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UV weathering effect on antibacterial performance in silicone rubber compounds

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Abstract. Silicone rubber compounded with three different types of antibacterial agents: namely; nano-Ag colloids, Silver substituted Zeolite compound (SSZ) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQM) were prepared and changes in antibacterial performance were assessed before and after exposure to UV light at different aging times. Drop plate and halo tests were performed to study the antibacterial performance of silicone rubber compounds. The results indicated that antibacterial activity of silicone compound changed when the UV aging time was increased. The antibacterial activity of the rubber added with HPQM extremely decreased considered by the inhibition zone and %reductions of *Staphylococcus aureus* and *Escherichia coli* bacteria for any given contact times. On the other hand, the UV light did not affect the antibacterial activity of silicone rubber compounds added with nano-Ag colloids and SSZ agents.

Introduction

Bacteria are normally found in the ground, water and in other living organisms. Some of them could turn in to human diseases [1]. Bacteria can be classified into two categories based on their responses to a laboratory technique; there are gram-positive and gram-negative bacteria with different micro structure and method to injurious to human [2]. These bacteria are also expected to be found in many household applications, including those made by silicone rubber, which is one of the most widely used in household applications such as children's toys, computer keyboards, phone case, ear phones and watch, that are likely to contact with human body. In this respect, the bacteria contamination has become a main concern for silicone rubber products when used in contact with human. The addition of antibacterial agents into the rubber products is one of the widely preferred methods to prevent the silicone rubber products from bacteria contaminations. Our previous study [3] used nano-Ag colloids, Silver substituted Zeolite compound (SSZ) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (HPQM) as antibacterial agents in silicone rubber compounds cured by peroxide and found that the HPQM exhibited the most effective antimicrobial agent amongst the three agents. This present work has extended the previous work [3] by investigating the effect of UV ageing on the antibacterial activity of silicone rubber added with these three antibacterial agents.

Experimental

Materials and Chemicals. Silicone Rubber (KE-951-U, Shin-Etsu Chemical Co., Ltd., Japan) was used as polymeric matrix, and. 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane (designated as TRigonox®101-45s-ps, supplied by Akzo Noble Polymer Chemicals Ltd., Shanghai, China) was used as a vulcanizing agent. Nano-silver colloids (supplied by Koventure Co., Ltd., Bangkok, Thailand), Silver Substituted Zeolite (designated as SSZ, supplied by Yamamoto Trading Co., Ltd., Thailand) and 2-Hydroxypropyl-3-Piperazinyl-Quinoline Carboxylic Acid Methacrylate (designated as HPQM, supplied by Micro Science Tech Co., Ltd, South Korea) were used as the antibacterial agents in content 0, 5,10 and 15 phr. *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923) were used as testing bacteria.

Sample Preparations: The formulation of the silicone rubber compound was given as follows: 100 phr silicone rubber and 0.5 phr 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane. Silicone rubber was vulcanized in peroxide systems. The rubber sample was prepared through mastication and compounding processes. The silicone rubber was first masticated on a laboratory two roll mill (Yong Fong Machinary Co., Ltd., Thailand) for 5 min and was then compounded with antibacterial agents and 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane for 10 min, and the resultant compounds were then compression-molded at a 90% cure using a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at pressure of 170 kg/cm^2 with a cure temperature of 165°C to produce vulcanized silicone rubber. After curing rubber, the silicone rubber added with the antibacterial agents were placed in UV weathering machine which followed ASTM G 154 (2006) whose conditions were UVA aging at 60°C for 6 h and condensation at 60°C for 8 h. The aging time was varied at 1, 3, 5, 7, 14 and 21 days.

Antibacterial performance: Plate Count Agar (PCA) and Halo tests were used in this work. *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923) were used and first incubated in nutrient broth for 24 h at 37 °C. In the case of PCA method, 5 mL of incubated bacteria was diluted with 45 mL of peptone water in a flask. A 5×5 cm silicone rubber sample was then dropped into the flask. The flask was then shaken by 0, 30, 90, 150 and 210 min. 100 µL of the solution was spreaded on agar. Agar was then incubated at 37 °C for 24 h. The percent reduction of living bacteria was then calculated.[4] For halo test, the incubated bacteria and nutrient agar were mixed in ratio 1:1 and the mixture was poured into plate. The silicone sample having 6mm in diameter was placed on the mixture on the plate. After that, it was incubated at the same temperature and time with PCA method. Clear zone was carefully measured.

Measurement of Contact angle. Contact angle measurements indicate quantitative changes in sensitivity of material surface properties (i.e., roughness and chemistry).[5] In this work, the contact angle or wettability of deionized water on silicone rubber surfaces was measured by a drop method using a Contact Angle Goniometer, Model 100-00 from Ramé-hart Instrument Co. (New Jersey, USA). The contact angle values were averaged for advancing stages of drops for 5 times/100 µL droplets using three independent samples.

Result and discussion

Fig. 1a and 1b show the results of inhibition zone from halo test for silicone rubber vulcanizates incorporated with 15 phr loadings of nano-silver colloid, SSZ and HPQM agents aging with UV weathering 21 days against *E. coli* and *S. aureus* bacteria, respectively. A filter paper doped with $CuSO_4$ (control+) and a blank filter paper (control-) were also considered for comparison purposes**.** It was found that silicone rubber vulcanizates with nano-silver colloid, SSZ and HPQM exhibited no inhibition zone. Fig. 1c and 1d show the effect of UV aging time on clear zone of the silicone rubber added with HPQM at 15 phr against *E. coli* and *S. aureus* bacteria, respectively. It was observed that without UV light, the HPQM resulted in large clear zone, but as the aging time was increased, the clear zone disappeared, suggesting that the UV light worsened the bacteria killing ability of the HPQM in the silicone rubber compounds.

The quantitative results for antibacterial performances of silicone rubber added with the HPQM agent for various loadings are given in Fig. 2**,** the results being assessed as a function of aging time and contact time. The results suggested that *E. coli* and *S. aureus* appeared to decrease with increasing contact times, indicating that bacteria killing has occurred for the silicone rubber vulcanizates with HPQM before UV aging. However, the killing efficiency seemed to diminished when increasing the UV aging times after 3 days. This corresponded to the clear zone results in Fig. 1. This could be explained by the peptidoglycan thickness of *S. aureus* that is far wider than that of *E. coli* structure and this would then be more difficult for HPQM to penetrate into the cell to kill the bacteria [6].

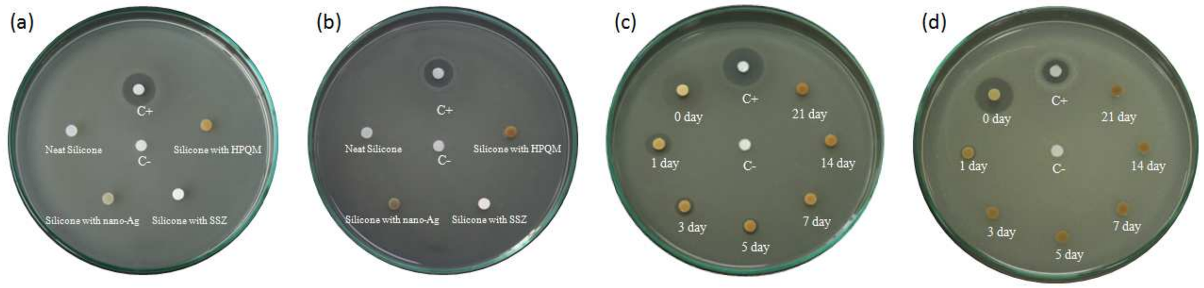

Figure 1. Effects of antibacterial agent type and UV aging on clear zone by Halo test. (a) and (b) silicone with various antibacterial agents at 21 day UV and 15 phr loading for *E.coli* and *S. aureus,* respectively, (c) and (d) silicone with HPQM at 15 phr loading for various UV aging times for *E.coli*, and *S. aureus,* respectively

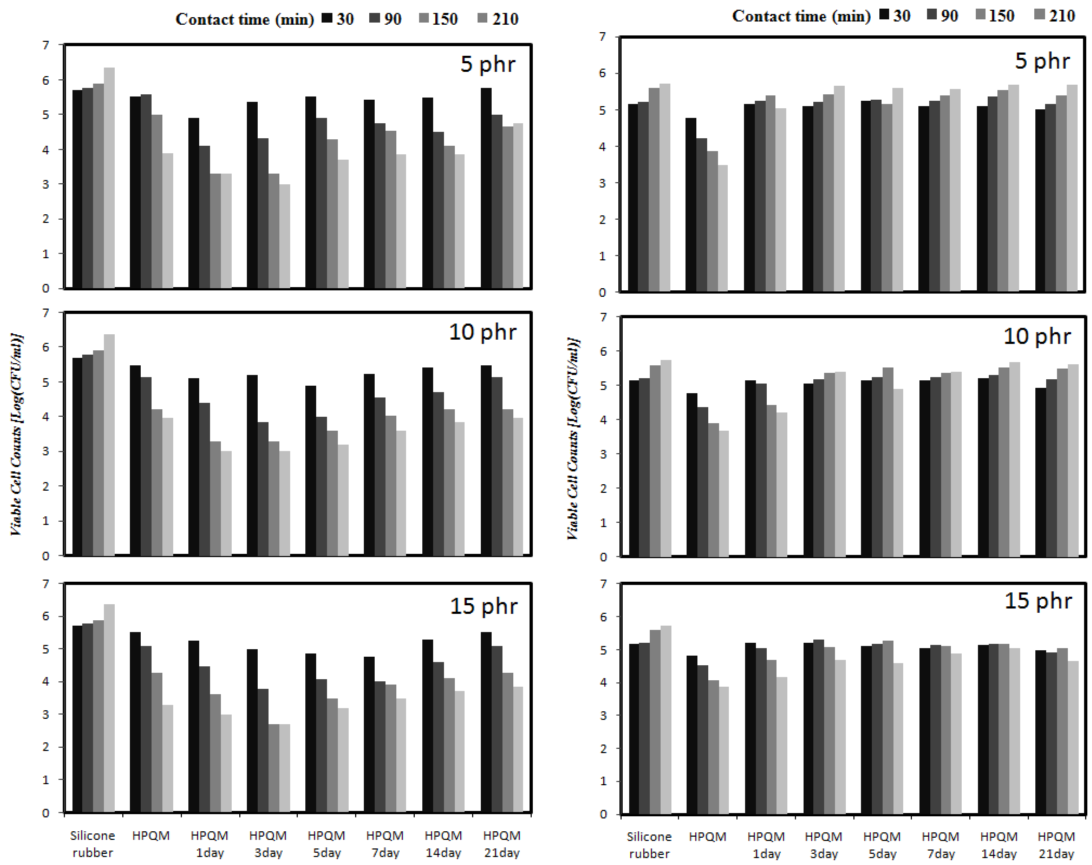

Figure 2. Viable Cell Count for *E. coli* (left) *and S. aureus* (right) colonies as a function of HPQM loadings at 5, 10 and 15 phr

Table 1 shows the results of contact angle values for the silicone rubber vulcanizates with the three antibacterial agents before and after UV aging at 21 days. It was found that the contact angle values for the rubbers with nano-silver colloid and SSZ slightly changed whereas those with HPQM decreased significantly from 111.8^{o} to 67.2^{o}. This suggests that the presence of PQM resulted in some chemistry changes on the rubber surfaces. The decrease in the contact angle suggested greater hydrophilicity on the silicone surface [7].

Table 1. Contact angle values for silicone rubbers with various types of anti-bacterial agents at 15 phr loadings

	Compound	Contact angle value (°)
Non aging	Neat Silicone Rubber	111.8 ± 2.8
	Silicone Rubber with nano -Ag colloid	108.1 ± 2.9
	Silicone Rubber withSSZ	97.2 ± 1.9
	Silicone Rubber with HPQM	67.2 ± 5,3
Aging 3 weeks	Neat Silicone Rubber	111.9 ± 2.3
	Silicone Rubber with nano -Ag colloid	93.0 ± 1.8
	Silicone Rubber with SSZ	105.0 ± 2.0
	Silicone Rubber with HPQM	96.9 ± 4.1

This was expected since HPQM, which is more hydrophilic than silicone, has migrated to the silicone surfaces to kill the bacteria, whereas the other two antibacterial agents did not.This explains all the results why the antibacterial efficiency of the rubber with HPQM was most pronounced. However, when experiencing the UV light, the contact angle value appeared to increased from 67.2^o to 96.9^o, but still lower than the neat silicone rubber (111.8^o).This means that the UV light has suppressed the migration of the HPQM on the silicone rubber surfaces.

Conclusion

The silicone rubber compound with HPQM agent exhibited the most satisfaction for antibacterial performance, which was experimentally evidenced by a progressive decrease in viable cell count with increasing contact time, and appearance of clear zone. The antibacterial activity for the HPQM added silicone rubber compounds occurred as a result of HPQM migration on the rubber surfaces which were revealed by a significant decrease in cintact angle value. The antibacterial activity of the HPQM added silicone rubber compounds worsened after UV aged at 3 days and longer. The changes in antibacterial activity were pronounced only for *E.coli*.

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