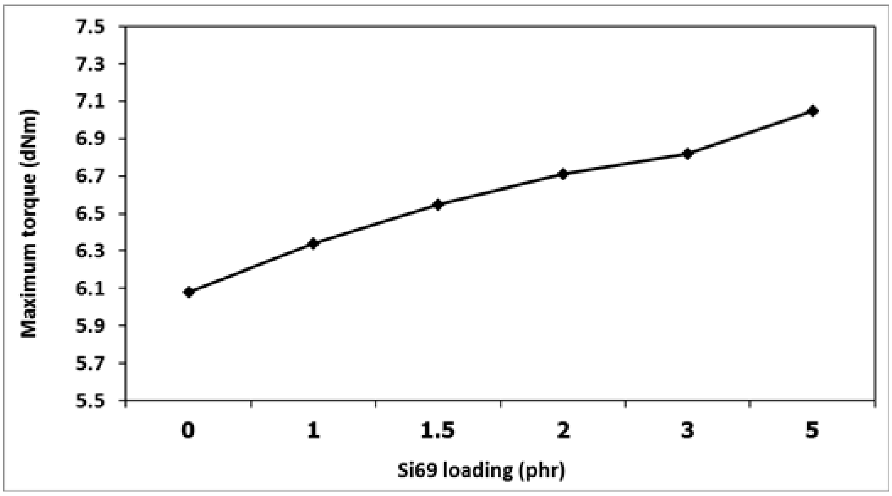

Figure 2. Effect of Si69 loading on maximum torque of the CCP filled NR composites

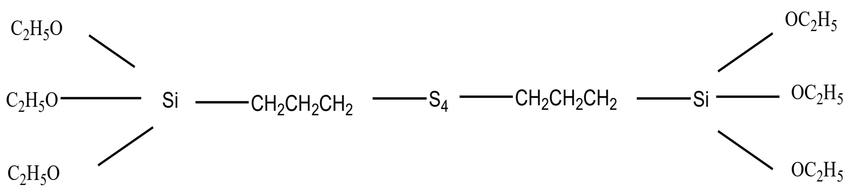

Figure 3. Structure of Si69

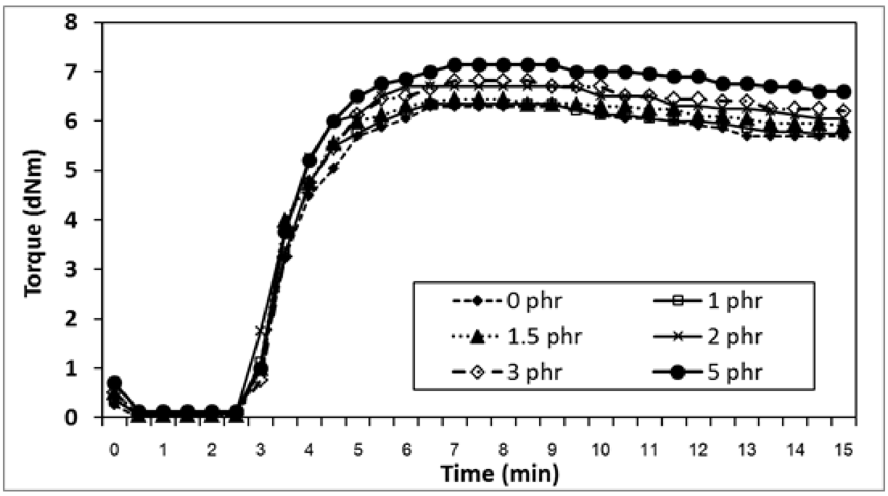

Figure 4. Rheographs of the RHP filled NR composites at different Si69 content

greater number of the crosslink, which reduces molecular mobility of the rubber chain and results in higher stiffness (or maximum torque).

Figure 4 represents rheographs of the CCP filled NR composites at different Si69 content. It was found that as Si69 loading is increased, higher maximum torque and higher torque during the test time were obtained. Moreover, all composites also show reversion tendencies in vulcanization.

3.2 Rubber-filler interaction

Figure 5 reveals the effect of Si69 loading on rubber-filler interaction of the CCP filled NR composites. Fundamentally, a lower Qf/Qg value implies greater rubber-filler interaction. From Figure 5, it can be concluded that the rubber-filler interaction of the composites increased with the increase in Si69 loading. Since Si69 possesses tetrasulphane and ethoxy groups in its molecules, the tetrasulphane groups can react with rubber molecules to form crosslinks whereas the ethoxy groups can react with hydroxyl groups on the surface of CCP to form hydrogen bonds. Therefore, these bonds could improve the rubber-filler interaction of the NR composites.

3.3 Tensile properties

Figure 6 shows the influence of Si69 loading on tensile strength of the CCP filled NR composites. The result exhibits that the tensile strength increased gradually with increasing Si69 loading (up to 2 phr) and tends to decrease afterwards. Hence, the addition of Si69 at 2 phr provided the highest tensile strength for the NR composites. The increase of the tensile strength with increasing Si69 up to 2 phr is due to the enhanced rubber-filler interaction from the performance of Si69 as coupling agent. This ultimately results in the reinforce-

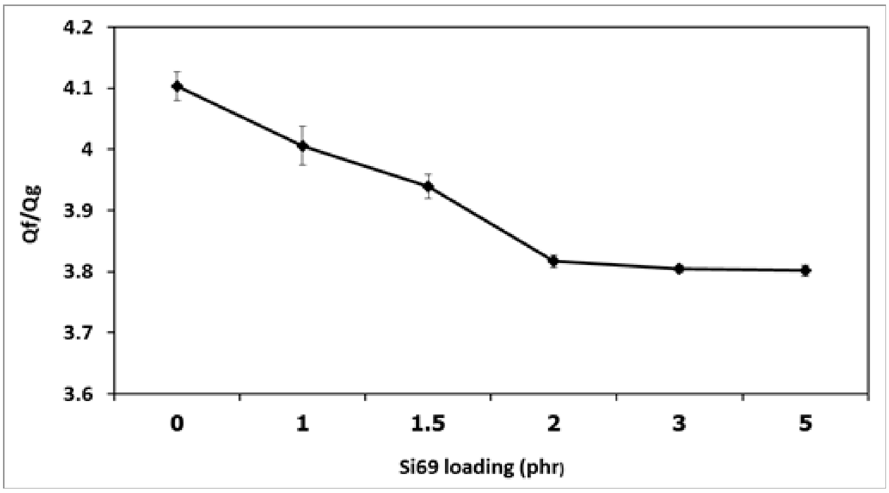

Figure 5. Effect of Si69 loading on rubber-filler interaction of the CCP filled NR composites

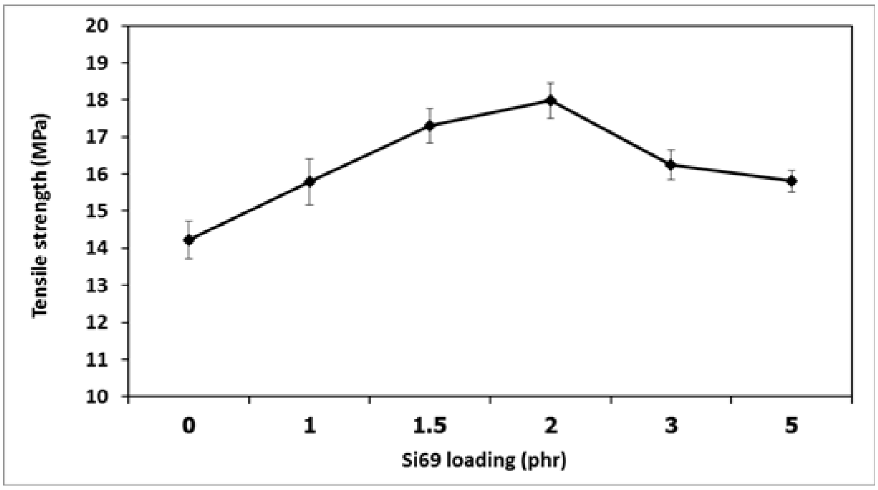

Figure 6. Effect of Si69 loading on tensile strength of the CCP filled NR composites

ment in tensile strength of the NR composites. Besides performance as coupling agent which improves the rubber-filler interaction, according to the sulphur contribution effect, Si69 can also contribute sulphur atoms to the NR matrix for vulcanization. This also promotes greater degree of crosslink density that consequently amplifies the tensile strength of the NR composites. The reduction in the tensile strength of the NR composites containing high loading of Si69 (more than 2 phr) is mainly due to plasticizing effect of excessive Si69. Moreover, the excessive crosslink density from sulphur contribution of Si69 which is beyond the optimum value can also cause the reduction in the tensile strength (Sae-oui et al., 2005; Sae-oui et al., 2006).

Figure 7 and 8 show the effect of Si69 loading on moduli at 100% elongation (M100) and modulus at 300% elongation (M300) of CCP filled NR composites respectively. From the results, it was found that both properties showed similar trend as shown by the tensile strength result. The increase in both moduli were pronounced at low Si69 contents (1-2 phr). Beyond that, at higher Si69 loading (3 and 5 phr), the moduli dropped significantly. Since the modulus of the rubber composites is directly proportional to the degree of crosslink density, the increase in crosslink density with increasing Si69 loading contributes to the increment in the moduli. At high quantity of Si69 (3 and 5 phr), both moduli of the CCP/NR composites showed a decreasing trend. This observation is mainly attributed to the plasticizing effect of excessive Si69.

The effect of Si69 loading on elongation at break of the CCP filled NR composites is depicted in Figure 9. It was found that the elongation at break of the NR composites decreased continuously with increasing

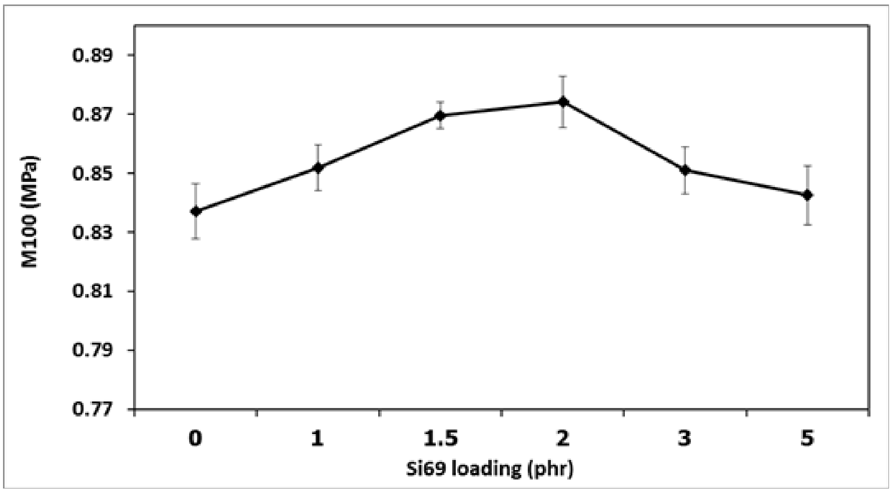

Figure 7. Effect of Si69 loading on modulus at 100% elongation (M100) of the CCP filled NR composites

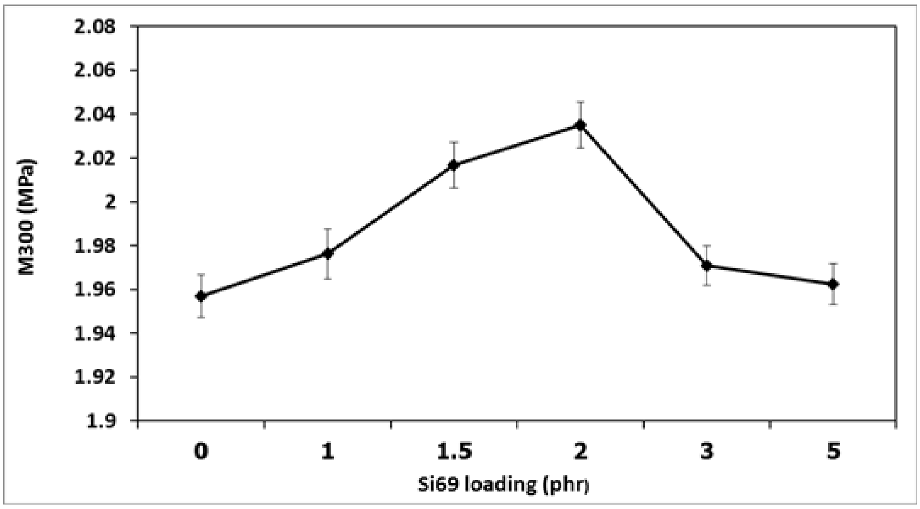

Figure 8. Effect of Si69 loading on modulus at 300% elongation (M300) of the CCP filled NR composites

Si69 loading until 3 phr. A possible explanation is the increase of the crosslink density with increasing Si69 content. The increase in the crosslink density gives rise to greater stiffness, and in consequence leads to lower elongation at break. Further increase of Si69 loading (5 phr) resulted in increment of the elongation at break owing to the plasticizing effect of the excess of Si69 in the NR composites.

3.4 Fatigue life measurement

Figure 10 represents the effect of Si69 loading on fatigue life of the CCP filled NR composites. The result shows that the fatigue life of the NR composites increased initially with the increase of Si69 loading and reached the maximum value when Si69 was added up to 2 phr. With further increase in Si69 loading, the fatigue life displayed a decreasing trend. Particularly at 5 phr Si69 loading, significant reduction in fatigue life could be observed. The enhancement of the fatigue life of the NR composites at low Si69 loading (1-2 phr) is due to the greater adhesion between CCP particles and rubber matrix that resulted from the role of Si69 as coupling agent in this system. The better interfacial adhesion is able to decrease the accumulated heat generated during the deformation, as well as promote the fatigue life of the composites (Ishak et al., 1997). In addition, Sae-oui et al. (Sae-oui et al., 2005) also reported that with increasing Si69 loading (maximum 3 phr), higher crosslink density and more flexible, longer sulphur linkage produced by Si69 can decrease hysteresis factor of rubber vulcanizates. This further results in the increase in fatigue life with increasing Si69 loading. Moreover, good quality of filler dispersion in the rubber

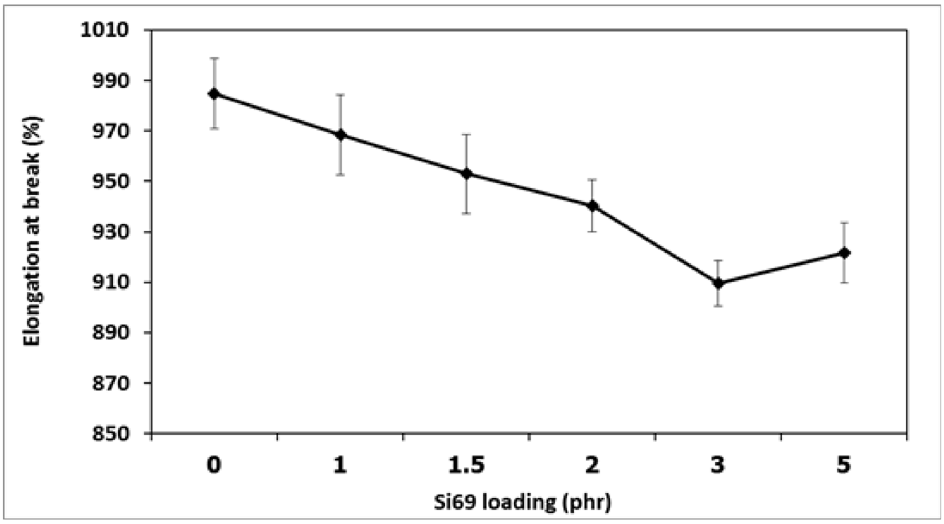

Figure 9. Effect of Si69 loading on elongation at break of the CCP filled NR composites

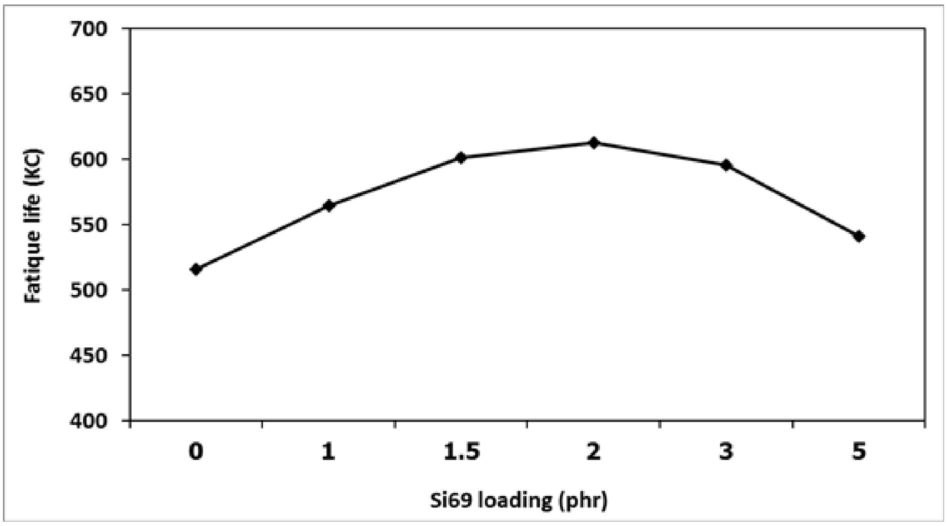

Figure 10. Effect of Si69 loading on fatigue life of the CCP filled NR composite

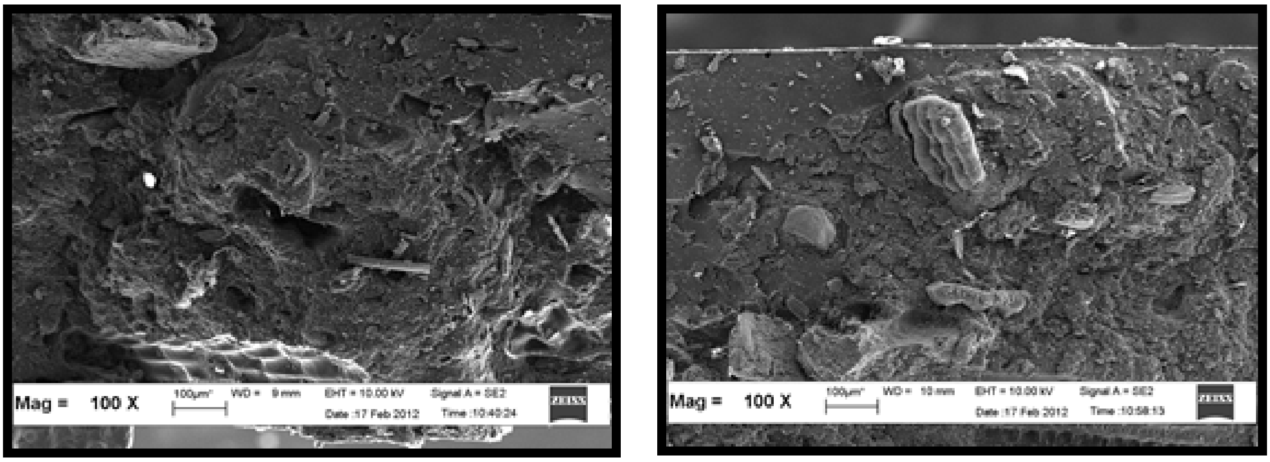

Figure 11. SEM micrographs of the tensile fracture surfaces of the CCP filled NR composites at different Si69 loadings; (a) 0 phr and (b) 2 phr (magnification 100X)

matrix and better wettability of filler particles by the rubber matrix also contribute to the higher cycles of fatigue life of the NR composites. The reduction in the fatigue life after 2 phr of Si69 loading might be attributed to the plasticizing effect of excessive Si69. At high Si69 loading, function of Si69 changes from the coupling agent to the plasticizer. Therefore, the hydrophilic filler and hydrophobic rubber cannot be coupled together with the presence of high content of Si69 as it would lead to the decrease in fatigue life of the NR composites.

3.5 Morphological studies

Figure 11 shows the SEM micrographs of the tensile fracture surfaces of the CCP filled NR composites at different Si69 loadings with the magnification 100X. Without Si69 (Si69 0 phr), the micrograph in figure 11 (a) shows many voids and relatively smooth nature of the void surface which indicates the poor adhesion between CCP particles and rubber matrix. Moreover, the rather smooth tensile fracture surfaces which indicate lower tensile strength could be observed.

With the presence of Si69 at 2 phr, the CCP filled NR composites exhibited more CCP particles embedded in rubber matrix, less voids and rougher fracture surfaces as shown in figure 11 (b). It is very clear that the CCP particles were wetted well by the rubber matrix. This is because of the improved rubber-filler interaction by Si69 in the system. These SEM results can substantially prove the results of the tensile properties and the rubber-filler interaction.

4. Conclusion

In conclusion, the addition of Si69 in the CCP filled NR composites could enhance the overall properties of the composites, namely the maximum torque, the tensile properties in terms of the tensile strength, modulus at 100% elongation, modulus at 300% elongation as well as elongation at break, fatigue life and rubber-filler interaction. However, it should be noted that as Si69 loading is increased up to 2 phr, the overall properties increased. Further increase in Si69 loading led to the reduction in all properties. Thus, the optimum content of Si69 for the CCP filled NR composites is 2 phr. The SEM studies also revealed better adhesion between CCP particles and rubber matrix due to the addition of Si69. However, Si69 content did not show significant effect on the scorch time and the cure time of the composites.

Acknowledgements

The authors wish to thank PERCH-CIC and Department of Chemistry, Faculty of Science, Mahasarakham University, Thailand for partial support of research facilities.

References

Abdelmouleh M., Boufi S., Belgacem M. N., Dufresne A. (2007). Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading. Composites Science and Technology, 67, 1627-1639.

Asim M., Jawaid M., Abdan K., Ishak M. R. (2018). The Effect of Silane Treated Fibre Loading on Mechanical Properties of Pineapple Leaf/Kenaf Fibre Filler Phenolic Composites. Journal of Polymers and the Environment, 26, 1520–1527.

Asyraf M. R. M., Rafidah M., Azrina A., Razman M. R. (2021). Dynamic mechanical behaviour of kenaf cellulosic fibre biocomposites: a comprehensive review on chemical treatments. Cellulose, 28, 2675–2695.

Chanda A. K., Hazra A., Kumar M. P., Neogi S., Neogi S. (2015). Chemical treatments of rice husk filler and jute fiber for the use in green composites. Fibers and Polymers, 16, 902–910.

Office of Agricultural Economics. (2021). Corn for Animal Feed. http://www.oae.go.th/view/1/ตารางแสดงรายละเอียดข้าวโพดเลี้ยงสัตว์/TH-TH

Formela K., Hejna A., Piszczyk Ł., Saeb M. R., Colom X. (2016). Processing and structure–property relationships of natural rubber/wheat bran biocomposites. Cellulose, 23, 3157–3175.

Fröhlich J., Niedermeier W., Luginsland H. D. (2005). The effect of filler–filler and filler–elastomer interaction on rubber reinforcement. Composites Part A: Applied Science and Manufacturing, 36, 449-460.

Huda M. S., Drzal L. T., Mohanty A. K., Misra M. (2007). The effect of silane treated- and untreated-talc on the mechanical and physico-mechanical properties of poly(lactic acid)/newspaper fibers/talc hybrid composites. Composites Part B: Engineering, 38, 367-379.

Ishak Z. A. M.,Bakar A. A.,Ishiaku U. S., Hashim A. S.,Azahari B. (1997). An investigation of the potential of rice husk ash as a filler for epoxidized natuaral rubber II: Fatigue behaviour. European Polymer Journal, 33, 73-79.

Jacob M., Thomas S., Varughese K. T. (2004). Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. Composites Science and Technology, 64, 955-965.

Kabir M. M., Wang H., Lau K. T., Cardona F. (2012). Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview. Composites Part B: Engineering, 43, 2883-2892.

Kengkhetkit N., Amornsakchai T. (2014). A new approach to “Greening” plastic composites using pineapple leaf waste for performance and cost effectiveness. Materials and Design, 55, 292-299.

Lee B. H., Kim H. S., Lee S., Kim H. J., Dorgan J. R. (2009). Bio-composites of kenaf fibers in polylactide: Role of improved interfacial adhesion in the carding process. Composites Science and Technology, 69, 2573-2579.

Lorenz O., Parks C. R. (1961). The crosslinking efficiency of some vulcanizing agents in natural rubber. Journal of Polymer Science, 50, 299-312.

Maziad N. A., EL-Nashar D. E., Sadek E. M. (2009). The effects of a silane coupling agent on properties of rice husk-filled maleic acid anhydride compatibilized natural rubber/low-density polyethylene blend. Journal of Materials Science, 44, 2665–2673.

Osabohien E., Egboh S. H. O. (2008). Utilization of bowstring hemp fiber as a filler in natural rubber compounds. Journal of Applied Polymer Science, 107, 210-214.

Poh B. T., Ng C. C. (1998). Effect of silane coupling agents on the mooney scorch time of silica-filled natural rubber compound. European Polymer Journal, 34, 975-979.

Sae-oui P., Sirisinha C., Hatthapanit K., Thepsuwan U. (2005). Comparison of reinforcing efficiency between Si-69 and Si-264 in an efficient vulcanization system. Polymer Testing, 24, 439-446.

Sae-oui P., Sirisinha C., Thepsuwan U., Hatthapanit K. (2006). Roles of silane coupling agents on properties of silica-filled polychloroprene. European Polymer Journal, 42, 479-486.

Xie Y., Hill C. A. S., Xiao Z., Militz H., Mai C. (2010). Silane coupling agents used for natural fiber/polymer composites: A review. Composites Part A: Applied Science and Manufacturing, 41, 806-819.

Yan H., Sun K., Zhang Y., Zhang Y., Fan Y. (2004). Effects of silane coupling agents on the vulcanization characteristics of natural rubber. Journal of Applied Polymer Science, 94, 1511-1518.

Zhou Y., Fan M., Chen L., Zhuang J. (2015). Lignocellulosic fibre mediated rubber composites: An overview. Composites Part B: Engineering, 76, 180-191.