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Antibacterial Efficacy and Mechanical Properties of Silica Reinforced Natural Rubber (NR) with HPQM based Neusilin

Piyaporn Niltui[1,a], Sirichai Kanking[1,b], Savaeng Techangamvong[2,c], Ekachai Wimolmala[1,d], Narongrit Sombatsompop[1,e]

[1]Polymer Processing and Flow (P-PROF) Group, Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi (KMUTT), Bangmod, Bangkok 10140, Thailand

[2]Koventure Co.,Ltd. 563 Moo 4 Bangpoo Industrial Estate Soi 10 Sukhumvit Road, Praeksa, Muang Samutprakarn 10280, Thailand.

[a]P.Niltui_23@hotmail.com, [b]k.sirichai.sk@gmail.com, [c]savaeng@purity.co.th, [d]ekachai.wim@kmutt.ac.th, [e]narongrit.som@kmutt.ac.th

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Abstract. This work studied the antibacterial performance and mechanical properties of natural rubber (NR) compound reinforced with commercial silica at various silica loadings form 0, 20, 40 and 60 parts per hundred rubber (phr). 2-Hydroxypropyl-3-Piperazinyl-Quinoline carboxylic acid Methacrylate (HPQM) based Neusilin at loadings of 0, 3 and 5 phr were used as anti-bacterial agent against *Escherichaia coli* (*E.coli*) ATCC 25923 and *Staphylococcus aureus* (*S.aureus*) ATCC 25922. The antibacterial performance was reported as a clear zone radius by diffusion test and a percentage reduction of bacteria by Plate-Count-Agar (PCA) method. The results suggested that the increasing silica loading in the NR vulcanizates improved the tensile modulus and hardness, but decreased elongation which had optimal tensile strength at 20 phr of silica. Additionally, the HPQM based Neusilin did not affect the mechanical properties of the rubber vulcanizates. The antibacterial results showed that the inhibition zone radius and the percentage reduction increased with increasing HPQM based Neusilin, but decreased with silica filler content. The antibacterial efficacy was inversely related to the reinforcement level of the NR vulcanizates by the silica. The percentage reduction of bacteria of NR compound filled with 5 phr of HPQM based Neusilin achieved 99.9%.

Introduction

Natural rubber is extensively used in medical and food industries, including, toys, gloves, pads, food conveyors and kitchen equipment. Usually the mechanical properties of the rubber products are improved by adding chemicals and reinforcing fillers. In the rubber industry, silica is widely used as a non-black reinforcing filler because it has high specific surface area and performance in improving the mechanical properties of the rubber composites, especially tensile and tear properties and hardness.[1] The rubber products must also be safe when contacting with human. In order to achive this, addition of anti-bacteria agent into the rubber products is one of the alternative methods to prevent the NR products from bacterial contaminations. Jai-eau et al.[2] revealed that 2-Hydroxypropyl-3-Piperazinyl-Quinoline carboxylic acid Methacrylate (HPQM) exhibited the most satisfactory anti-bacterial efficacy for the conventional vulcanization (CV) system without reinforcing filler and appearance of inhibition zone and the efficacy of anti-bacterial. Yang and Park [3] studied mechanical properties of the silicone rubber with antimicrobial agent addition and found that the tensile strength decreased with increasing amount of antimicrobial agent.

Based on the above literature reviews [2-3], it is suggested that the incorporation of reinforcing fillers may affect the anti-bacterial performance of the rubber since its presence may make the anti-bacterial agent to release and kill the bacteria on the rubber surface. This present work aimed to seek the optimum contents of HPQM based Neusilin and silica content for most promising antibacterial efficacy and mechanical properties of the natural rubber vulcanizates.

Experimental

Materials and Chemicals. Natural Rubber STR 5L (Chemical Innovation Co., Ltd., Thailand) was used as polymeric matrix in 100 part. Zinc oxide (Thai-Lysaght Co., Ltd., Thailand) in content of 5.0 phr and Stearic acid (Imperial Industrial Chemicals Co., Ltd., Thailand) in content of 2.0 phr were used as activators. 2-Mercaptobenzothiazole (CMC advance Co., Ltd., Thailand) in content of 0.5 phr and 1,3-Diphenylguanidine (Siam Chemicals Co., Ltd., Thailand) in content of 0.2 phr were used as accelerators. Silane coupling agent (Behn Meyer Chemical T Co., Ltd., Thailand) in content of 2wt% of silica, Poly (ethylene glycol) grade 4000 (Cosan Co., Ltd., Thailand) in content of 5wt% of added silica with silane coupling agent, and precipitated silica grade Tokusil 233 (Tokuyama Siam Silica Co., Ltd., Thailand) varying from 0-60 phr were used as filler activator/processing aid and reinforcing filler, respectively. Sulfur (Zeon advanced Polymix Co., Ltd., Thailand) vulcanizing agent was used in content of 3.0 phr. 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate based Neusilin (Micro Science Tech Co., Ltd., South Korea) was used as the antibacterial agent varying from 0-5 phr. *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 25923 were used as testing bacteria.

Sample Preparations. The compounding recipe was prepared through a two roll mill (Yong Fong Machinary Co., Ltd., Thailand) for 30 min. The cure time used was determined using an Oscillating Disk Rheometer (GT 7070-S2, GOTECH Testing Machine, Inc., Taiwan) at a test temperature of 160^{o}C. then compression-molded at a 90% cure using a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at pressure of 150 kg/cm^2 using the same cure temperature. The NR vulcanizates were tested in inhibition zone, antibacterial performance and mechanical testing.

Mechanical properties. The mechanical properties; tensile modulus, tensile strength and elongation at break of NR vulcanizates were examined using a universal testing machine (Autograph AG-I, Shimadzu, Tokyo Japan), according to ASTM D412 (2006). The speed rate for testing was used at 500 mm/min. The hardness was studied by hardness durometer (Shore A Model GS-719G, Japan), following ASTM-D2240 (2005).[4]

Antibacterial performance. Disk diffusion and PCA technique were utilized for anti-bacterial perforamnce evaluations in this work. *E.coli* and *S.aureu*s were used and first incubated in nutrient broth for 24 h at 37^{o}C. In disk diffusion technique, the incubated bacteria and nutrient agar were mixed in the ratio of 1:1 and the mixture was poured into a plate. The NR sample having 6 mm in diameter was placed on the mixture on the plate. After that, it was incubated at 37^{o}C for 24 h. For PCA test, a 5x5 cm rubber sample was dropped into the flask which had been cultivated with bacteria of 5 mL, which was shaken on reciprocal shaker at 100 rpm of speed for contacted times varying from 0, 1, 2, 3 and 4 h. The prepared solution 100 μL was spreaded on agar which was then incubated at the same conditions with disk diffusion technique. The percent reduction of living bacteria was then calculated based on the methods already described by our previous works.[2, 5]

Result and discussion

Fig. 1 summarises the results of tensile modulus, hardness, tensile strength and elongation at break of the NR vulcanizates filled with silica filler. Tensile modulus and hardness in Figs. 1(a) and 1(b) were found to increase as the silica loading was increased. This result was expected due to the incorporation of more rigid silica filler into the NR vulcanizates. It was also observed that tensile strength increased with increasing silica content until a maximum level reached at approximately 20 phr in Fig. 1(c) indicating the increment in strength caused by silica reinforcement in NR vulcanizate. The reduction in tensile strength with using 40-60 phr of silica loading occurred due to the agglomeration of silica particles which formed as obstacles in the molecular flow of the rubber vulcanizates during deformation.[6-7] Fig. 1(d) shows the decrease in elongation at break as a function of silica loading. This is simply explained by the fact that rubber chains mobility were resticted because of the presence and reinforcement of the silica. In addition, it was interesting to note that the addition of HPQM based Neusilin had a slightly effect on the overall mechanical properties, the changes being within the experimental errors (+/-5.0%).

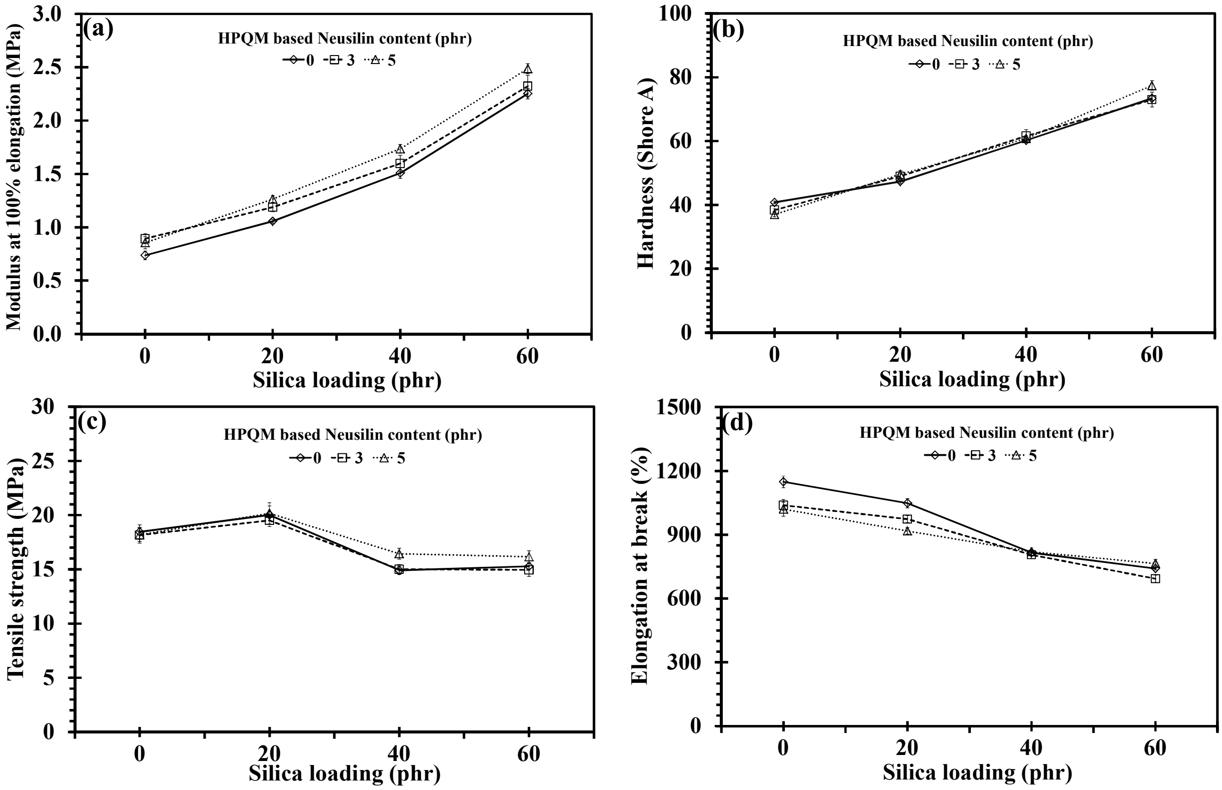

Figure 1 Mechanical properties; (a) tensile modulus, (b) hardness, (c) tensile strength and (d) elongation of NR vulcanizates on a function of silica loading and antibacterial agent content.

Table 1 shows the diffusion ability of HPQM based Neusilin as a function of inhibition zone. It was found that the radius of inhibition zone of the non-reinforced NR vulcanizates was greater than that of the silica-reinforced vulcanizates. This suggested that the presence of silica or the reinforcement effect reduced the diffusability of the HPQM based Neusilin, and HPQM based Neusilin seemed to have more sensitive effect with *E.coli* as compared with *S.aureus*.Similar behavior was observed by Jai-eau et al [2].

Table 1 Inhibition zone of NR vulcanizates filled with antibacterial agent

Types of bacteria	HPQM based Neusilin content (phr)	Radius of inhibition zone (mm) Silica loading (phr)			
		0	20	40	60
***Escherichia coli* (ATCC 25922)**	**0**	0.00	0.00	0.00	0.00
	3	3.00	1.75	2.00	1.25
	5	4.00	2.75	1.75	2.50
***Staphylococcus aureus* (ATCC 25923)**	**0**	0.00	0.00	0.00	0.00
	3	0.00	0.00	0.00	0.00
	5	1.75	0.00	0.00	0.00

Figs.2(a) and 2(b) show the percent reduction as function of anti-*E.coli* and anti-*S.aureus* efficacy, respectively. It was found that the addition of HPQM based Neusilin of 3 and 5 phr in NR compounds could achieved 99.9% anti-bacterial efficacy against *E.coli* for the contact times of greater than 2 h, the higher the HPQM dosage the lower the contact time. It was noted that at 1 h contact time, the anti-bacterial efficacy was dependent on the silica loading and interestingly it was associated with the reinforcement level as discussed in Fig. 1. That was, the higher the reinforcement level (highest strength) the lower the anti-bacterial efficacy. This could be explained that the reinforcement would make the HPQM diffusion in the NR vulcanizates more difficult and thus lower anti-bacterial efficacy. This was why at higher loadings of silica (40 and 60) where the reinforcement level diminished due to the agglomeration of the silica particles, the anti-bacterial efficacy has improved as compared with that at silica loading of 20 phr. The anti-bacterial efficacy against *S.aurues* had no definite trend and relatively low as compared with that against *E.coli*.

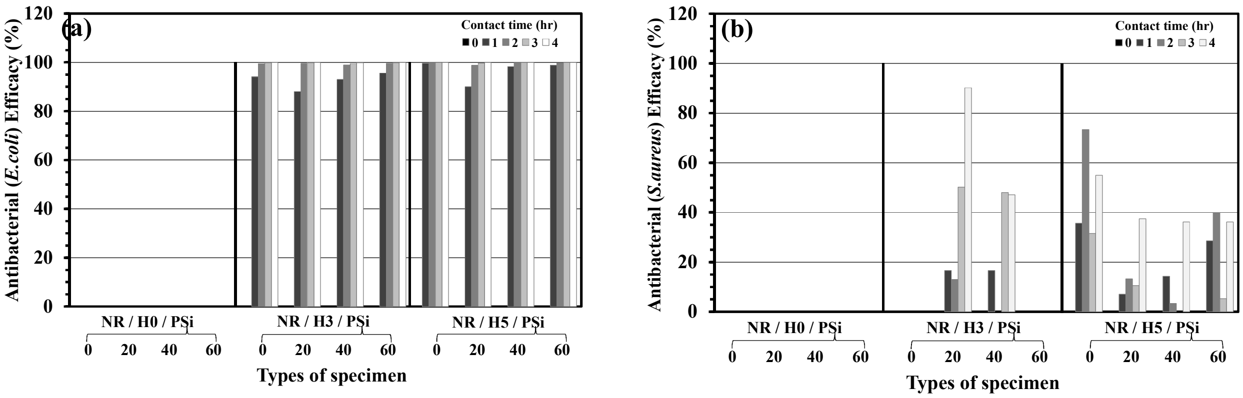

Figure 2 Effect of silica loading and HPQM based Neusilin content (a) *E.coli* and (b) *S.aureus* on antibacterial efficacy of NR vulcanizates.

Conclusion

Silica filler could be used as reinforcing filler in NR vulcanizates at the optimum content of 20 phr. The addition of HPQM based Neusilin anti-bacterial agent did not affect the overall mechanical properties of the NR vulcanizates. The antibacterial results showed that the inhibition zone radius and the percentage reduction increased with increasing HPQM based Neusilin, but decreased with silica filler content. The antibacterial efficacy was inversely assocaited with the reinforcement level of the NR vulcanizates by the silica.

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