Physical properties of natural rubber filled with pottery stone

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Abstract

Silica is the most important reinforcing filler for natural rubber (NR) when compare with others non-black fillers, due to its ability to improve physical properties such as tensile and tear strength. There are silanol groups, -Si-OH, appears on the surface of silica particle. Because of its hydrophilic surface of silica, when composite with NR, coupling agent should be added for enhancing compatibility between silica and NR. Moreover, particle size of silica also affects their compatibility as well. The silica is obtain from the precipitation of aqueous sodium silicate solution called precipitated silica, or from natural resources such as rice husk ash and fly ash. According to its chemical composition, pottery stone composing of 75.9% of silica may be the alternative non-black filler. The probability of using pottery stone as reinforcing filler for NR was investigated in this work. Effects of pottery stone content particle size and coupling agent content on physical properties of NR were studied.

Keywords: *Natural rubber, pottery stone, silica, physical properties*

1. Introduction

Although natural (NR) is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into NR in most cases in order to gain the appropriate properties for specific applications.

In recent years, synthetic precipitated silica has been used in rubber reinforcement and proved to be as effective as carbon black. The surfaces of silicas poessess siloxane and silanol groups. The silanol groups are acidic and interact with the basic accelerators causing long cure time and slow cure rates, and loss of crosslink density in sulphur-cured rubbers. Moreover, the surfaces of silica are polar and hydrophilic, and they is a strong tendency to adsorb moisture, which adversely influences cure and properties of the rubber vulcanisates. The amount of water adsorbed on the surfaces of silica affects the ionization of the silanol groups, and this in turn affects cure. Strong interaction between the silica particles increases viscosity, which is not desirable in rubber processing and can cause excessive wear and tear of the processing equipment.

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A wide variety of particulate fillers from are used in the rubber Industry for various purposes, of which the most important are reinforcement, reduction in material costs and improvements in processing. Reinforcement is primarily the enhancement of strength and strength-related properties. Silica (Si) is the most important reinforcing filler in NR when compares with others in category of non-black filler when Si is compounded with rubbers, physical properties are increased. Nowadays many attempts have been made to use silica from the natural resources as alternative reinforcing filler. In this research, Si from pottery stone is a natural mineral stone, and used as reinforcing filler in natural rubber. According to its chemical composition, pottery stone composing of 76.6% of silica. The probability of using pottery stones reinforcing filler for NR was investigated in this work. Furthermore, To add coupling agent, silane 69, will improve the compatibility in natural rubber. It will be studied the physical properties and compared with precipitated Si.

2. Experimental

2.1. Materials

The compound formulations are given in Table 1. The NR used in this study was standard Thai natural rubber grade 5L (STR 5L). Other ingredients: *2,2,4*-trimethyl-*1,2*-dihydro-quinloine (TMQ) and *N-1,3*-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD) (antioxidants), sulfur (S) (curing agent), zinc oxide (ZnO) and stearic acid (activators), *N*-cyclohexyl-*2*-benzothiazole sulfonamide (CBS) (accelerator) were of reagent grade. Pottery stone containing about 75 wt% SiO_2 with various particle sizes from Lopburi Province was used in the present study. It was sieved to generate 3 grades according to size range (coarse: 63-106 m, medium: 45-62 μm and fine: below 45 μm). The designation NR-PS in Table 1 meant the NR compound filled with pottery stone. Precipitated silica (Tokusil 255 with specific surface area of 150-180 m^2/g) was manufactured by Tokuyama Siam Silica Co., Ltd. The NR compound filled with precipitated silica was named NR-Silica.

Table 1 Compound formulations

Ingredient (phr)	**Compound**		
	Gum NR	**NR-PS**	**NR-Silica**
NR	100	100	100
Pottery stone	0	30	0
Precipitated silica	0	0	30
ZnO	8	8	8
Stearic acid	1	1	1
TMQ	1	1	1
6PPD	1	1	1
CBS	2.7	2.7	2.7
S	4.16	4.16	4.16

2.2. Preparation of rubber compounds

The rubber compounds were prepared using a two roll-mill. The mixing step was divided into 2 steps. For the first step, all ingredients, except the curatives, were mixed with NR. Then, the compound was sheeted-off and left at room temperature until it cooled down to avoid excessive heat. In the second step, the compound was further masticated for 1 min. Then, the curatives were added slowly and mixed for four more minutes. Finally, the compound was rolled-up 10 times to assure homogeneous mixing before sheeting off.

2.3. Determination of cure characteristics and sample preparation:

Cure characteristics were determined at 160 ^{o}C using a moving die rheometer (MDR). All rubber compounds were compression molded into sheets in a hydraulic press at 160 ^{o}C according to their t_c100 (time at which the rheometer torque is highest on the cure curve). The moldings were cooled quickly in the water at the end of the curing cycle.

2.4. Equilibrium swelling measurement of the vulcanizates

Sample for swelling test was cut from cured sheets having a thickness of 1 mm. Then, the sample was immersed in 30 ml of toluene for 1 week at room temperature. The swollen sample was removed from the toluene and blotted with a paper towel to remove the excess toluene. Then the sample was quickly put into a weighing bottle to determine swollen weight. Swollen sample was dried to constant weight at room temperature. Dried weight then was determined. The swelling ratio (Q) was determined using equation (1). The value of swelling ratio of each vulcanizate was the average of five specimens:

$$Q = (W_s - W_u) / W_u, \qquad (1)$$

where Ws is the weight of swollen sample and Wu the weight of dried sample before swelling.

2.5. Mechanical property measurement

Tensile and tear properties were determined following ISO 37 and ISO 34 (die B), respectively. The values of tensile and tear properties were the average of 4-5 specimens.

The hardness was measured using a Wallace Shore A durometer according to ASTM D2240.

3. Results and discussion

3.1. Cure characteristics and swelling ratio

Cure characteristics and swelling ratio of the NR compounds are given in Table 2. As can be seen, the addition of precipitated silica significantly increases cure time. The cure retardation by precipitated silica is attributed to the fact that some of accelerators and Zn complex, which acts as cure activator, could be trapped by the silanol groups on the silica surface (Byers,1998). The vulcanization reaction is therefore retarded. As a consequence, with the same curative level, crosslink density of the NR vulcanizate filled with precipitated silica is lower than that of Gum NR. This can be supported by swelling ratio, which is inversely proportional to crosslink density. The result in Table 2 shows that the NR vulcanizate filled with precipitated silica has the lowest crosslink density. On the other hand, for the NR compounds filled with pottery stone, no matter which pottery stone grade is added into NR compound, both scorch time and cure time are similar to those of gum NR compound. The swelling ratios of the NR filled with pottery stone with various pottery stone grades, are slightly higher than that of gum. This might be due to the dilution effect, i.e. the amount of swellable part, rubber matrix, is lower.

Table 2 Effect of pottery stone and precipitated silica on the cure characteristics and swelling ratio of the NR compounds*

	t_s2 (min)	t_c100 (min)	Swelling Ratio
Gum NR	3.06	5.39	5.11
NR-PS(F)	3.08	5.54	4.38
NR-PS(M)	2.48	5.30	4.38
NR-PS(C)	2.58	5.51	4.55
NR-Silica	2.00	17.3	7.50

*The letters in parentheses after NR-PS indicate pottery stone grade (F = fine, M = medium, and C = coarse grade)

3.2. Mechanical properties

Table 3 represents mechanical properties of the NR vulcanizates. It should be noted that cure package of all vulcanizates was similar. The results reveal that incorporating 30 phr of precipitated silica into rubber matrix results in decreasing of tensile and tear strength. It has long been known that tensile and tear strength strongly depend on crosslink density. As shown in the swelling test results, the NR vulcanizate filled with precipitated silica forms less crosslink point. Thus, the explanation is given as the decrease in crosslink density. Moreover, the polar feature of precipitated silica leads to the poor rubber-filler interaction and rise to high tendency for filler agglomeration in the rubber matrix (Wolff and Wang, 1992). Therefore, the detrimental effect on strength is also due to bad dispersion of precipitated silica. The silica-elastomer interaction can be improved by chemically bonding the two with a silane coupling agent (Sae-oui et a.,2004). However, this results often in an undesirable cost penalty for their use in rubber compositions. For 100% modulus and hardness of the NR vulcanizate filled with precipitated silica, in spite of adding filler which has higher modulus than that of rubber, these two properties only slightly increase. Again, this is attributed to the reduction of crosslink density. Elongation at break of the NR filled silica is found to decrease.

For the NR vulcanizates filled with pottery stone, the results show that pottery stone greatly enhances 100% modulus, tear strength and hardness though it has little effect on tensile strength. No marked difference in the 100% modulus and hardness of the NR vulcanizates is observed between three pottery stone grades. However, it is found that particle size of pottery stone is an important factor which determines tear strength. Only fine and medium grade of pottery stone can significantly increase tear strength.

Table 3 Effect of pottery stone and precipitated silica on mechanical properties of the NR vulcanizates*

	100% Modulus	**%Elongation at Break**	**Tensile Strength**	**Tear Strength (Die B)**	**Hardness**
Gum NR	0.53	878	17.1	48.4	31.6
NR-PS(F)	0.84	713	17.8	60.8	40.4
NR-PS(M)	0.83	742	18.2	63.8	42.3
NR-PS(C)	0.85	729	18.4	49.2	42.2
NR-Silica	0.58	772	9.20	24.5	35.0

*The letters in parentheses after NR-PS indicate pottery stone grade (F = fine, M = medium, and C = coarse grade)

4. Conclusion

In this study, pottery stone which is an inexpensive and abundant raw material in Thailand can be successfully used as reinforcing filler for natural rubber. Without addition of silane coupling agent, pottery stone consisting of 70%wt SiO_2 can enhance physical properties of the NR vulcanizates. With the same composition, reinforcing efficiency of pottery stone is superior to that of precipitated silica.

References

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