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Antibacterial Ability of HPQM base Neusilin / Natural Rubber Reinforced with Carbon Black

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Abstract
This work studied antibacterial ability of natural rubber (NR) reinforced carbon black N330 at loadings 0, 20, 40 and 60 parts per hundred rubber (phr) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline carboxylic acid Methacrylate (HPQM) based Neusilin at loadings 0 , 3 and 5 phr were used against *Escherichia coli* (*E.coli*) ATCC 25923 and *Staphylococcus aureus (S.aureus)* ATCC 25922. The Inhibition zone (Disk diffusion) and Plate Count Agar (PCA) methods were employed to assess the ability of the anti-bacterial performance, cure characteristics and mechanical properties such as tensile modulus, tensile strength, elongation at break and hardness. The results suggested that increasing HPQM in appearance of inhibition zone and 99.9 percent reduction of *E.coli*. The antibacterial ability HPQM base Neusilin at loadings 5 phr and carbon black at loadings 20 phr were better. The antibacterial ability of NR vulcanizates depends on the level of reinforcement. The tensile strength with using 40 phr of carbon black loading was suggested in this work.

Introduction
Carbon black is one of the most important reinforcing filler that widely used in rubber compounding. Due to it has high specific surface area and performance in improving the mechanical properties of the rubber composites, especially tensile and tear properties and abrasion resistance.[1] In the present natural rubber is used as a health product such as medical rubber floor, food conveyor belts and rubber layer in livestock. In generally, bacteria can be contaminated on surrounding and consumer goods. There were many antibacterial agents such as nano-silver, triclosan and sorbic acid anhydride which may be able to reduce growth of bacteria. [2] Based on available evidence for natural rubber research. Jai-eau et al.[3] studied the effect of vulcanizing systems on antibacterial performance of natural rubber compounds. It shown that 2-Hydroxypropyl-3-Piperazinyl-Quinoline carboxylic acid Methacrylate (HPQM) exhibited the most useful anti-bacterial efficacy for the conventional vulcanization (CV) system without reinforcing filler and appearance of inhibition zone and the anti-bacterial efficacy of 99.9%, for *E.coli*. Seentrakoon et al.[4] studied antibacterial performance and mechanical properties of NR with nano-TiO_2 addition and found that the tensile strength increasing with amount of antibacterial agent. Based on the above literature reviews [3-4], it is suggested that the incorporation of reinforcing fillers may affect to release and kill the bacteria on the NR surface. This present work aimed to seek the optimum contents of HPQM based Neusilin and corbon black content for most promising cure characteristics, antibacterial efficacy and mechanical properties of the natural rubber vulcanizates.

Experimental

Materials. The compounds used as received. Details of the compounds are shown in Table 1

Table 1 Formulation of rubber compounds

Compound/Grade	**Content** (phr*)	**Supplier**
Natural rubber / STR5L	100	Chemical Innovation Co., Ltd., Thailand
Zinc Oxide (ZnO)	5.0	Thai-Lysaght Co., Ltd., Thailand
Stearic acid	2.0	Imperial Industrial Chemicals Co., Ltd., Thailand
Mercaptobenzothaizole, MBT	0.5	CMC advance Co., Ltd., Thailand
DiphenylGuanidune, DPG	2.0	Siam Chemicals Co., Ltd., Thailand
Sulphur	3.0	Zeon advanced Polymix Co., Ltd., Thailand
Antioxidant / 6PPD	1.0	Behn Meyer Chemical Co., Ltd., Thailand
Carbon Black / N330	Varying 0 / 20 / 40 / 60	Thai carbon black Public Co., Ltd., Thailand
HPQM base Neusilin	Varying 0 / 3 / 5	Micro Science Tech Co., Ltd., South Korea

*Parts per hundred parts of rubber

Preparation of rubber compound, Cure characteristics and Mechanical properties. The compounds was masticated with Two-roll-mill (Yong Fong Machinary Co., Ltd., Thailand) for 30 min. Scorch time, cure time of rubber compounds were Oscillating Die Rheometer (ODR) (GOTECH testing machine 70-70-S2, Taiwan) at temperature of 160°C . Prepared sample by compression molding at 160°C with pressure of 15 MPa using hydraulic hot press. Rubber compound vulcanizes for tested in mechanical properties with a universal testing machine (Autograph AG-I, Shimadzu, Tokyo Japan), according to ASTM D412-06. The speed rate for testing was used at 500 mm/min. The hardness was tested by hardness durometer (Shore A Model GS-719G, Japan), following ASTM-D2240-05.

Antibacterial performance. Inhibition zone and PCA method were used 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 Inhibition zone, the incubated bacteria and nutrient agar were mixed in ratio 1:1. Prepare rubber samples (6 mm diameter) and were gently placed over the plate. After that, it was incubated at 37±0.5^{o}C and examined after 24 h. For plate count agar method, prepare rubber samples (A: 5x5 cm^2) was dropped into the flask which had bacteria 5 mL shaken on reciprocal shaker at 100 rpm of speed at temperature of 37±1 °C for contacted time of 0, 1, 2, 3 and 4 hr. The prepared solution 100 µL was spreaded on agar. Agar was then incubated at the same condition with Inhibition zone test. The percent reduction of living bacteria was then calculated.

Results and Discussion

Table 2 Cure characteristics of NR filled carbon black and HPQM base Neusilin.

HPQM base Neusilin (phr)	**Scorch time** (sec)				**Cure time** (sec)			
	Carbon black loading (phr)							
	0	**20**	**40**	**60**	**0**	**20**	**40**	**60**
0	70±1.4	64±1.7	55±3.5	53±1.4	371±1.2	329±1.4	328±5.6	330±2.0
3	67±2.8	54±2.8	43±4.0	45±2.1	367±5.6	339±6.3	333±3.5	339±3.8
5	60±0.7	51±1.4	42±1.7	46±2.8	352±0.8	342±2.1	343±2.0	349±2.3

Table 2 shows the scorch time and cure time of natural rubber compounds. It was found that the various of carbon black and HPQM based Neusilin loading did not affect both of the scorch time and cure time due to amount of carbon black increased in the compound viscosity thus the shear heating effect together which some surface alkalinity and the good thermal conduction property [5]
Fig.1 summarises the result of the tensile modulus, hardness, tensile strength and elongation at break of NR vulcanizates. Figs. 1(a) and 1(b) were found that the tensile modulus and hardness had increase with increasing the carbon black content because of rigidity of carbon black. Additionally,

the tensile strength increased with increasing carbon black content until a maximum level reached at approximate 40 phr result from the higher level of reinforcement. Then, the tensile strength decreased with using 60 phr of carbon black loading because of agglomeration is shown Fig. 1(c).[6] While the elongation at break had decrease because rubber chains mobility were restricted because of the presence and reinforcement of the carbon black. However, HPQM based Neusilin did not significantly affect the overall mechanical properties.

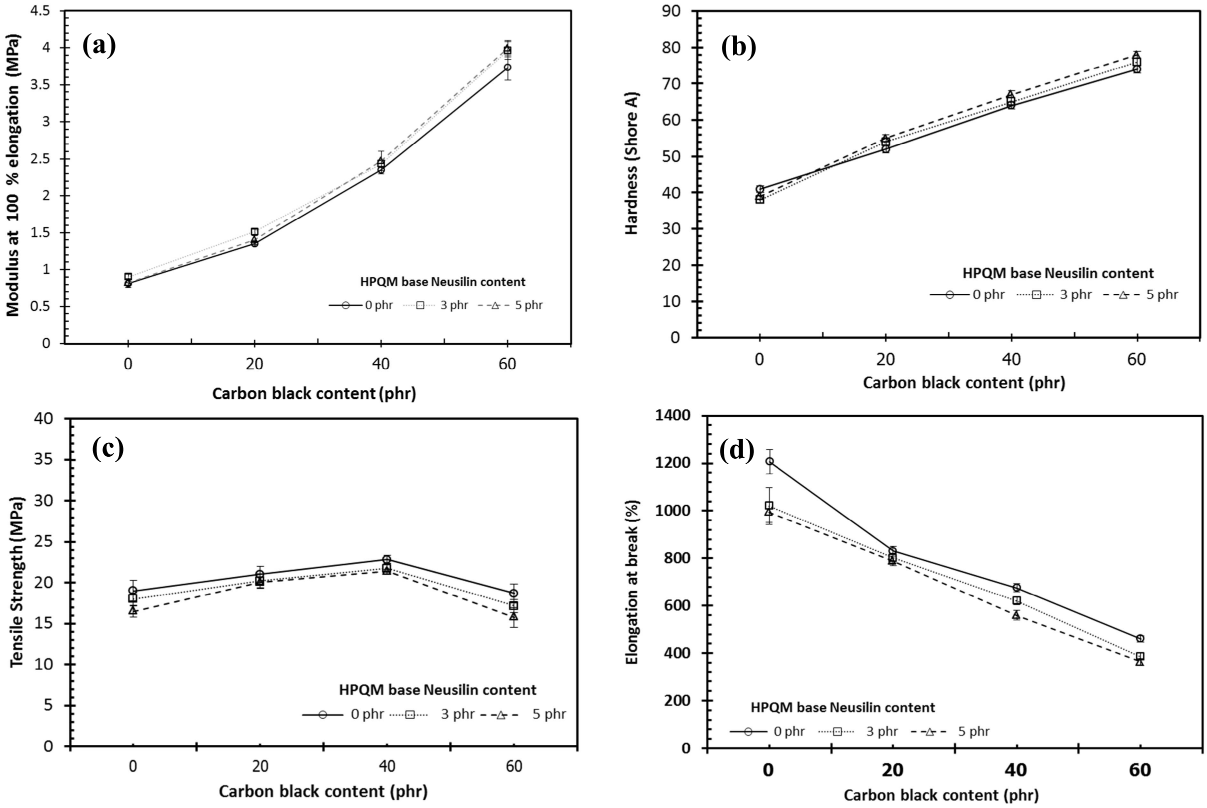


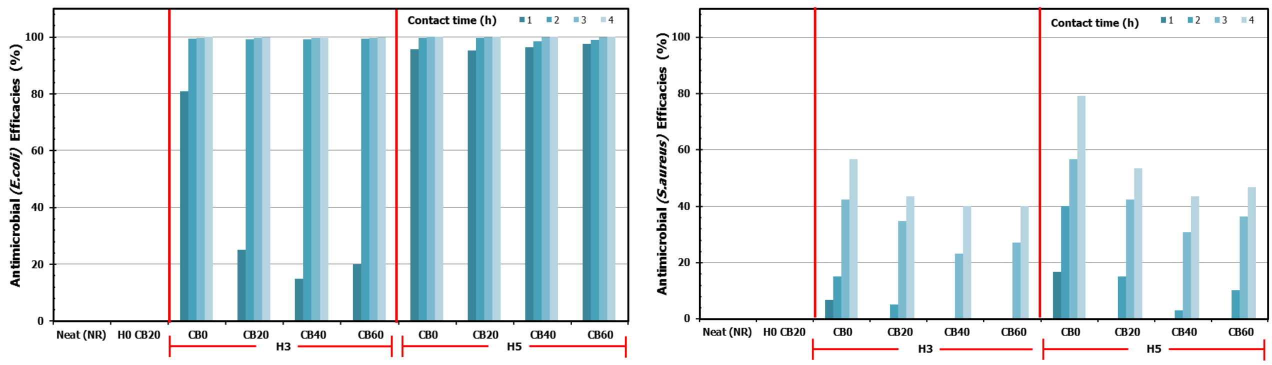
Figure 1 Mechanical properties of NR rubber compound filled carbon black and HPQM base Neusilin (a) tensile modulus (b) hardness (c) tensile strength and (d) elongation at break

Table 3 Antibacterial ability of NR filled carbon black on inhibition zone

Type of bacteria	HPQM based Neusilin (phr)	Radius of inhibition zone (mm)			
		Carbon black content (phr)			
		0	20	40	60
E.coli	0	0.00	0.00	0.00	0.00
	3	1.75	1.25	0.75	0.50
	5	2.50	1.75	1.00	0.75
S.aureus	0	0.00	0.00	0.00	0.00
	3	0.00	0.00	0.00	0.00
	5	2.00	0.00	0.00	0.00

Table 3 shows the diffusion ability of HPQM based Neusilin as a function of clear zone. It was found that the radius of clear zone of the neat NR vulcanizates was better than that of the carbon black-reinforced vulcanizates. This suggested that the presence of 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*.[3]

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 carbon black 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 carbon black 60 phr where the reinforcement level diminished due to the agglomeration of the carbon black particles, the anti-bacterial efficacy has improved as compared with that at carbon black loading of 40 phr. The anti-bacterial efficacy against *S.aurues* had no definite trend and relatively low as compared with that against *E.coli*.



(a) *E.coli* bacteria **(b)** *S.aurues* bacteria

Figure 2 Antibacterial ability with carbon black content on reduction of bacteria

Conclusion

The optimum content of carbon black filled NR vulcanizates could be used as reinforcing filler at 40 phr. The addition of HPQM based Neusilin anti-bacterial agent did not affect cure characteristics and the overall mechanical properties of the NR vulcanizates. The antibacterial results showed that the clear zone radius and the 99.9 percentage reduction reached with increasing HPQM based Neusilin, but decreased with carbon black filler content. The antibacterial efficacy was contrarily assocaited with the reinforcement level of the NR vulcanizates by the carbon black.

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